Polymer Blends: Introduction

1

Leszek A. Utracki, P. Mukhopadhyay, and R. K. Gupta

Contents

Leszek A. Utracki: Deceased.

L.A. Utracki
National Research Council Canada, Industrial Materials Institute, Boucherville, QC, Canada

P. Mukhopadhyay
IPEX Technologies Inc., Montreal, Canada
e-mail: Prithu.Mukhopadhyay@ipexna.com

R.K. Gupta
Department of Chemical Engineering, West Virginia University Benjamin M. Statler College of Engineering and Mineral Resources, Morgantown, WV, USA
e-mail: rakesh.gupta@mail.wvu.edu

L.A. Utracki, C.A. Wilkie (eds.), *Polymer Blends Handbook*,
DOI 10.1007/978-94-007-6064-6_3,

Abstract

While this chapter serves as an introduction to all the subsequent chapters, it is quite comprehensive. A brief history as well as information on polymer synthesis, nomenclature, and properties is provided. The need to formulate polymer alloys and blends and the resulting benefits are explained. Since the vast majority of polymer pairs are thermodynamically immiscible, compatibilization and reactive extrusion are necessary to improve interfacial adhesion and to optimize blend performance. How polymer morphology is influenced both by blend

composition and the imposed process conditions is discussed first. This provides the theoretical basis for understanding the concept of polymer blending.

The raison d'etre of polymer blending is developing materials having enhanced performance. Performance itself depends on the polymer pair types employed, their relative amounts, extent of miscibility, nature and amount of compatibilizer used, and the method of blending. A key issue is the process of mixing polymers during which blends undergo a complex combination of shear and elongation and the evolution of blend microstructure becomes crucial and requires close attention. Each category of polymer pairs, from commodity resins and their blends, to engineering resins and their blends, and to specialty polymers and their blends is discussed in detail. Pertinent theoretical as well as experimental results are presented and reviewed.

The concern over environmental issues and sustainability has opened up another vibrant research field, namely, biobased and biodegradable polymer blends. An overview of major developments and recent trends in biodegradable blends with an emphasis on PLA blends are also discussed. This chapter closes with an outlook for the future of this important subject.

1.1 Introduction

The world production of plastics in 1900 was about 30,000 t – in the year 2010 it had reached 265 Mt, with thermoplastics contributing about 90 % of this amount, while the rest was thermosets. For the last 20 years, plastic production has increased at the rate of about 5 % per year, with no saturation in sight. In 2010, China accounted for 23.5 % of plastic production, whereas Europe and the North American (NAFTA) region contributed 21.5 % and 20.5 %, respectively (Plastics-the facts 2011, PlasticsEurope, 20th ed). According to a report by Global Industry Analysts Inc., global plastic consumption is set to reach 297.5 Mt by 2015.

Polymers are classified as either *natural*, those that resulted from natural biosynthesis, or *synthetic*. The *natural* (polysaccharides, proteins, nucleic acids, natural rubbers, cellulose, lignin, etc.) has been used for tens of thousands of years. In Egypt the musical string instruments, papyrus for writing, and styrene (in a tree balsam) for embalming were used 3,000 BC. For millennia shellac has been used in Indian turnery (Chattopadhyaya 1986). The natural rubber was used by *Olmecs* at least 3,000 years ago (Stuart 1993).

The term *synthetic* polymer refers equally well to linear, saturated macromolecules (i.e., *thermoplastics*), to unsaturated polymers (i.e., *rubbers*), or to any substance based on cross-linkable monomers, macromers, or prepolymers (i.e., *thermosets*). The focus of this handbook is on blends of thermoplastics made of predominantly saturated, linear macromolecules.

In the last quarter century, there have been two major developments, one technical and one economic, which have given a new direction to the polymer industry. There has been a revolution in polyolefin technology that started during the last decade of the twentieth century, and this is related to the development of metallocene and single-site catalysts. The use of these catalysts allows for the synthesis of improved polymers with well-defined structures and closely controlled molecular architectures. Separately, there has been a shift toward green chemistry, promoted by concerns about sustainability and raw material availability. The need to provide alternatives to petroleum-based products has led to the development and commercialization of biobased plastics. Simultaneously, there has been increasing emphasis on the recycling of postconsumer plastics (Yeh et al. 2009). Additionally, there has been consolidation in the industry and an overall shift in production of commodity resins to countries in Asia.

There are many sources of information about polymer history (Martuscelli et al. 1987; Seymour and Cheng 1987; Vogl and Immergut 1987; Alper and Nelson 1989; Morris 1989; Seymour 1989; Sperling 1992; Mark 1993; Sparke 1993; Utracki 1994, 1998a; Freinkel 2011; Strom and Rasmussen 2011).

The abbreviations used in this text are listed at the end of this chapter.

1.2 Early Polymer Industry

1.2.1 The Beginnings

The polymer industry traces its beginning to the early modifications of shellac, natural rubber (NR, an amorphous *cis*-1,4-polyisoprene), gutta-percha (GP, a semicrystalline *trans*-1,4-polyisoprene), and cellulose. In 1846, Parkes patented the first polymer blend: NR with GP partially co-dissolved in carbon disulfide. Blending these two polyisoprene isomers resulted in partially cross-linked (co-vulcanized) materials whose rigidity was controllable by composition. The blends had many applications ranging from picture frames, tableware, ear trumpets, to sheathing the first submarine cables.

1.2.2 Modified Natural Polymers

The first man-made polymer was nitrocellulose (NC). The main use of the NC resins was a replacement of the natural and expensive materials, viz., ivory, tortoise shell products, amber, ebony, onyx, or alabaster. The use of cellulose acetate (CA), as a thermoplastic, began in 1926. Cellulose ethers and esters became commercially available in 1927. Casein cross-linked by formaldehyde gave hornlike materials – *Galalith*™ has been used to manufacture shirt buttons or as imitation of ivory and porcelain (Pontio 1919).

1.2.3 Synthetic Rubbers

The first polymerization of isoprene in sealed bottles was reported in 1884 by Tilden. *Methyl rubber* was thermally polymerized at 70 °C – the reaction required 3–6 months, giving poor quality products. In 1926 BASF developed sodium-initiated polymerization of butadiene known as *Buna*™ for butadiene + natrium. The first successful, general-purpose rubbers were copolymers of butadiene with either styrene, *Buna-S*, or acrylonitrile, *Buna-N* (Tschunkur and Bock 1933; Konrad and Tschunkur 1934). Poly(2-chlorobutadiene), *chloroprene* (Carothers et al. 1931), was introduced in 1931 by du Pont. Elastomeric polysulfides (Patrick 1932), were commercialized in 1930 as *Thiokol*™. In 1937 butyl rubber (copolymer of isobutylene with isoprene) was invented. The synthetic rubber production took a big leap during the Second World War (WW2) (Morton 1982).

1.2.4 Synthetic Thermosetting Polymers

The first commercially successful *synthetic* polymer was phenol-formaldehyde (PF) resin (Smith 1899). The resin was introduced in 1909 by Baekeland as *Bakelite*™. The urea-formaldehyde (UF) resins were discovered in 1884, but production of *Beetle*™ moldable resin commenced in 1928. Three years later, *Formica*™, phenolic paper covered with decorative layer protected by UF, was introduced. The thiourea-formaldehyde molding powders were commercialized in 1920, while in 1935, Ciba introduced *Cibanite*™, aniline-formaldehyde (AF) resins, molding materials, and then, 2 years later, the melamine formaldehyde (MF).

Epoxy compounds were discovered by Prileschaiev in 1909, but its importance was realized only during WW2. In 1956, glass fiber reinforcements were introduced. The thermoset polyesters (TS) were developed by Ellis in 1933–1934. The first use of glass-reinforced TS dates from 1938.

1.2.5 Synthetic Thermoplastic Polymers

The synthetic polymers are divided into three categories:

1. Commodity
2. Engineering
3. Specialty

The five large-volume polymeric families that belong to the commodity resins are polyethylenes (PE), polypropylenes (PP), styrenics (PS), acrylics (PMMA), and vinyls (PVC). According to the web site, www.icis.com, the market share of these plastics in 2011 was 178 Mt – in other words, they represent about 70 % of all plastics.

The five engineering polymer families are polyamides (PA), thermoplastic polyesters (PEST), polycarbonates (PC), polyoxymethylenes (POM), and polyphenylene ethers (PPE). According to a March 2013 Industry Experts report entitled “Engineering Plastics – A Global Market,” 19.6 Mt of engineering plastics were produced in 2012. In other words, these polymers constitute only about 10 % by volume of all polymers produced. However, due to superior properties, they command a much larger percentage by value of the plastic consumption.

Table 1.1 High-performance materials: a comparison

		Strength (GPa)		Modulus (GPa)	
No.	Material	Theoretical	Observed	Theoretical	Observed
1.	Polyethylene (standard)	21	≤ 0.03	316	0.2
2.	Polyethylene gel-spun	21	6.0	316	220
3.	Polyester (standard)	24	0.07	124	2.2
4.	Polyester oriented	24	1.2	124	21
5.	Aromatic polyamide	21	3.6	190	125
6.	Aromatic polyester (EFK)	–	4.1	–	139
7.	Poly(phenylene benzothiazole)	–	4.2	371	365
8.	Polyazomethin	–	4.7	–	125
9.	Carbon fiber	–	3.1	–	235
10.	Steel	29	2.1–3.5	–	210

The engineering and specialty polymers show high mechanical performance, and the continuous use temperature $150 \leq \text{CUT}(^\circ\text{C}) \leq 500$.

The polymer industry increasingly favors high technology and high value-added materials. These are obtained either by means of new polymerization methods, by new processing technologies, or by alloying and reinforcing. For example, new syndiotactic PP or PS (sPP or sPS, respectively) surpasses the performance of their predecessors. The gel-spun PE fibers have 200 times higher tensile strength than standard PE. Aromatic polyester (EKF from Sumitomo) has tensile strength of 4.1 GPa, to be compared with 70 MPa of a standard polyester resin (see Table 1.1).

New types of polymers are also being introduced, e.g., dendritic-structure polymers (Fréchet et al. 1992; Schluter and Rabe 2000), carbosilane dendritic macromolecules (Roovers et al. 1993), the “hairy rod” molecular structures where rigid-rod chain macromolecules are provided with short and flexible side branches (Wegner 1992), etc. However, the polymer technology invariably moves away from the single-phase materials to diverse combinations of polymers, additives, and reinforcements. While synergistic effects are often cited, the main reason is a need for widening the range of properties, for development of materials that would have the desired combination of properties – tailor-made polymeric systems. With single-phase polymers, one can only change the molecular weight or form copolymers. This can require significant effort. By contrast, blending is easy and inexpensive, and it is especially useful when only small volumes are required. Also, scale-up is straightforward. At present, about a third of the synthetic resins are used in blends and another third in composites.

1.2.6 Compounding and Processing

The first mixer was an annular container with a spiked rotor for rubber compounding (Hancock 1823). The calendar/two-roll mill was patented by Chaffe in 1836 and manufactured by Farrel Co. A counterrotating twin-shaft internal mixer with elliptical rotating disks or sigma blades was developed by the end of the 1800s (Freyburger 1876; Pfleiderer 1880). The first hand-operated extruder was a ram press, used for forming NR or GP and then later NC.

The first belt-driven extruders with Archimedean screw were patented much later (Gray 1879). In 1939, Paul Leistritz Maschinenfabrik built electrically heated, air-cooled extruder, with nitrided barrel, having L/D = 10, an automatic temperature control, variable screw speed. The machine is considered a precursor of the modern single-screw extruders, SSE. During the WW2 breaker plates, screen packs, crosshead dies, coextrusion, monofilament extrusion, film blowing, and biaxial sheet orientation were introduced. In the 1950s, a coextrusion process, venting, and two-stage screws were developed. In the 1980s the microprocessor control evolved into computer-integrated manufacturing, and the helical grooved feed barrels, high-pressure gear pumps, air lubricated die flow, and biaxial film orientation were introduced (Utracki 1991a, c).

Pfleiderer patented the first modular counterrotating twin-screw extruder (TSE) in 1882. An intermeshing, corotating TSE, the predecessor of the modern machines, was designed for extrusion of CA. The TSE was used by I. G. Farbenindustrie for the production of PA-6 (Colombo 1939). In 1959, Werner and Pfleiderer introduced ZSK machines (vented, intermeshing, corotating, with segmented screw and barrel, twin-screw extruders). These provided good balance between the dispersive and distributive mixing at relatively high output rates. In 1979 Japan Steel Works (JSW) developed TEX-series TSEs for reactive compounding, permitting an easy change of the screw direction from co- to counterrotation. In collaboration with Sumitomo Chem., barrel elements with sampling ports were designed, providing ready access to the processed material for determining the reaction progress and morphology (Nishio et al. 1990). American Leistritz has been active in designing TSE kneading elements that improved mixing capability by maximizing the extensional flow field. More information on the evolution of the extrusion technology can be found in ▶ Chap. 9, “Compounding Polymer Blends”.

Injection molding of NC dates from 1872. The early machines were hand operated. They used an axially movable screw or plunger and were equipped for devolatilization. The commercial-scale injection molding of PS has begun in 1931. In 1932 Gastrow developed the first automatic unit, *Isoma-Automat* (30 g capacity per shot), with torpedo-type heating chamber. In 1951, Willert invented an in-line reciprocating screw plasticization that revolutionized the injection molding industry. The first automated injection molding plant was developed by Eastman Kodak in 1950.

Hayatt used blow molding in 1880 to produce baby rattles out of CA tubes or sheets. In 1942, Plax Corp. started manufacturing *squeezable* LDPE bottles. By the end of the 1950s, blow molding was the most rapidly developing processing method. In 1965 Wyeth, using the stretch blow molding, produced polyethylene terephthalate (PET) bottles. In 1972, Toyo Seikan started to produce multilayered blow molded bottles from PP and EVAl. In 1976 Ishikawajima-Harima introduced intermittent coextrusion blow-molding system for large parts.

1.2.7 Development of Polymer Science

1.2.7.1 Polymerization

Cellulose modification dates from 1833 (Braconnot). In 1838 Regnault photopolymerized vinylidene chloride. A year later, Simon observed that heating styrene in the presence of air generated a tough gelatinous material – a low molecular weight PS. Polyoxymethylene (acetal) was discovered in 1859. In 1872 several new polymers were announced, viz., PVC, polyvinyl bromide (PVB), and phenol-formaldehyde (PF). Polymethacrylates were discovered by Kahlbaum in 1880, polymethylene in 1897, 1 year later polycarbonate by Einhorn, polyamide-6 (PA-6) in 1907, etc. In the 1920s, the list of polymers rapidly started to increase, viz., polysulfide (PSF), polyvinyl alcohol (PVAl), poly(styrene-co-maleic anhydride) (SMA), polyvinyl formal (PVFO), etc. During the next decade, polyacetylene (PACE), styrene-acrylonitrile copolymer (SAN), low-density polyethylene (LDPE), polyvinylidene chloride (PVDC), epoxy resins (EP), polyamides (e.g., PA-66, PA-610, PA-106), polysiloxanes (PDMS), polychlorotrifluoroethylene (PCTF), polytetrafluoroethylene (PTFE), and many others were discovered (Utracki 1989a).

Most early thermoplastics, e.g., PVC or PS, were obtained in the free radical polymerization, initiated either by heat or by sunlight. The first systematic studies of the free radical chemistry commenced 80 years later (Ostromislensky 1911, 1915, 1916). Fikentscher empirically determined which one of the 30-or-so monomers *liked* or *disliked* to copolymerize with each other. The advantage of latex blending was also established. The theory of the free radical copolymerization was only developed in the 1940s (Alfrey et al. 1952).

The polycondensation reactions have been known since the mid-1800 (Lourenço 1859; Wurtz 1859, 1860). In 1927, Carothers and his colleagues provided the basis for understanding the nature of these reactions (Carothers, 1931). Good agreement between Flory's theoretical predictions and the experimental observations of the average molecular weight (MW) provided convincing arguments for the acceptance of the linear macromolecule model.

The alkyl-lithium-initiated, *living* anionic polymerization of elastomers was described in 1928 by Ziegler. To polymerize styrene-isoprene block copolymers, Szwarc et al. (1956) used sodium naphthalene as an anion-radical di-initiator, while Shell used an organolithium initiator. The polymerization mechanism was described by Bywater (1965).

In the early 1950s, Ziegler found that in the presence of $ZrCl_4 + AlR_3$ ethylene can be polymerized at low temperature and pressure into linear, high-density polyethylene (HDPE). The catalysts developed by Ziegler, and later by Natta, become known as *Ziegler-Natta*, *Z-N* catalysts. These can be defined as polymerization initiators created from a catalyst (1) and cocatalyst (2), where (1) is halide or oxyhalide of transition metals from groups IV to VII and (2) is an organometallic compound of metal from groups I to III. The *Z-N* catalyst is prepared by mixing ingredients (1) and (2) in a dry, oxygen-free solvent (Natta and Danusso 1967). A more recent Z-N catalyst development is

$MgCl_2$-supported catalysts that have a 100-fold more active sites per mole of Ti and about ten times higher propagation rate (Rieger et al. 1990).

The newest, single-site metallocene catalyst makes it possible to control MW, molecular weight distribution (MWD), comonomer placement, stereoregularity, and lifetime of the reactive chain end (Kaminsky et al. 1985, 1992; Kaminsky 1998; Swogger 1998; Choi and Soares 2012). The use of either $(Cp)_pR'_s(Cp)MeQ_{3\text{-}p}$ or $R''_s(Cp)_2MeQ'$ (where Cp is cyclopentadienyl (substituted or not) radical; Me is metal from group 4b, 5b, or 6b; and R′, R″, Q, and Q′ are radicals (viz., aryl, alkyl, alkenyl, alkylaryl, or arylalkyl), s = 0−1, p = 0−2), for the polymerization of ethylene copolymers, provides independent control of MW and density. The catalyst is used in combination with a large amount of alumoxanes.

In 1975 Mitsui Petrochemicals introduced metallocene-made LLDPE *Tafmer*™, with controlled comonomer placement, but rather low MW. In 1991, Dow Plastics produced developmental quantities of ethylene copolymers with up to 25 mol% of butene, hexene, or octene, *Affinity*™ resins. The use of a metallocene catalyst with a single cyclopentadiene ring resulted in a certain degree of randomization of the polymerization process. The catalyst produced PP with narrow molecular weight distribution, *and a long-chain branching*, similar to LDPE. In the early 1990s, Exxon Chemical Company (now ExxonMobil) worked to develop metallocene catalysts for use in Union Carbide's (now Dow Chemical) gas-phase UNIPOL™ PE process. Later, in 1997, the two companies formed a joint venture called Univation Technologies which introduced XCAT™ metallocene catalysts. The resulting linear low-density polyethylene finds application in flexible packaging, pallet stretch wrap, and food packaging and agricultural films. The most recent development is PRODIGY™ bimodal catalyst that allows for the synthesis of bimodal film resins in a single reactor, resulting in a PE with improved performance and processability.

The metallocene catalysts are also used to produce high melting point polymers out of *commodity* monomers, e.g., sPS, with $T_g = 100\ °C$, and $T_m = 266\ °C$, or syndiotactic poly(*p*-phenyl styrene), (sPhPS), with $T_g = 196\ °C$, $T_m = 352\ °C$, and the decomposition temperature, $T_{decomp} = 380\ °C$. Since sPhPS is miscible with sPS in the whole range of concentration, blends of these two syndiotactic polymers can be processed at any temperature above 266 °C (Watanabe et al. 1992). Polycyclohexylethylene (PCHE) is a metallocene resin, developed by Dow as a replacement for PC in the production of optical disks. PCHE has low shrinkage (0.02 % after 24 h), higher light transmission than PC (91.9 % vs. 89.8 %, respectively) and high flex modulus of 71 GPa.

1.2.7.2 Polymer Physics

Molecular Weight (MW)

Osmotic pressure measurements for the determination of MW were used in 1900 to characterize starch. Twenty years later, the solution viscosity measurements were introduced by Staudinger for this purpose. However, it was Mark and his collaborators who developed the concept of the intrinsic viscosity ([η]) and demonstrated that it provides information on the volume of individual colloidal particles, thus on MW.

For the freely rotating chains, the dependence (today known as *Mark-Houwink-Sakurada* equation) was obtained (Guth and Mark 1934):

$$[\eta] \equiv \lim_{c \to 0}[(\eta/\eta_o) - 1]/c = KM_v^a \qquad (1.1)$$

where η and η_o are viscosities of the solution and solvent, M_v is the viscosity-average molecular weight, and K and a 0.5–0.7, are equation parameters. In 1933 the ultra-centrifugation was developed (Kraemer and Lansing 1933). Utility of light scattering for the determination of MW was demonstrated 11 years later (Debye 1944, 1946).

Free-Volume Concept

The free-volume theory of liquids dates from the beginning of the twentieth century. Two expressions for *the free-volume fraction*, f, have been proposed, either $f = (V - V_{occ})/V$ or less frequently used $f = (V - V_{occ})/V_{occ}$ (V_{occ} is the occupied volume). The theory was used to interpret the temperature (T) and pressure (P) dependencies of liquid viscosity (Batschinski 1913). The V_{occ} was defined as the specific volume at which the liquid viscosity is immeasurably high, $\eta \to \infty$. Good correlation was found between V_{occ} and either the critical volume or the van der Waals constant b, viz.

$V_{occ}/(V_{crit}/3) = V_{occ}/b = 0.921 \pm 0.018$. Batschinski wrote:

$$\eta = a_o + a_1/f = a_o + a_1 V/(V - V_{occ}) \qquad (1.2)$$

where a_i are equation parameters. Forty years later, more accurate data of viscosity (spanning several orders of magnitude) and specific volume for a series of paraffin's with molecular weight MW = 72–1,000 g/mol led to the logarithmic dependence (Doolittle 1951):

$$\ln \eta = a_o + a_1 V/(V - V_{occ}) \qquad (1.3)$$

where v_o is the value of v at a characteristic solidification temperature, T_o, at which the fluid viscosity increases to infinity. Equation 1.3 provided a basis for the derivation of well-known WLF time-temperature shift factor a_T (Williams et al. 1955).

The free-volume model has been also incorporated into thermodynamic theories of liquids and solutions (Prigogine et al. 1957), and it is an integral part of theories used for the interpretation of thermodynamic properties of polymer blends (Utracki 1989a). In particular, it is a part of the most successful equation of state (EoS) derived for liquids and glasses (Simha and Somcynsky 1969), critically examined using data for 56 principal polymers (Rodgers 1993). Since the mid-1960s, the lifetime of ortho-positronium has been used to measure the free-volume fraction f. Accordingly, f increases linearly with the temperature:

$$f = -0.13556 + 6.2878(T/T^*) \quad \text{for} \quad 0.0165 \le T/T^* \le 0.0703$$

where T* is the temperature reducing parameter in Simha-Somcynsky theory (Utracki 1998b). More detailed analysis indicated that the free volume should be discussed in terms of distribution of the holes. For example, the measurements showed that above T_g the number of holes does not increase, but their volume does (Kobayashi et al. 1989). In PS/PPE blends, the size of the free-volume spaces in PS was found smaller than that in PPE (Li et al. 1999b).

Viscoelasticity

In 1874, Boltzmann formulated the theory of viscoelasticity, giving the foundation to the modern rheology. The concept of the relaxation spectrum was introduced by Thompson in 1888. The spring-and-dashpot analogy of the viscoelastic behavior (Maxwell and Voigt models) appeared in 1906. The statistical approach to polymer problems was introduced by Kuhn (1930).

Busse (1932) observed that "green" rubber under stress shows a dual behavior, suggesting the presence of two types of interactions: few widely separated strong ones, acting as physical cross-links, and many weak ones of the van der Waals type, which make it possible for one macromolecule to slip by the others. This postulate was the first connotation of the chain entanglement. Bueche (1952, 1956, 1962) adopted the entanglements' concept for the interpretation of polymer flow. He calculated the molecular friction constant per statistical segment as the unit force needed to pull the undeformed macromolecule through the surrounding medium at unit speed, $f_o = F/N$ (with N being the number of statistical segments per macromolecule), deriving the relations (see Eq. 1.4) between the diffusion constant, D, or zero-shear viscosity, η_o, and such molecular parameters as density, ρ, molecular weight, M, and radius of gyration, R_g:

$$
\begin{aligned}
&D\eta_o = (\rho N_A/36)\left(R_g^2/M\right)k_B T; \quad \text{and} \quad \eta_o = (\rho N_A/36)\left(R_g^2/M\right)N^* f_o \\
&\text{for}: \quad M \le 2M_e \qquad N^* = M/M_o \\
&\text{for}: \quad M > 2M_e \qquad N^* = \beta(M/M_o)(\rho N_A/48)(M/M_e)^2\sqrt{M}\left(R_g^2/M\right)^{3/2}
\end{aligned}
\tag{1.4}
$$

where numerical constant $\beta \cong 0.6$. The dependence predicts that for low molecular weight liquids (M below the value of the critical molecular weight for entanglement, $M_c = 2M_e$, where M_e is the molecular weight between entanglements), η_o should be proportional to M, while for high molecular weight macromolecules (above M_c), to $M^{3.5}$. Thus, predictions of the entanglement-based theory are in good agreement with the observations: $\eta_o \propto M^{3.4}$ (Gupta 2000). The correlation between the plateau modulus and entanglement concentration soon followed (Ferry et al. 1955). The long disputes on the nature of entanglement led to defining it as "a special type of interactions, affecting mainly the large-scale motions of the chains, and through them, the long time end of the viscoelastic relaxation time spectrum" (Graessley 1974).

Entanglement-based theories have now been largely superseded by reptation theories that owe their origins to the work of de Gennes (1979) and of Doi and Edwards (1986) and Doi (1995). The essential idea here is that entangled polymer molecules can be considered to be contained within a tube; the orientation of the tubes and the motion of the chains within the tubes relax over different timescales. This concept has been developed by a large number of authors over the years, and a simple and readable model that accounts for the main mechanisms has been published by Marrucci and Ianniruberto (2003). A major success of the reptation theory has been in establishing the molecular weight dependence of polymer diffusion.

Work to further expand the reptation-tube model has been explored. Pokrovskii (2008), for example, has shown that the underlying stochastic motion of a macromolecule leads to two modes of motion, namely, reptative and isotropically diffusive. There is a length of a macromolecule $M^* = 10M_e$ where M_e is “the macromolecule length between adjacent entanglements” above which macromolecules of a melt can be regarded as obstacles to motions of each other and the macromolecules reptate. The transition to the reptation mode of motion is determined by both topological restriction and the local anisotropy of the motion.

1.3 Polymer Structure and Nomenclature

1.3.1 Basic Considerations

A *polymer* is a substance composed of *macromolecules*, built by covalently joining at least 50 molecular mers, or the *constitutional repeating units or CRU*. The longest sequence of CRU defines the *main chain* of a macromolecule. The main chain may be composed of a series of *subchains*, identified by some chemical of physical characteristic (e.g., tactic placement). The main chain may also contain long or short *side chains* or *branches*, attached to it at the *branch points*. A small region in a macromolecule from which at least four chains emanate constitutes a *cross-linking point*. A macromolecule that has only one cross-link is the *star macromolecule*.

A macromolecule consisting of several cross-linked chains, but having a finite molecular weight, is a *micronetwork*. A highly ramified macromolecule in which each CRU is connected to every other CRU is a *polymer network*. When the main chain of a macromolecule has numerous branch points from which linear side chains emanate, it is *comb macromolecule*. The CRU is defined as a bivalent organic group, not necessarily identical to the source from which the macromolecule was prepared – it is the largest identifiable group in the polymer dictated by the macromolecular structure. To discuss the structure of polymer molecules, one may consider the chemical nature of CRU, type of the linkages, the global macromolecular arrangement, and the topochemical character of the macromolecule, tacticity, etc. These are summarized in Table 1.2.

Table 1.2 Macromolecular structures

No.	Characteristic	Examples
1	*Recurring constitutional repeating units*, *CRU*	
1.1	*Structure*	Aliphatic, aromatic, heterocyclic, metallo-organic
1.2	*Joining similar CRU*	Homopolymers (linear, branched, dendritic, cross-linked, etc.)
1.3	*Joining different CRUs*	Copolymers, multipolymers, polyadducts, polycondensates. . .
1.4	*Joining polymer segments*	Block copolymers, graft copolymers, ladder polymers
2	*The nature of bond between CRU*	For example, ether, ester, amide, urethane, sulfite
3	*Macromolecular structure*	Linear, branched, cross-linked, dendritic
4	*Topochemical characteristics of macromolecule*	
4.1	*Geometrical isomers*	For example, rubber and gutta-percha are poly(1,4-isoprene), *cis*- and *trans*-, respectively
4.2	*Optical isomers*	Having optically active C*; e.g., polypeptides, polysaccharides
4.3	*Tacticity*	Isotactic, syndiotactic, and atactic
4.4	*Helical structures*	Polypeptides, tactic polymers
4.5	*Head-to-tail*, *head-to-head*	For example: PIB or PS

1.3.2 Polymer Nomenclature

Macromolecular compounds can be classified according to (Kumar and Gupta 2003):

1. The chemical structure of the repeating unit (viz., polyamides, polyesters, polyolefins)
2. The structure (viz., linear, branched, ladder, or cross-linked)
3. The phenomenological behavior or technological use
4. The source of the compounds (viz., synthetic, natural, and derived products)

The Commission on Macromolecular Nomenclature defined 52 terms related to polymer structure, including *polymer*, *constitutional units*, *monomer*, *polymerization*, *regular polymer*, *tactic polymer*, *block polymer*, *graft polymer*, *monomeric unit*, *degree of polymerization*, *addition polymerization*, *condensation polymerization*, *homopolymer*, *copolymer*, *bipolymer*, *terpolymer*, *and copolymerization* (IUPAC 1974). The Commission remains the leading nomenclature body in the polymer field. Table 1.3 lists the pertinent sources for information on the nomenclature of polymeric materials.

Since there are difficulties in assigning systematic and unique abbreviations to polymers, only a short list has the IUPAC's official sanction. The IUPAC Macromolecular Nomenclature Commission has published three sets of rules for naming polymers:

1. Traditional, *trivial names* are sanctioned by the historical use and approved by IUPAC as an alternative (examples are listed in Table 1.4)
2. *Structure-based* nomenclature
3. *Source-based* nomenclature proposed by the Commission

Table 1.3 Polymer nomenclature proposed by the IUPAC

No.	Title	References
1.	*Report on Nomenclature Dealing with Steric Regularity in High Polymers*	Huggins et al. 1962, 1966
2.	*Basic Definitions of Terms Relating to Polymers*	IUPAC 1974, 1996
3.	*Nomenclature of Regular Single-Strand Organic Polymers*	IUPAC 1976
4.	*Stereochemical Definitions and Notations Relating to Polymers*	IUPAC 1981
5.	*Note on the Terminology for Molar Masses in Polymer Science*	IUPAC 1984
6.	*Nomenclature for Regular Single-Strand and Quasi-Single-Strand Inorganic and Coordination Polymers*	IUPAC 1985a
7.	*Source-Based Nomenclature for Copolymers*	IUPAC 1985b
8.	*Use of Abbreviations for Names of Polymeric Substances*	IUPAC 1987
9.	*Definitions of Terms Relating to Individual Macromolecules, Their Assemblies, and Dilute Polymer Solutions*	IUPAC 1989a
10.	*Definitions of, Terms Relating to Crystalline Polymers*	IUPAC 1989b
11.	*A Classification of Linear Single-Strand Polymers*	IUPAC 1989c
12.	*Compendium of Macromolecular Nomenclature*	Metanomski 1991
13.	*Source-Based Nomenclature for Non-Linear Macromolecules and Macromolecular Assemblies*	Jenkins et al. 1993

Table 1.4 Traditional and systematic names of polymers

No.	Traditional name	Systematic name
1.	Polyethylene	Poly(methylene)
2.	Polypropylene	Poly(propylene)
3.	Polyisobutylene	Poly(1,1-dimethyl ethylene)
4.	Polybutadiene	Poly(1-butenylene)
5.	Polyisoprene	Poly(1-methyl- 1-butenylene)
6.	Polystyrene	Poly(1-phenyl ethylene)
7.	Polyacrylonitrile	Poly(1-cyano ethylene)
8.	Polyvinyl alcohol	Poly(1-hydroxy ethylene)
9.	Polyvinylacetate	Poly(1-acetoxy ethylene)
10.	Polyvinylchloride	Poly(1-chloro ethylene)
11.	Polyvinylidenefluoride	Poly(1,1-difluoro ethylene)
12.	Polytetrafluoroethylene	Poly(difluoro methylene)
13.	Polyvinylbutyral	Poly[(2-propyl-1,3-dioxane-4,6-diyl) methylene]
14.	Polymethylacrylate	Poly[1-(methoxycarbonyl) ethylene]
15.	Polymethylmethacrylate	Poly[1-(methoxycarbonyl)-1-methyl ethylene]
16.	Polyformaldehyde	Poly(oxy methylene)
17.	Polyethylene oxide	Poly(oxy ethylene)
18.	Polyphenylene ether	Poly(oxy-1,4-phenylene)
19.	Polyethylene terephthalate	Poly(oxyethylene-oxyterephthaloyl]
20.	Poly-ε-caprolactam	Poly[imino(1-oxohexamethylene)]
21.	Polyamide-6,6 or polyhexamethyleneadipamide	Poly[imino(1,6-dioxohexa methylene) iminohexa methylene]; or poly(iminoadipoyliminohexa methylene)

1.3.2.1 Structure-Based Nomenclature

For organic, regular, single-strand polymers, the structure-based system of naming polymers should be used. This nomenclature describes chemical structures rather than substances. Three steps are to be followed in a sequence:

1. Identify the constitutional repeating unit, CRU.
2. Orient the CRU.
3. Name the CRU.

The name of the polymer is *poly(CRU)*. The preferred CRU is one beginning with the subunit of highest seniority. The order of seniority is heterocyclic rings, chains containing heteroatoms (in the descending order O, S, Se, Te, N, P), carbocyclic rings, and chains containing only carbon. The seniority is expressed by brackets and internal parentheses (see examples in Table 1.4).

After the CRU and its orientation, reading left to right, have been established, the CRU or its constituent subunits are named. The name (the largest identifiable unit) includes description of the main chain and the substituents. The subunits are named according to the rules for nomenclature of organic chemistry. The name of the CRU is formed by citing, in order, the names of the largest subunits within the CRU. More complicated, regular single-strand polymers can be represented as multiples of repeating units, such as $[ABC]_n$. The name of the polymer is *poly(ABC)*, where (ABC) stands for the names of A, B, and C, taken in the order of seniority. An extension of the structure-based method to linear inorganic and/or coordination polymers is limited by the general lack of a system for naming bivalent radicals. Few polymers with inorganic, covalently bonded backbones have trivial names (viz., poly(dimethylsiloxane) or poly(dichlorophosphazene)), some can be named by (as organic polymers) using bivalent radicals, e.g., poly[oxy(dimethyl silylene)] or poly[nitrilo (dichlorophosphoranylidyne)].

Structure-based nomenclature is also applicable to copolymers having a regular structure, regardless of the starting materials used (viz., poly(oxyethylene-oxyterephthaloyl)). In principle, it should be possible to extend the existing structure-based nomenclature beyond regular, single-strand polymers to polymers that have reacted, cross-linked polymers, ladder polymers, and other more complicated systems.

1.3.2.2 *Source-Based* Nomenclature

Traditionally, polymers have been named by attaching the prefix *poly* to the name of the CRU, real or assumed monomer, the source from which it is derived. Thus, PS is the polymer made from styrene. When the name of the monomer consists of two or more words, parentheses should be used, but for common polymers such as polyvinylchloride, polyvinylacetate, etc., it is customary to omit them. Different types of polymerization can take place with many monomers, and there are different ways for obtaining a polymer. For example, name such as polyvinyl alcohol refers to a hypothetical source, since this polymer is obtained by hydrolysis of polyvinylacetate. In spite of deficiencies, the source-based nomenclature is still entrenched in the literature. It is also the basis for naming and classifying copolymers (see Table 1.5).

Table 1.5 Nomenclature of copolymers

No.	Type	Connective	Example
1.	Short sequences		
1.1.	Unknown or unspecified	-co-	Poly(A-co-B)
1.2.	Statistical	-stat-	Poly(A-stat-B)
1.3.	Random	-ran-	Poly(A-ran-B)
1.4.	Alternating	-alt-	Poly(A-alt-B); (AB)n
1.5.	Periodic with at least three monomeric units	-per-	Poly(A-per-B-per-C); $(ABC)_n$; $(ABAC)_n$; $(AABB)_n$
2.	Long sequences		
2.1.	Block	-block-, or -b-	Poly A-block-poly B; poly(A-b-B)
2.2.	Graft (polymeric side chain different)	-graft-or -g-	Poly A-graft-poly B; poly(A-g-B); AAAAA (g-BBB)AAAAAAA
2.3.	Star	-star-	Star-poly A
2.4.	Star block	-star-. . .-block-	Star-poly A-block-poly B
3.	Networks		
3.1.	Cross-linked	-cross-	Cross-poly A
3.2.	Interpenetrating	-inter-	Cross-poly A-inter-cross-poly B
3.3.	Conterminous	-cross-	Poly A-cross-poly B

1.3.3 Copolymers

When mers are not identical, the polymerization leads to a *copolymer*. For divalent mers, a *linear copolymer* is obtained, but when at least some mers are able to join more than two units, the polymerization leads to *branched* or *cross-linked copolymer*. When the polymerization starts on a polymer chain of different chemical character than the one that is subsequently forming, the resulting structure is known as *grafted copolymer*. Thus, the arrangement of the different types of monomeric units must be specified. Several types of arrangements are shown in Table 1.5, where A, B, and C represent different CRUs. The systematic source-based nomenclature for copolymers involves identification of the constituent monomers and description of their arrangement. This is achieved by citing the names of the constituent monomers after the prefix “poly” and by placing between the names of each pair of monomers an italicized connective to denote the kind of arrangement by which those two types of monomeric units are related in the structure.

The structures listed in Table 1.5 are divided into three categories: *short sequences*, *long sequences*, *and networks*. Within the first category, a sequence of placement of individual CRU is considered, within the second the placement of long sequences of CRU defines the copolymer type, while to the third belong cross-linked networks, cross-linked polymers, and chemical-type interpenetrating polymer networks. The network is a cross-linked system in which macromolecules of polymer A are cross-linked by macromolecules of polymer B (Sperling 1992). The composition can be expressed as, e.g., *block*-co-poly(butadiene/styrene) (75:25 wt%) or *graft*-co-poly[isoprene/(isoprene; acrylonitrile)] (85:15 mol%).

Table 1.6 Descriptors for nonlinear macromolecules and macromolecular assemblies

Polymer structure	Descriptor
Cyclic	*cyclo*
Branched (unspecified)	*branch*
Short-chain	*sh-branch*
Long-chain	*l-branch*
With *f* (give numerical value) branch points	*f-branch*
Comb	*comb*
Star (unspecified)	*star*
With *f* (give numerical value) arms	*f-star*
Network	*net*
Micronetwork	*m-net*
Polymer blend	*blend*
Interpenetrating polymer network	*ipn*
Semi-interpenetrating polymer network	*sipn*
Macromolecule-macromolecule complex	*compl*

1.3.4 Macromolecular Assemblies

To describe polymers or polymer blends with greater precision, the qualifiers listed in Table 1.6 have been suggested (Jenkins et al. 1993). In a series of four papers, Wilks (1997a–d) has compared the polymer nomenclature styles and structure representation systems used by Chemical Abstracts Service (CAS), the IUPAC, and MDL Information Systems, Inc. (MDL).

1.3.5 Polymer Blend Terminology

The terminology used in polymer blends' science and technology is summarized in Table 1.7 (Utracki 1989a, b). Universal adoption of a consensus nomenclature is vital to the description of chemical structures in online searching and in publishing works. For instance, different kinds of surfaces, interfaces, and interphases provide challenges to develop consistent nomenclature. This is a continuous process as polymers, its variations, and their blends are studied. The definition and nomenclature relating to polymer liquid crystals are recommended in IUPAC (2001), regular single-stranded polymers in IUPAC (2002), terms related to polymers containing ionizable or ionic groups and of polymers containing ions in Jones (2009), and so is the graphical representation of single-strand (copolymers) and irregular polymers in IUPAC (2012).

1.4 Introduction to Polymer Blends

Polymer blends constitute almost one third of the total polymer consumption, and their pertinence continues to increase. According to bcc Research, the global

Table 1.7 Terminology of polymer blends

Term	Definition
Polymer	A substance composed of large molecules, the *macromolecules*, built by covalently joining at least 50 molecular mers, segments, or recurring *constitutional repeating units*, *CRU*. Commercial polymers may contain up to 2 wt% of another polymeric modifier
Copolymer	Polymeric material synthesized from more than a single monomer
Engineering polymer (EP)	Processable polymeric material, capable of being formed to precise and stable dimensions, exhibiting high performance at the continuous use temperature CTU > 100 °C and having tensile strength in excess of 40 MPa
Polymer blend (PB)	Mixture of at least two macromolecular substances, polymers or copolymers, in which the ingredient contents is above 2 wt%.
Homologous polymer blend	Mixture of two homologous polymers (usually a mixture of narrow molecular weight distribution fractions of the same polymer)
Miscible polymer blend	Polymer blend, homogenous down to the molecular level, associated with the negative value of the free energy of mixing: $\Delta G_m \approx \Delta H_m \leq 0$ and a positive value of the second derivative $\partial^2 \Delta G_m \partial \phi^2 > 0$. Operationally, it is a blend whose domain size is comparable to the dimension of the macromolecular statistical segment
Immiscible polymer blend	Polymer blend whose free energy of mixing $\Delta G_m \approx \Delta H_m > 0$
Compatible polymer blend	Term to be avoided! At best a utilitarian, nonspecific term indicating a marketable, visibly homogeneous polymer mixture, with enhanced performance over the constituent polymers
Polymer alloy	Immiscible, compatibilized polymer blend with modified interface and morphology
Compatibilization	Process of modification of the interfacial properties in immiscible polymer blend, resulting in reduction of the interfacial tension coefficient and stabilization of the desired morphology, thus leading to the creation of a polymer alloy
Interphase	Third phase in binary polymer alloys, enhanced by interdiffusion or compatibilization. Thickness of this layer varies with the blend components and compatibilization method from 2 to 60 nm
Compatibilizer	Polymer or copolymer that either added to a polymer blend or generated there during reactive processing modifies its interfacial character and stabilizes the morphology
Chemical compatibilization	Compatibilization by incorporation of a compatibilizer, usually either a copolymer or multipolymer
Physical compatibilization	Compatibilization by physical means: high stress field, thermal treatment, irradiation, etc.
Reactive compatibilization	Compatibilization during reactive processing, extrusion, or injection molding
Engineering polymer blend	Polymer blend or polymer alloy that either contains or has properties of an engineering polymer
Interpenetrating polymer network (IPN)	Polymer alloy, containing two or more polymers in the network form, each chemically cross-linked. Sequential, simultaneous (SIN), and latex type IPNs are known
Thermoplastic IPN	Polymer alloy, containing two or more polymers in a co-continuous network form, each physically cross-linked. The cross-linking originates in crystallinity, ion cluster formation, presence of hard blocks in copolymers, etc.

market in volume for engineering resins and their blends was more than 22 billion pounds in 2012; polycarbonates and polyamides are the most prominent, and these account for about 60 % of the total market.

1.4.1 Benefits and Problems of Blending

The following material-related benefits can be cited:

(i) Providing materials with a full set of desired properties at the lowest price
(ii) Extending the engineering resins' performance
(iii) Improving specific properties, viz., impact strength or solvent resistance
(iv) Offering the means for industrial and/or municipal plastic waste recycling

Blending also benefits the manufacturer by offering:

(i) Improved processability, product uniformity, and scrap reduction
(ii) Quick formulation changes
(iii) Plant flexibility and high productivity
(iv) Reduction of the number of grades that need to be manufactured and stored
(v) Inherent recyclability, etc.

1.4.2 Compatibilization

The topic is extensively treated in ▶ Chap. 4, "Interphase and Compatibilization by Addition of a Compatibilizer" and ▶ Chap. 5, "Reactive Compatibilization", and thus only the key features are mentioned below. Several books and reviews also provide extensive information on the topic (Newman and Paul 1978; Kotliar 1981; Porter et al. 1989; Porter and Wang 1992; Brown 1992; Ajji and Utracki 1996; Datta and Lohse 1996; Utracki 1998a; Bucknall and Paul 2000; Robeson 2007).

It is noteworthy that in the absence of the configurational entropy effects (see ▶ Chap. 2, "Thermodynamics of Polymer Blends"), the miscibility of polymer blends depends on the balance of small enthalpic and/or non-configurational entropic effects. Sensitivity of this balance to small variation of the macromolecular structure is illustrated in the series of papers on miscibility of model polyolefins – e.g., see (Rabeony et al. 1998). Another example is provided by the photoisomerization initiated, reversible phase separation of PVME blends with stilbene-substituted PS (Ohta et al. 1998).

While miscibility is limited to a specific set of conditions, the immiscibility dominates – most polymers form immiscible blends that require compatibilization. Alloys' performance depends on the ingredients, their concentration, and morphology. The alloying process must result in *stable* and *reproducible* properties of polymer blends. Thus, the morphology must either be stable, unchanged during the forming steps, or the changes must be well predicted. The alloying makes use of an appropriate dispersing method (viz., mechanical mixing, solution, or latex blending) and compatibilization.

The latter process must accomplish three tasks:

1. Reduce the interfacial tension, thus giving a finer dispersion.
2. Stabilize the morphology against thermal or shear effects during the processing steps.
3. Provide interfacial adhesion in the solid state.

The compatibilization strategies comprise (i) addition of a small quantity of cosolvent – a third component, miscible with both phases, (ii) addition of a copolymer whose one part is miscible with one phase and another with another phase, (iii) addition of a large amount of a core-shell copolymer – a compatibilizer-cum-impact modifier, (iv) reactive compounding that leads to modification of at least one macromolecular species that result in the development of local miscibility regions, and (v) addition of a small quantity of nanoparticles which influence blend structure similarly to particle-stabilized water/oil emulsions.

Commercial alloys may comprise six or more polymeric ingredients. The increased number of components, n, increases the number of interfaces between them: $N = n(n-1)/2$. For such complex systems, it may be necessary to use an ingredient with highly reactive groups, capable of interacting with several polymeric components, e.g., such multicomponent copolymer as ethylene-glycidyl methacrylate, triglycidylisocyanurate, etc. Alternatively, one may carry a sequential blending, incorporating one polymer within another and then combining the preblends into the final alloy, hence reducing the number of interfaces that must be simultaneously controlled.

While the reduction of the interfacial tension, ν, is relatively easy by introduction of a macromolecular "surfactant," the stabilization of morphology and improvement of the interfacial adhesion in the solid state may not be so. One may use either a single compatibilizer that can perform all three compatibilization tasks, or a combination of agents, each playing one or two different roles. For example, stabilization of the desired dispersion (accomplished by addition of "surfactant" to mechanically mixed compound) may be accomplished by partial cross-linking of one of the three phases: matrix, dispersed, and the interphase. In the latter case, the interfacial adhesion in the solid state is also improved.

The density profile across the interface follows an exponential decay (see Fig. 1.1). The intercepts of the steepest tangential line with the horizontal lines defining the volume fraction of either one of the two polymeric ingredients, $\phi = 0$ and 1, define the thickness of the interphase, Δl (Helfand and Tagami 1971, 1972). Experimentally Δl varies from 2 to 60 nm (Kressler et al. 1993; Yukioka and Inoue 1993, 1994). Measurements of Δl have been used to map the miscibility region of PC/SAN blends when varying the AN content and temperature (Li et al. 1999a).

For high molecular weight polymer blends ($M \to \infty$), the Helfand and Tagami theory predicts that in binary blends (i) the interfacial thickness, Δl_∞, is inversely proportional to the interfacial tension coefficient, ν_∞, the product, $\Delta l_\infty \nu_\infty$, being independent of the thermodynamic interaction parameter, χ; (ii) the surface free energy is proportional to $\chi^{1/2}$; (iii) the chain ends of both polymers concentrate at the interface; (iv) any low molecular weight third component is repulsed to the interface; and (v) the interfacial tension coefficient increases with molecular weight

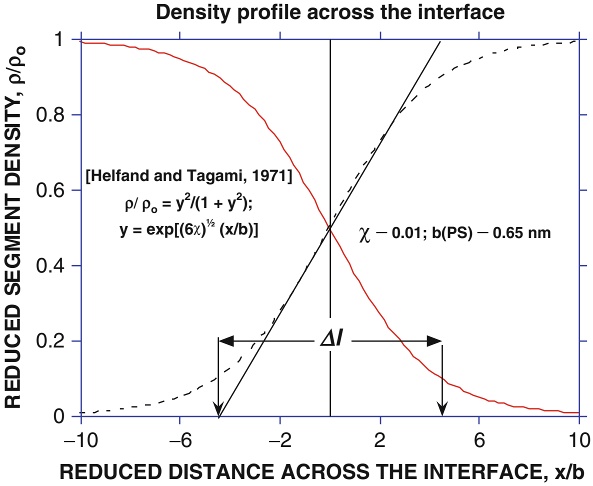

Fig. 1.1 Density profile across the interface, defining thickness of the interphase

to an asymptotic value: $\nu = \nu_\infty - a_o M^{-2/3}$. The value of ν can be measured or calculated from the molecular structure of two polymers, e.g., by means of the Hoy's group contribution method. The computed and experimental values of ν for 46 polymer pair showed good correlation with an average error of ± 36 % (Luciani et al. 1996, 1997).

The concentration dependence of ν_∞ may be expressed as (Tang and Huang 1994; Ajji and Utracki 1996)

$$\begin{aligned} \nu &= \nu_{CMC} + (\nu_o - \nu_{CMC})\exp\{-a\chi Z_c\phi\}; \\ d &= d_{CMC} + (d_o - d_{CMC})\exp\{-a\chi Z_c\phi\} \end{aligned} \tag{1.5}$$

where a and a_1 are adjustable parameters, Z_C is the copolymer's degree of polymerization, and subscript CMC indicates the "critical micelles concentration." It is important to note that ν and the diameter of the dispersed phase follows the same mathematical dependence.

The amount of compatibilizer required to saturate the interface, w_{cr}, can be expressed by the two limiting equations:

$$w_{cr} = 3\phi M / aRN_A; \qquad w_{cr} = 27\phi M / \left[\langle r^2 \rangle RN_A\right] \tag{1.6}$$

where ϕ is the volume fraction of the dispersed phase, R is the radius of the dispersed drop, N_{Av} is the Avogadro number, M is the copolymer molecular weight, $a \geq 5\ \mathrm{nm}^2$ is the specific cross-sectional area of the copolymer macromolecule, $\langle r^2 \rangle = KM$ is square end-to-end distance of the copolymer, and K is the characteristic parameter of the polymeric chain. The first equation in Eq. 1.6 was derived assuming that *all* compatibilizer's molecules cross the interface once, while the second assuming that di-block copolymer macromolecular coils are randomly deposited on the interface (Mathos 1993; Ajji and Utracki 1996). The reality is somewhere in between these two ideal cases. Both relations predict that the amount of copolymer required to saturate the interface is proportional to the total interfacial area expressed as ϕ/R.

Measurements of ν for the commercial resins' blends depended on the contact time of the two polymers. Helfand et al. theory predicts that owing to diffusion of low molecular weight ingredients to the interphase, ν should decrease with time. This indeed was observed for most blends, but an opposite effect was also seen for some PA/PO blends. The effect depended on the nature and amount of antioxidants and stabilizers in each resin. POs frequently contain acidic stabilizers, viz., sterically hindered phenols, (hydro)-peroxide decomposers (e.g., tris(2,4-di-tert-butyl phenyl)-phosphite), radical scavengers such as thio-derivatives (Herbst et al. 1995, 1998). When blending thus stabilized PO with PA, chemical reactions between the acidic stabilizers and -NH_2 of the PA chain ends result in formation of a rigid membrane. Measuring the interfacial tension coefficient as a function of the contact time shows increasing values of the interfacial tension coefficient. These time effects should be incorporated when predicting the blends' morphology (Luciani et al. 1996, 1997).

Initially, the most common method of compatibilization was an addition of a third polymeric component, either a block or a graft copolymer. It was assumed that the compatibilizer would migrate to the interface, broadening of the segmental concentration profile, Δl. There are several reports indicating that addition of a block or graft copolymer reduces ν and alters the molecular structure at the interface, but it rarely increases the interphase thickness. Another disadvantage of the addition method is the tendency for a copolymer to migrate to at least five different locations, forming saturated solutions and micelles in both phases, as well as the interphasial layer (block copolymers may also form mesophases). Hence, the copolymeric compatibilizer that is to be added to a blend should have:

(i) Maximum miscibility with the respective polymeric components.
(ii) Molecular weight of each block only slightly higher than the entanglement M_e.
(iii) Concentration just above CMC. In industry the time effects are important – the higher is the viscosity of the blend's components, the longer is the diffusion time, thus the slower the processing.

The morphology of commercial blends usually is far from equilibrium. Preparation of the alloys must take thermodynamic and kinetic parameters into account if the desired effects are to be achieved. The effects of copolymer addition on the dispersion size and blend performance have been studied (Hobbs et al. 1983; Fayt et al. 1986a; Armat and Moet 1993; Alsewailem and Gupta 2002). The interface/morphology relationship in polymer blends with thermoplastic starch has also been studied (Taguet et al 2009).

From the economic as well as the performance points of view, the reactive compatibilization is most interesting (see ▶ Chap. 5, "Reactive Compatibilization"). The process involves (i) sufficient dispersive and distributive mixing to ascertain required renewal of the interface; (ii) presence of a reactive functionality, suitable to react across the interphase; (iii) sufficient reaction rate making it possible to produce sufficient quantity of the compatibilizing copolymer within the residence time of the processing unit. The method leads to particularly thick interphase, thus good stability of morphology.

The reactive blending has been used since the beginning of the plastic industry. For example, two polyisoprene isomers, NR and GP, were softened by addition of $SCl_2 + CS_2$ and milled in a hot rubber mill. During milling, the solvent partially decomposed co-vulcanizing NR with GP (Parkes 1846). A patent from 1939 describes reactive blending of PVAl with multicomponent acrylic copolymers containing maleic anhydride (I. G. Farbenindustrie 1939). In the early 1940s, BASF used a corotating TSE for reactive extrusion of PA-6. Since the mid-1960, the reactive extrusion has been used for toughening and general modification of the engineering resins, viz., PA, PET, PC, or PBT. In 1971, Exxon patented styrene grafting of PE in reactive extrusion followed by blending with PPE for improved processability and excellent performance. Oxazoline-grafted polymers were used as compatibilizers in reactive blending of PC with PA. In 1975 du Pont started to manufacture the *super tough PA*, *Zytel-ST*™, by reactive blending of PA-66 with maleated ethylene-propylene-diene elastomer (EPDM-MA). The reactive compatibilization of the PPE/PA was developed in 1977 (Ueno and Maruyama 1979). More details on reactive compatibilization can be found in ▶ Chap. 5, "Reactive Compatibilization" as well as in a monograph published by Utracki (1998a).

It has been known for a long time that emulsions of low viscosity liquids can be stabilized not just by the use of surfactants but also by means of added nanoparticles (Pickering 1908). This behavior is found to carry over to polymer blends as well (Vermant et al. 2008; Fenouillot et al. 2009; Yoo et al. 2010). It is found that the morphology that results with the use of nanoparticles is finer than that in the case of pure blends since the interfacial tension is lowered. The morphology is also more stable against annealing. This effect is the result of the nanoparticles locating themselves at the blend interface and forming a solid barrier that inhibits drop coalescence. For this result to be observed, though, the size, shape, surface chemistry, and loadings of the nanoparticles must be tailored such that the Gibb's free energy of the interface is minimized when nanoparticles are located there. Else, there can even be transfer of nanoparticles from one phase to another (Goldel et al. 2012). A benefit of using nanofillers like carbon nanotubes in immiscible polymer blends is that the electrical percolation threshold can be significantly lowered (Goldel and Potschke 2011). This topic is explored in ▶ Chap. 17, "Polymer Blends Containing "Nanoparticles"".

It is imperative to mention that component polymer surfaces and interfaces play a major role in the properties and applications of blends such as in biocompatibility, switching, or adaptive properties. Whether it is an everyday plastic part or parts in automotives or in an airplane, not only the development of interfacial morphology but also the analyses of blends interfaces are equally important. The compatibilizing effect is primarily due to the interfacial activity of the constituent partners. This in turn raises the question of what are the effects of the molecular weight, concentration, temperature, and molecular architecture of the compatibilizer. Anastasiadis (2011) has reviewed interfacial tension in binary polymeric blends and the effects of copolymers as emulsifying agents. The diffused interface widths in binary blends such as PVC/EVA and PS/PMMA have been studied (Ramya 2013). When there is a large difference in compressibility between constituent polymers, Cho (2013) interpreted pressure coefficient of interfacial tension and argued that there exist a region that $\delta_\gamma/\delta P < 0$. Polymer surface and interface characterization techniques differ based on the environments (such as air, vacuum, liquid, etc.). Stamm (2008) has lucidly described several aspects of surface and interface characterization and provided a list of different techniques in which those could be applied. The other technique known as grazing incidence small-angle neutron scattering is also gaining attention due to its surface sensitivity in the investigation of nanostructures in thin films and at surfaces (Buschbaum 2013).

1.4.3 Morphology

The morphology depends on the blend concentration. At low concentration of either component, the dispersed phase forms nearly spherical drops, and then, at higher loading, cylinders, fibers, and sheets are formed. Thus, one may classify the morphology into dispersed at both ends of the concentration scale and co-continuous in the middle range. The maximum co-continuity occurs at the phase inversion concentration, ϕ_I, where the distinction between the dispersed and matrix phase vanishes. The phase inversion concentration and stability of the co-continuous phase structure depend on the strain and thermal history (Song et al. 2009, 2011). For a three-dimensional (3D) totally immiscible case, the percolation theory predicts that $\phi_{\mathrm{perc}} = 0.156$. In accord with the theory, the transition from dispersed to co-continuous structure occurs at an average volume fraction, $\phi_{\mathrm{onset}} = 0.19 \pm 0.09$ (Lyngaae-Jørgensen and Utracki 1991; Lyngaae-Jørgensen et al. 1999). The co-continuity contributes to synergism of properties, e.g., advantageous combination of high modulus and high impact strength in commercial blends. Detailed discussion of the phase co-continuity and its effect on morphology and rheology is given in ▶ Chap. 7, “Rheology of Polymer Alloys and Blends”.

When discussing the morphology, it is useful to use the *microrheology* as a guide. At low stresses in a steady uniform shear flow, the deformation can be expressed by means of three dimensionless parameters – the viscosity ratio, the capillarity number, and the reduced time, respectively:

$$\lambda \equiv \eta_d/\eta_m; \qquad \kappa = \sigma d/\nu; \qquad t^* = t\dot{\gamma}/\kappa = \gamma/\kappa \tag{1.7}$$

where σ is the local stress, η_d and η_m is the dispersed phase and matrix viscosity, respectively, $\dot{\gamma}$ is the deformation rate, and d is the droplet diameter. The capillarity number may be used in its reduced form $\kappa^* \equiv \kappa/\kappa_{\mathrm{cr}}$, where the critical capillary number κ_{cr} is defined as the minimum capillarity number sufficient to cause breakup of the deformed drop. The drop can break when $1 < \kappa^* < 2$.

For $\kappa^* > 2$ the drops deform into stable filaments, which only upon reduction of κ^* disintegrate by the capillarity forces into mini-droplets. The deformation and breakup processes require time – in shear flows the reduced time to break is $t_b^* \geq 100$. When values of the capillarity number and the reduced time are within the region of drop breakup, the mechanism of breakup depends on the viscosity ratio, λ – in shear flow, when $\lambda > 3.8$, the drops may deform, but they cannot break. Dispersing in extensional flow field is not subjected to this limitation. Furthermore, for this deformation mode κ_{cr} (being proportional to drop diameter) is significantly smaller than that in shear (Grace 1982).

The use of microrheology for the description of drop deformation and break was found to provide a surprisingly good agreement with experimental observations for the morphology evolution during compounding in a TSE (Utracki and Shi 1992; Shi and Utracki 1992; 1993). The predictive model (without adjustable parameters) was further improved by incorporation of the coalescence (Huneault et al. 1995a). A similar model has also been proposed (Moon and Park 1998).

The flow affects the blend morphology, but the structure variations also engender changes to the rheological response. The flow affects morphology in two ways – it changes the degree and type of dispersion on a local level and imposes global changes of morphology in formed parts. The latter effects originate from the flow-imposed migration of the dispersed phase that, for example, may cause formation of skin-core structures, weld lines, etc. The flow-imposed morphologies can be classified as (i) dispersion (mechanical compatibilization), (ii) fibrillation, (iii) flow coalescence, (iv) interlayer slip, (v) encapsulation, and others (Utracki 1995).

Flow may also cause mechanochemical degradation that generates reactive components, viz., radicals, peroxides, acids, etc. Transesterification, *trans*-amidation, and ester-amide exchange reactions during processing are well documented (their rate depends on the total interfacial area that in turn depends on flow) (Walia et al. 1999). These reactions may be responsible for the formation of compatibilizers that increase the interfacial area, affect the phase equilibria and the regularity of the main chain, and thus modify the degree of dispersion, blend's crystallinity, and, hence, performance. Use of cross-linked PE (XLPE) and different elastomers (EPDM, EVAc, butyls) as insulation materials is well known in the power distribution cable industries. Flow behavior and morphology of melt mixed blends of XLPE and silicone elastomers with and without compatibilizer (vinyl silane) have been studied (Mukhopadhyay et al. 1990). Surface morphology of the blends revealed the presence of a cross-linked microgelled silicone elastomer that seemed to disperse as a filler in the continuous XLPE matrix.

Miscibility of the blend components has an obvious effect on morphology (for detailed discussions, see ▶ Chap. 8, "Morphology of Polymer Blends"). During processing, the hydrostatic and shear stresses can change the lower critical solubility temperature (LCST) by at least 60 °C. This may result in formation (inside the processing unit) of a miscible blend. The blend emerging from the extruder may phase separate by the spinodal decomposition mechanism into a co-continuous structure, whose degree of dispersion can be controlled, for example, PBT/PC blends.

Stress-induced fibrillation occurs in a steady-state shearing or extension, when the capillarity ratio $\kappa > 2$. Under these conditions, flow is co-deformational. Since, $\kappa \propto d$, it is easier to fibrillate coarser dispersions where $\phi > a\lambda^b$ (the numerical value of the a and b parameters depends on the composition of the blend) (Krasnikova et al. 1984). Flow through a capillary of POM dispersed in a copolyamide (CPA) at $T = T_m(\text{POM}) + 6$ °C resulted in fibrils with diameters of about 20 μm and length 3.2 mm. Fibrillation of POM in EVAc strongly varied with λ. For $\lambda \approx 1$, the finest morphology was found (Tsebrenko et al. 1976, 1982). At temperatures slightly above the melting point, $T > T_m$, coalescence combined with stress-induced crystallization resulted in the formation of long fibers. The effect has been explored for performance improvement of blends comprising liquid-crystal polymers (LCP) (La Mantia 1993; Champagne et al. 1996).

The shear-induced interlayer slip was theoretically predicted – it creates a tree-ring structure in the extrudates (Utracki et al. 1986; Utracki 1991b; Bousmina et al. 1999). The relation may be used to describe the steady-state viscosity of antagonistically immiscible polymer blends, such as PP/LCP (Ye et al. 1991; Utracki 1986, 1991b).

The shear-induced segregation takes place in any system comprising flow elements with different friction coefficient, either miscible or immiscible (Doi and Onuki 1992). Migration of the low viscosity component toward the high stress regions may result in a flow-induced encapsulation. The effect has been well documented and successfully explored in polymer processing (Utracki 1987, 1988, 1989a, 1991a, 1995). For example, the high viscosity engineering resins with poor resistance to solvents, e.g., PC, PEST, or PEEK, can be blended with a low melt viscosity LCP. Extrusion through a die with sufficiently long land causes LCP to migrate toward the high stress zone near the die land, thus lubricating the die flow, improving the throughput, and enveloping the resin in a protective layer of LCP (Cogswell et al. 1981, 1983, 1984).

From an industrial viewpoint, polymer morphology can change due to physical aging even after a part has been extruded or injection molded, and this has implications on the performance of a polymer during service. Amorphous polymer melts when rapidly cooled to below their T_g form nonequilibrium structures which can relax over time by losing free volume (Struik 1978). As a consequence, mechanical properties can change, often for the worse. The use of polymer blends can retard this process since specific interactions such as hydrogen bonding and dipole-dipole interactions can restrict molecular mobility and increase long-term stability (Cowie and Arrighi 2010). Cowie and Ferguson (1989) have studied the physical aging of blends of PS and PVME using enthalpy relaxation and determined that the blend aged at a slower rate as compared to PVME alone.

In closing this section, we note that research interest in polymer blend miscibility is quite active as it affects final blend morphology. Recently, using a lattice-based equation of state, White and Lipson (2012) provided new correlations between the microscopic character of blend components and their bulk miscibility. These authors studied twenty-five polymer blend systems divided into two categories UCST and LCST and have found that the averaged difference between pure component energy parameters is significantly greater for LCST blends than for UCST blends.

1.4.4 Rheology

The rheology of polymer blends is discussed in detail in ▶ Chap. 7, "Rheology of Polymer Alloys and Blends". Here only an outline will be given. Since the flow of blends is complex, it is useful to refer to a simpler system, e.g., for miscible blends to solutions or a mixture of polymer fractions, for immiscible blends to suspensions or emulsions, and to compatibilized blends to block copolymers (Utracki 1995; Utracki 2011). It is important to remember that *the flow behavior of a multiphase system should be determined at a constant stress*, *not at a constant deformation rate*.

For miscible blends, the free-volume theory predicts a positive deviation from the log-additivity rule, PDB. However, depending on the system and method of preparation, these blends can show either a positive deviation, negative deviation, or additivity (Utracki 1989a). Upon mixing, the presence of specific interactions may change the free volume and degree of entanglement, which in turn affect the flow behavior (Steller and Żuchowska 1990; Couchman 1996). For immiscible blends, the flow is similarly affected, but in addition there are at least *three* contributing phases: those of polymeric components and the interphase in between. Flow of suspensions provides good model for blends with high viscosity ratio, $\lambda > 4$, while for blends with $\lambda \approx 1$, the emulsion model is preferred. The block copolymer is a good model for well-compatibilized polymer alloys.

The fundamental assumption of the classical rheological theories is that the liquid structure is either stable (Newtonian behavior) or its changes are well defined (non-Newtonian behavior). This is rarely the case for flow of multiphase systems. For example, orientation of sheared layers may be responsible for either dilatant or pseudoplastic behavior, while strong interparticle interactions may lead to yield stress or transient behaviors. Liquids with yield stress show a *plug flow*. As a result, these liquids have drastically reduced extrudate swell, $B \equiv \equiv d/d_o$ (d is diameter of the extrudate, d_o that of the die) (Utracki et al. 1984). Since there is no deformation within the plug volume, the molecular theories of elasticity and the relations they provide to correlate, for example, either the entrance pressure drop or the extrudate swell, are not applicable.

The concentration dependence of the constant-stress viscosity provides information on the inherent flow mechanism. The experimental data should be evaluated considering the log-additivity rule, $\ln \eta_b = \sum \phi_i \ln \eta_i$. There are five possible types of behavior, described as (1) positively deviating blend (PDB), (2) negatively deviating blends (NDB), (3) log-additive blends, (4) PNDB, and (5) NPDB. These can be described combining the emulsion model of polymer blends with the interlayer slip (Utracki 1991b; Bousmina et al. 1999). Owing to the variability of the blend structure with flow, the rheological responses are sensitive to the way they are measured. Since the structure depends on strain, the responses measured at high and low values of strain are different. For this reason, the selected test procedure should reflect the final use of the data. When simulation of flow through a die is attempted, the large strain capillary flow is useful. However, when the material characterization is important, the dynamic tests are recommended. The dynamic measurements of polymer blends at small strains are simple and reliable. The storage and loss shear moduli (G' and G'', respectively) should be first corrected for the yield stress and then analyzed for the relaxation spectrum (Utracki and Schlund 1987; Riemann et al. 1995; Friedrich et al. 1995).

Two types of rheological phenomena can be used for the detection of blend's miscibility: (1) influence of polydispersity on the rheological functions and (2) the inherent nature of the two-phase flow. The first type draws conclusions about miscibility from, e.g., coordinates of the relaxation spectrum maximum; cross-point coordinates (G_x, ω_x) (Zeichner and Patel 1981); free-volume gradient of viscosity, $\alpha = d(\ln\eta)/df$; the initial slope of the stress growth function, $S = d(\ln\eta_E^+)/d\ln t$; the power-law exponent $n = d(\ln\sigma_{12})/d\ln\dot{\gamma} \cong S$, etc. The second type involves evaluation of the extrudate swell parameter, $B \equiv \equiv D/D_o$, strain (or form) recovery, apparent yield stress, etc.

Compatibilization enhances dispersion, increases the total apparent volume of the dispersed phase, rigidifies the interface, and increases interactions not only between the two phases but also between the dispersed drops. These changes usually increase the blend's viscosity, elasticity, and the yield stress. The compatibilizer effects are especially evident at low frequencies. There are two mechanisms that may further affect these behaviors: (i) the copolymer may form micelles inside one or both polymeric phases instead of migrating to the interphase and (ii) an addition of compatibilizer may increase the free volume resulting in decreased viscosity.

The time-temperature, t-T, superposition principle is not valid even in miscible blends well above the glass transition temperature, T_g (Cavaille et al. 1987; Ngai and Plazek 1990; Chung et al. 1994). In miscible blends, as either the concentration or temperature changes, the chain mobility changes and relaxation spectra of polymeric components in the blends show different temperature dependence, thus the t-T principle cannot be obeyed. Furthermore, at the test temperatures, the polymeric components are at different distance from their respective glass transition temperatures, $T - T_{g1} \neq T - T_{g2}$, which affects not only the t-T superposition but also the physical aging time (Maurer et al. 1985). In immiscible PO blends, such as PE/PP, at best, the superposition is limited to the melt within narrow temperature ranges (Dumoulin 1988).

For most blends, the morphology changes with the imposed strain. Thus, it is expected that the dynamic low strain data will not follow the pattern observed for the steady-state flow. One may formulate it more strongly: *in polymer blends the material morphology and the flow behavior depend on the deformation field*, *thus under different flow conditions*, *different materials are being tested*. Even if low strain dynamic data could be generalized using the t-T principle, those determined in the steady state will not follow the pattern. Chuang and Han (1984) reported that for blends at constant composition, the plots of N_1 versus σ_{12} and G' versus G'' are independent of T. However, for immiscible blends, the steady-state relation may be quite different from the dynamic one. The agreement can be improved by means of the Sprigg's theory (Utracki 1989a).

Four measures of melt elasticity have been used: the first normal stress difference, N_1; the storage modulus, G'; and the two indirect ones, the entrance-exit pressure drop, P_e (*Bagley correction)*, and the extrudate swell, B. In homogeneous melts, the four measures are in a qualitative agreement. In the blends where the dispersed phase is rigid, B and P_e is small. By contrast, for the readily deformable dispersed phase, the deformation-and-recovery provides a potent mechanism for energy storage, leading to a large elastic response. In short, neither Bagley's entrance-exit pressure drop correction, P_e, nor the extrudate swell, B, should be used as a measure of blends' elasticity. In both cases, not the molecular deformation but the *form recovery* dominates the observed dependence.

Two contributions to the tensile stress growth function, η_E^+, should be distinguished: one due to the linear viscoelastic response, η_{EL}^+, and the other originating in the structural change of the specimen during deformation, η_{ES}^+. The first can be calculated from any linear viscoelastic function, while the second depends on the intermolecular interactions or entanglements, and its value depends on the total strain, $\varepsilon = t\dot{\varepsilon}$, and either strain rate $\dot{\varepsilon}$ or straining time, t (Utracki 1988, 1989, 1995; Takahashi 1996). Owing to the industrial importance of strain hardening, $SH \equiv \log(\eta_{ES}^+/\eta_{EL}^+)$, a large body of literature focuses on the optimization of blend composition to maximize SH. Since SH depends on the entanglement, either interchain reactions that lead to branched macromolecules, blending linear polymers with branched ones, synthesizing bimodal resins, or widening the molecular weight distribution may result in improved SH. Extensive work on SH has been done for PE blends, especially the ones comprising LDPE (Utracki and Schlund 1987). Several other resins with long-chain branching (viz., bPC, bPP, or a biodegradable polybutylenesuccinate, etc.) have been introduced as special grades for, e.g., film blowing, blow molding, wire coating, or foaming (Imaizumi et al. 1998).

The convergent flow at the die entrance provides strong elongational flow. In 1989 Laun and Schuch derived for Newtonian liquids that $P_e \approx 1.64\sigma_{12}$. The relation is satisfactory for homopolymers, but for the blend, the prediction is about one decade too low. On the other hand, this type of flow provides excellent means for mixing highly viscous dispersed phase. An extensional flow mixer (EFM) was developed. The device provides good mixing for multicomponent polymer systems, e.g., for blends with components having widely different viscosities, viz., PE with UHMWPE, PP with high elasticity EPR, and PC with PTFE (Nguyen and Utracki 1995; Utracki and Luciani 1996a; Luciani and Utracki 1996; Tokohisa et al. 2006).

1.4.5 Developing Commercial Blends

There are several methods of blending, viz., mechanical (dominant), solution, latex, fine powder, as well as several techniques adopted from the IPN technology. Not always the finest dispersion is desirable – the size and shape of the dispersed phase must be optimized considering the final performance of the blend.

The polymer blends' performance depends on the properties of the ingredients, their content, and morphology. Since the cost is virtually fixed by the material and the compounding method, the economy depends on blend's morphology, tailored for a specific application. Blends have been developed for economic reasons, viz., improvement of either a specific property (e.g., impact strength) or engendering a full set of required properties, extending engineering resin performance, improving processability, recycling, etc.

There are several approaches to evaluation of the blend economy. For example, the cost of a blend equals the weight average of material cost, plus the compounding cost per unit mass, e.g., $C_b = \Sigma w_i C_i + K$. Another approach is to calculate the cost-to-performance ratios for diverse materials and/or compositions. For example, one may ask *how much a unit of the tensile modulus or the strength at yield will cost* and optimize the composition accordingly. However, with growing frequency, the blend economy is based on the replacement calculations, comprising the total cost, that of material, compounding, forming, assembling, customer satisfaction, esthetics, service life-spans, and then the ease of disposal or recycling.

For a major resin manufacturer, blending provides means to improve and broaden the resin performance, and therefore, it enhances the demands and sale. By contrast, the resin user starts with a set of performance parameters that the material must possess. In both cases, the basic preposition is the same: *to have a blend with desired characteristics*, *one must use a component that already shows this characteristic*, or simply, *one cannot create something out of nothing*.

While extension of the engineering resin performance constitutes the largest part of the high-performance blends' production, the most difficult and interesting task is the development of blends with a full set of desired properties. To achieve this goal, a systematic approach has been developed (Utracki 1994). The procedure starts with the selection of blend components, each possessing at least one of the desired properties. For example, to improve impact strength, an elastomer should be used; to induce flame retardancy, a nonflammable polymer; to improve modulus, a stiffer resin should be incorporated; etc. Since for each property there are several candidates to select from, the selection is guided by the principle of the compensation of properties – advantages of one component should compensate for deficiencies of the other, e.g., the disadvantages of PPE (processability and impact strength) can be compensated for by those of HIPS. Next, the method of compatibilization, compounding, and processing must be selected. Since polymer blends' performance depends on morphology, the goal is to ascertain the desired structure by selecting an appropriate resin grade (rheology) as well as the methods of compatibilization, compounding, and processing.

Interesting studies on the morphology development during dispersive mixing were published by Kozlowski (1994, 1995). In this fundamental work, a rotating disk mixer was used. The disk had a milled grove in which stationary spreader was inserted. The gap clearance, speed of rotation, temperature, shape of the spreader, and pressure were controlled. The device simulated the dispersive processes that take place in internal mixers or extruders. A model of stepwise generation of morphology was proposed, where the original pellet (of the dispersed phase) undergoes deformation into elongated plates, which under stress break into fibers and finally into drops. The final morphology is a result of dispersion and coalescence processes that depend on the viscoelastic character of the component, the interfacial tension properties, and the stress history (see ▶ Chap. 9, “Compounding Polymer Blends”).

The ideal compounding unit should have (i) uniform elongational and shear stress field; (ii) flexible control of temperature, pressure, and residence time; (iii) capability for homogenization of liquids having widely different rheological properties; (iv) efficient homogenization before onset of degradation; and (v) flexibility for the controllable change of mixing parameters.

Most blends described in the patent literature have been prepared using either an internal mixer or a single-screw extruder (SSE). In standard configuration, SSE is inadequate for the preparation of blends with controlled morphology. Furthermore, due to the presence of “dead spaces,” the run-to-run reproducibility of the SSE-extruded blends may be poor. SSE should not be used for reactive blending. However, there are several designs of mixing screws, profiled barrel elements, and add-on mixing devices that ameliorate SSE mixing capability. From between the latter devices, RAPRA’s cavity transfer mixer (CTM) or the patented extensional flow mixer (EFM) should be mentioned. The first of these is a sort of “dynamic motionless mixer,” where material is transferred from the cavities in the barrel to those on the screw, enhancing the distributive mixing (Gale 1980). The EFM is a motionless device in which the extensional forces provide dispersive mixing for blends with components having widely different viscosities, viz., PE with UHMWPE, PP with high elasticity EPR, PC with PTFE, gel particles in reactor powders, etc. (Utracki and Luciani 1996a).

More expensive but easier to control is a twin-screw extruder, TSE. Owing to the modular design with many types of elements fulfilling different functions, TSE can be optimized for specific tasks. The ratio of the dispersive-to-distributive mixing can be adjusted, and the width of the residence time can be controlled. TSE is excellent chemical reactor for polymerization, modification of polymers, and reactive compatibilization (Rauwendaal 2001). As a result, the blend quality and run-to-run reproducibility are improved. Computer models have been developed to predict variation of blend’s morphology along the screw length in these machines (Shi and Utracki 1992, 1993; Huneault et al. 1993, 1995b).

1.4.6 Blends’ Performance

The quality of compounded blend affects the processing and performance. Layering, poor weld lines in injection molded parts, and skin-core extrudate structure with low notched Izod impact strength all indicate poor blend quality – either not adequate dispersion or poor stabilization of morphology. Compounding demands precise control of process variables. At the present, most alloys are prepared by reactive processing. It has been reported that pellet blending of two blend lots may lead to apparent immiscibility and bad weld-line strength. Evidently, even a small variation in the extent of reaction may make them immiscible. The mixed lots may pass standard tests, but still yield unacceptable products.

Historically, blending was used to improve the impact strength of the early resins, i.e., toughening of PS, PVC, PMMA, PET, PA, etc. With time, blends evolved into multipolymer systems that not only have to be impact modified but also compatibilized. Many blends have been formulated with a multicomponent modifier that simultaneously compatibilizes and impact-modifies the mixtures.

The following observations can be made: (1) The maximum toughening of brittle polymers has been obtained dispersing ca. 10 vol.% of a ductile resin with domain diameter of $d \approx 0.1–1.0\ \mu m$ –the lower limit is for resins that fracture by the shear banding, whereas the higher for those that fracture by the crazing and cracking (Bucknall 1977; Bucknall et al. 1984). (2) The phase co-continuity provides the best balance of properties, e.g., high rigidity in the presence of large deformability (or elongation). The properties depend on the thickness of the interpenetrating strands, thus also on compatibilization. (3) For the best barrier properties, the lamellar structure is desirable. To create it, the blend should comprise large but stable drops with diameter $d \approx 5–50\ \mu m$. During biaxial stretching (e.g., in blow molding or film-blowing processes), the large drops easily deform into lamellae.

Two types of mechanical tests are recognized: low speed (tensile, compressive, or bending) and high speed (impact). Poor compatibilization affects both. For example, in tensile tests the maximum strain at break and the yield stress can be dramatically reduced by poor inter-domain adhesion. Similarly, the lack of adhesion is responsible for low-impact strength – the specimens are brittle. Several toughening mechanisms have been proposed, viz., crazing, shear-banding, cavitation, particle debonding, elastic deformation of the toughening particles, etc. (Arends 1996).

Polymeric systems are roughly classified as either brittle or pseudo-ductile. The first type has low crack initiation as well as propagation energy and it fails by the crazing-and-cracking mechanism. Typical examples are PS, PMMA, and SAN. The second type has high crack initiation energy, but low crack propagation energy, and it tends to fail by yielding and shear banding. Typical examples are PA, PEST, and PC. As usual, there are some polymers, e.g., POM and PVC, which show intermediate behaviors – in many systems the fracture takes place by a mixed mode. The transition from brittle to ductile mode of fracture depends on the intrinsic properties of the material as well as on the external variables such as geometry, temperature, loading mode, test rate, etc. To detect the mechanism of fracture, the stress-strain, and the volume-strain dependencies should be known. “Toughness” is defined as the total area under the stress-strain curve, thus abruptly ending curves without the yield point are characteristic of brittle materials. The volume-strain dependence provides means for quantitative identification of the fracture mode – pure shear banding shows no volume expansion, whereas pure crazing and cracking show the maximum volume expansion.

Wu (1985, 1987, 1988, 1990) postulated that the brittle/ductile behavior of a neat amorphous polymer is controlled by two intrinsic molecular parameters: the entanglement density, ν_e, and the chain stiffness (given by the characteristic chain constant, C_∞). Assuming that crazing involves chain scission, the stress, σ_z,

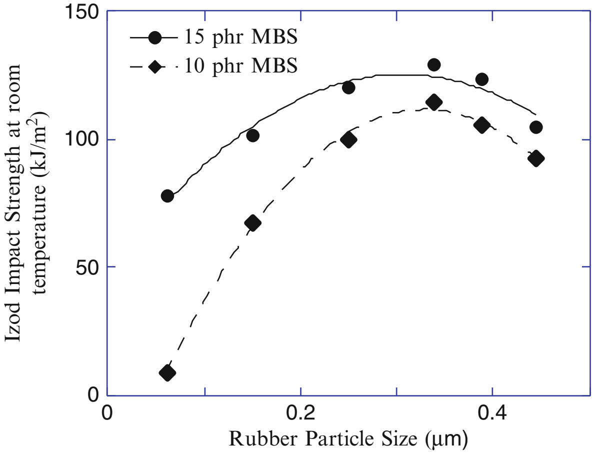

Fig. 1.2 Izod impact strength at room temperature as a function of diameter of elastomeric particles in methylmethacrylate-butadiene-styrene copolymer used for toughening polyvinylchloride resin (After Bartelo and Mori 1994)

should be proportional to $\nu_e^{1/2}$ and the yield stress, σ_y, proportional to C_∞. In consequence, $\sigma_z/\sigma_y \propto \nu_e\sqrt{3M_v/\rho_a}$, where M_v is the average molecular weight of a statistical segment and ρ_a is the polymer density. For brittle polymers, $\nu_e < 7.5$.

Effectiveness of the toughening process depends on the diameter of the elastomeric particles and their concentration. At constant concentration, the toughness versus particle diameter dependence goes through a maximum – abscissa of its location, d_{opt}, does not depend on concentration, whereas the ordinate does (see Figure 1.2). The optimum particle size, d_{opt}, depends on the entanglement density of the matrix resin, as well as on the fracturing and toughening mechanisms. In general, small particles, having weight-average diameters in the range of 0.2–0.4 µm, work well in the presence of shear yielding, while larger particles in the range of 2 and 3 µm are more effective in the presence of crazing (Bucknall and Paul 2009). Another important characteristic is interparticle spacing (Bucknall and Paul 2009, 2013).

However, the determination of the d_{opt} may be ambiguous, owing to the polydispersity of sizes as well as to inclusion of the matrix polymer inside the elastomeric particle. For example, it has been accepted that to toughen PS into HIPS, the optimum diameter is defined as a diameter of the elastomeric particles expanded by inclusion of the PS mini-drops. In PVC, the diameter of the elastomer was defined as the diameter of the original butadiene latex particle before grafting it with styrene and methylmethacrylate. In PC, the "optimum" diameter was defined by availability of the core-shell toughening agent – it is difficult to find toughness with elastomeric particles having diameter $d < 100$ nm. The strategy for the preparation of polymer blends with stable morphology demands that blends have thick interphase, $\Delta l \leq 60$ nm. Frequently it is impossible to decide how far the toughening by rubber core extends into the interphase. Many impact-resistant engineering resin blends have been formulated using a core-shell multicomponent copolymer with a *rigid* core and elastomeric shell whose thickness and affinity with the matrix resin was adjusted.

In many cases, toughening of a brittle polymer can be achieved by introduction of stiffness heterogeneity, viz., incorporation of an elastomer, immiscible polymer, solid particles, gas bubbles (i.e., foaming or microfoaming), etc. However, the size and concentration of these heterogeneities should be optimized. For most thermoplastics, the optimum diameter of the dispersed elastomeric particle is $d < 3$ μm and its volume fraction $0.05 < \phi < 0.10$. The accepted mechanism of toughening considers the heterogeneity to be a stress concentrator, generating excessive crazing and/or shear banding of the matrix, thus requiring higher amount of energy to cause fracture. The stress concentration factor was defined as $\gamma \propto 1/(1 - a\phi^{2/3})$ where the parameter a depends on the matrix (Bucknall 1977; Partridge 1992). For blends with pseudo-ductile matrix, d_{opt} depends on concentration, as it is important to keep the distance between the elastomeric particles approximately constant.

During the early works on compatibilization of PE/PS blends in Prof. Heikens laboratories, it was noted that addition of a small amount of one polymer to another improved impact properties. Since these two polymers are antagonistically immiscible and upon solidification void formed around the dispersed particles, it was concluded that it is the presence of the voids that accounts for the toughening effect (D. Heikens, 1982, private communication). About 15 odd years later, the microcellular blends have been introduced. For example, microfoamed blends of HDPE with PP (using CO_2 in an autoclave) showed significantly improved impact strength (Dorudiani et al. 1998). Similar enhancement of mechanical performance was reported earlier for N_2-microfoamed PS, SAN, or PC (Collias and Baird 1995). Now, microfoaming is being used to reduce the material consumption, part weight (by 30–50 %) (Kumar and Suh 1990), but it can also help to improve the mechanical performance, especially of the injection molded parts.

Under the triaxial stresses in the region ahead of the sharp crack, a particle may cavitate at a certain strain, changing the stress field of the matrix from the dilatation to the distortion dominated. Thus, the matrix may deform plastically, what consumes energy. The mechanism depends on the size of the dispersed toughening particles and the inherent plastic deformation capability of the matrix (Borggreve and Gaymans 1989; Lazzeri and Bucknall 1993; Yee and Shi 1995; Groeninckx et al. 1995). In PC cavitation occurred well before shear yielding (Parker et al. 1992). Blends comprising relatively high concentration of two engineering resins may require toughening of both phases by sequential reactive blending.

Formation of co-continuous structures in blends of either a brittle or pseudo-ductile resin with an elastomer may result in a quantum jump of toughness, without greatly affecting the key engineering properties of the high-performance resin. Commercial blends of this type, e.g., POM, PA, PC, or PET with an elastomer, are available (viz., *Triax*™ series).

1.4.7 Evolution of Polymer Alloys and Blends

The historical evolution of the polymer blend technology is presented in the following order:

1. Commodity resins (styrenics, PVC, acrylics, PE's, PP)
2. Engineering resins (PA, PEST, PC, POM, PPE)
3. Specialty resins (PSF, PAE, PARA, PAr, PPS, LCP, PEI, PEA, etc.)

Blends of polymer A with polymer B will be discussed following the adopted rules: (i) symbol A/B is used to identify any mixture of polymer A with B, independently of the concentration range or morphology, and (ii) the A/B blends are discussed under the name of the lower category polymer, i.e., blends of engineering or specialty polymers with a commodity resin are discussed in the category of commodity resin blends, blends of specialty polymers with engineering resins are discussed in the category of engineering resins, hence "specialty resin blends" consider only mixtures of two (or more) specialty resins.

1.5 Commodity Resins and Their Blends

Five large-volume polymeric groups belong to this category: polyethylenes, polypropylene, styrenics, acrylics, and vinyls. Their world market share remains relatively stable – the commodity resins represent 71 % of all consumed plastics.

1.5.1 Polystyrene (PS)

Simon in 1839 named the distillate of *Styrax officinalis* a *styrol*. By 1845, the thermal polymerization of styrene as well as the thermal depolymerization of PS was known. In 1915, I. G. Farbenindustrie started commercial production of PS, *Trolitul*™. Until the 1950s, PS was produced in small quantities – the resin was brittle, thermally unstable, with poor solvent and scratch resistance. The main use of styrene was in the manufacture of styrenics, viz., *Buna-S*, SBR, or ABS.

Common PS is atactic and amorphous. It has good optical clarity, low dielectric loss factor, modulus E = 3.2 GPa, strength σ = 45–65 MPa, density ρ = 1,050 kg/m^3, and CUT = 50–70 °C. Because of brittleness and low chemical resistance, the demand for neat PS has decreased, and except for foaming, PS is rarely used. PS can also be polymerized into crystalline forms: isotactic (iPS) or syndiotactic (sPS) with T_m = 230 °C or 272 °C, respectively. The former was polymerized using Ziegler-Natta catalyst (Ishihara et al. 1986), while the latter using a single-site metallocene titanium-based catalyst (Imabayashi et al. 1994).

The high-impact PS, HIPS, has been known since 1911 (Matthews 1911, 1913). In the USA, Ostromislensky (1924, 1926–1928) patented copolymerization of styrene with *rubber*, *balata*, *or other elastic and plastic gum*. Production of HIPS, *Victron*™, by the Naugatuck Chemical started in 1925, but soon it was discontinued.

PS is miscible with several polymers, viz., polyphenylene ether (PPE), polyvinylmethylether (PVME), poly-2-chlorostyrene (PCS), polymethylstyrene (PMS), polycarbonate of tetramethyl bisphenol-A (TMPC), co-polycarbonate of bisphenol-A and tetramethyl bisphenol-A, polycyclohexyl acrylate (PCHA), polyethylmethacrylate (PEMA), poly-*n*-propyl methacrylate (PPMA), polycyclohexyl methacrylate (PCHMA), copolymers of cyclohexyl methacrylate and methylmethacrylate, bromobenzylated or sulfonated PPE, etc. Information on other miscible blends may be found in ▶ Chap. 21, "Miscible Polymer Blends".

Similarly, poly-α-methylstyrene is miscible with PMMA, PEMA, PBMA, and PCHMA. Poly-*p*-methylstyrene and poly-*p*-t-butylstyrene show miscibility with polyalkyl(meth)acrylates. However, PS is immiscible with PMMA, PMA, polyethylacrylate (PEA), polybutylacrylate (PBA), or PBMA (Somani and Shaw 1981).

In miscible blends, it is important that both components are in the entangled state. In particular, during processing in the extensional flow field (e.g., blow molding, film blowing, wire coating, calendering, or foaming), an enhancement of strain hardening (SH) can only be obtained when the concentration of the high molecular weight component is at least comparable to the critical concentration of entanglement, $c \geq c^*$. Under these circumstances, large increases of SH were observed, e.g., for PS blended with ultra-high molecular weight PS (UHMW-PS) or SAN blended with ultra-high molecular weight PMMA (UHMW-PMMA). By contrast, addition of immiscible UHMW-PS to SAN did not show any improvement of SH (Takashi 1996; Takahashi et al. 1996; Koyama et al. 1997; Minegishi et al. 1997, 1998). Examples of blends that were evaluated for SH are listed in Table 1.8.

1.5.1.1 PS/Commodity Resin Blends

The most common immiscible PS blends are those prepared to improve the impact strength of PS or its copolymers, viz., HIPS or SBR (Table 1.9).

It was reported that incorporation of 0.1–18 vol.% of either acrylic or olefinic elastomer particles (e.g., in HIPS) into a thermoplastic (viz., PE, PP, PS, SAN, PEST, PPE/HIPS, PC, PEI, PA, fluoropolymers, etc.) resulted in excellent control of the foaming process (Campbell and Rasmussen 1994). The bubble diameter could be calculated from the concentration of rubber particles. When these were lightly cross-linked, the stretched membrane provided an excellent barrier against coalescence of gas bubbles. Thus, reliable nucleation and absence of coalescence lead to foaming stability. For example, in autoclave foaming of PS with N_2, the cell size was less than 40 μm, independently of the saturation pressure and only slightly increasing with the foaming temperature.

Postulating that the rubber particles are stretched to membranes all having the same thickness, the foam cell size can be expressed as

$$D_{cell} = D_o + \left(d^3_{rubber}/nt\right)^{1/2}; \quad n = 3 \text{ to } 6 \tag{1.8}$$

where D_{cell} is the cell size, d_{rubber} is the initial diameter of rubber particle, D_o is the diameter of foam cell in the absence of rubber particles, and t is thickness of the rubber shell after foaming. Depending on the initial assumption of

Table 1.8 Strain hardening in molten polymer blends

Polymers	Type	SH behavior (references)
PMMA/ UHMW-PMMA	Miscible	General rule: large enhancement of SH only for c(UHMW) $>$ c* $=$ 1.2 wt%; SH $\leq$ 10 (Minegishi et al. 1997)
PS/UHMW-PS	Miscible	Large enhancement of SH increasing with T; SH $\leq$ 10 (Minegishi et al.1998)
SAN/UHMW-PS	Immiscible	At 145 °C no effect on SH; SH $\leq$ 2 (Koyama et al. 1997)
SAN/UHMW-PMMA	Miscible	Large enhancement of SH; SH $\leq$ 10 (Koyama et al. 1997)
PE/UHMWPE	Miscible	Large enhancement of SH; SH $\leq$ 10 (Okamoto et al. 1998a, b; Kotaka 1998)
Bimodal POs	Miscible	Large enhancement of SH; SH $\leq$ 10 (Münstedt and Kurzbeck 1998)
LLDPE/LLDPE	Miscible	Average SH for the narrow and broad MWD LLDPEs (Schlund and Utracki 1987)
LLDPE/LDPE	Immiscible	Presence of LDPE increased linearly SH of LLDPE (Schlund and Utracki 1987)
		Enhancement of SH for c $\geq$ 10 wt% LDPE
LDPE/PS	With 0–5 wt% of SEBS	SEBS (micelles in LDPE phase) reduced the strain at break; additive SH; yield stress (Utracki and Sammut 1987, 1990)
LDPE/PS	Compatibilized	Better SH; the blends are suitable for foaming (Y. Horiuchi, 1998, personal communication)
PMMA/PVDF	Miscible	30 wt% of PVDF reduced SH of PMMA at 160 °C (Kotaka 1998)

Table 1.9 Toughening of PS

Composition	Reason	References
PS with SBR	Impact performance	Seymour 1951
PS with PIB and PSIB	Toughness	Sparks and Turner 1952
PS with PB and SBR	Toughness	Hayes 1956, 1967
PS with SBR and a cross-linked SBR	Toughness	Conrad and Reid 1963
PS with SBR and PEG	Toughness, adhesion, electrostatic dissipation	Briggs and Price 1963
HIPS (PS toughened by styrene-grafted EPR)	To improve weatherability	*Hostyren*™
HIPS with SBS	Enhanced properties	Durst 1970
PB reacted with styrene, ethyl- or methylstyrene, t-butyl styrene, and/or vinyl silanes	Low-density PO foams for marine or submarine applications	Dawans and Binet 1981
PS with SBR, $(SB)_n$, and PP	Toughness	Grancio et al. 1981, 1983
HIPS with a star-block copolymer, $(SB)_n$	Enhanced properties	Gausepohl et al. 1982
HIPS with a SB-block copolymer having small size of the rubber particles	Transparent HIPS	Asahi Chemical Industry 1982
HIPS with HDPE and SEBS	Enhanced properties	Murray 1982
HIPS with $BS(B'S')_n$ terminated with 2,4-di-*tert*-butyl-*p*-cresol and *tris* (nonyl-phenyl)phosphite	For adhesiveness	Shiraki et al. 1986

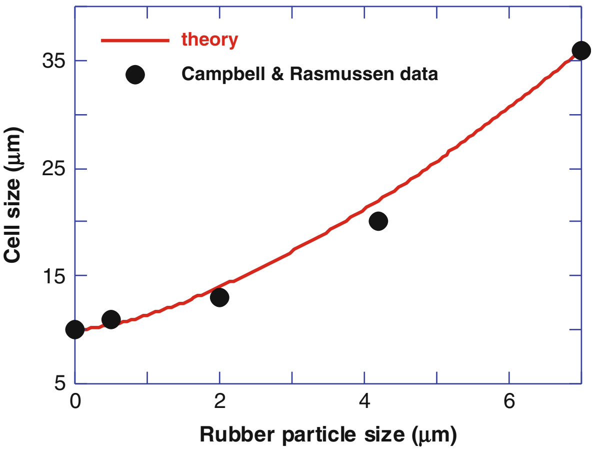

Fig. 1.3 Cell size versus the initial rubber particle diameter. Data points: (Campbell and Rasmussen 1994) *solid line* – Eq. 1.8 with n = 6, and the cell wall thickness t = 85 nm

Table 1.10 PS or HIPS with polyolefins

Additive	References
PE and CSR	Herbing and Salyer 1963
PE and styrene-ethylene bulk copolymer	Gorham and Farnham 1964
PO and EVAc	Yamamoto et al. 1971
Either PP or PE	Ogawa et al. 1973
5–95 wt% PS with 95–5 wt% PO and 0.5–10 wt% SEBS (foaming)	Zeitler and Mueller-Tamm 1977
PP and SEBS	Holden and Gouw 1979
1–99 wt% of either LDPE, LLDPE, HDPE, EVAc, PP, or EPR (chemical foaming to open-cell structures)	Tashiro et al. 1983
LLDPE	Canterino and Freudemann 1985; Canterino et al. 1986
Reprocessed PE/PS, compatibilized with 0.5–40 wt% of EVAc	McCullough and Stevens 1985
$\geq$ 60 wt% of partially neutralized ionic PS (e.g., a copolymer of styrene and acrylic acid) with $\geq$ 1 wt% PE ionomers, foamed with 3–20 wt% of $NaHCO_3$	Park 1986a, 1986b, 1988
PE or PP compatibilized with a nonsymmetrical 3-block copolymer, S1-D-S2	Hoenl et al. 1993
HDPE and either SBS or SIS	Swartzmiller et al. 1993, 1994

the cell geometry, the geometrical factor can be calculated as n = 3 to 6. Adequacy of Eq. 1.8 is shown in Fig. 1.3.

The second large group of styrenic blends comprises these with polyolefins – they are summarized in Tables 1.10 and 1.11. These blends are mainly used in packaging. Formulated for extrusion, injection, and blow molding, they show excellent processability, improved impact strength, low moisture absorption, and shrinkage. The performance characteristics (e.g., modulus, toughness, ductility, transparency, or gloss) can be controlled by composition and morphology.

Table 1.11 Addition of styrenics to PO

Additive to PE	Reason	References
1. Addition of styrenics to PE		
SAN	Improved crack resistance	Jankens 1963
5–20 wt% SBR	Impact strength	Dow Chem. 1963
SB, SBS, or a *p*-methylstyrene-b-isoprene copolymer	Improved crack resistance	Minekawa et al. 1971
Styrene-grafted HDPE	Higher modulus	Yui et al. 1978
ABS with CPE or low molecular weight PS	Impact strength	Kamosaki et al. 1978
SEBS	Mechanical properties	Davison and Gergen 1977, 1980
SBS or SEBS as compatibilizers for PS/PE	Recyclability	Lindsey et al. 1981
HIPS with HDPE and SEBS	Impact strength	Castelein 1982
PS/LDPE; MI ratio $R = MI_{PS}/MI_{PE} = 790$, weight ratio $Y = 10$ to $Y = [394.7 + 1.18R - 295.1 \log D]$; density: $D = \rho = 15–30\ kg/m^3$. R and Y control the co-continuous blends morphology	Flexibility, dumping small vibrations, stiffness, heat insulation, low water permeability	Hoki and Miura 1987
5–50 wt% PS with LDPE a chemical blowing agent and a peroxide (0.05–0.1 pph DCP)	Dimensionally stable, $\rho = 20–30\ kg/m^3$, cells 1.5 mm	Park 1986c, 1987, 1995
LDPE/PS = 80/20 blends compatibilized in a twin-screw extruder with supercritical CO_2	Studies of the rheology during closed-cell foaming	Lee et al. 1998
2. Addition of styrenics to PP		
PS or HIPS	For nacreous soda-straw tubes	Ogawa et al. 1973
ABS with either CPE or low molecular weight PS	Impact strength	Kamosaki et al. 1978
PS with HIPS and SEBS	Mechanical performance	Holden and Gouw 1979
PS was compatibilized by adding either SBS or $(SB)_n$	Higher modulus	Grancio et al. 1981, 1983
PS or HIPS and a nonsymmetrical, linear 3-block copolymer of styrene and butadiene, S1-D-S2, where the polystyrene blocks $S1 \geq S$	Processability, impact and stress-cracking resistance, impermeability to H_2O	Hoenl et al. 1993
PS with recycled PP – co-continuous morphology	Performance, recyclability	Morrow et al. 1994
sPP-co-sPS from single-site metallocene catalyst	Compatibilization of sPP/sPS	Razavi 1994
PP, EPR, EVAc, and PS blended with 1–50 wt% of the silane-modified-based resin, cross-linking catalyst and 1–20 wt% of a foaming agent	Resilient foams with superior, compression strength, and heat-insulating properties	Kobayashi et al. 1997

Other patents described similar blends prepared either by different methods or comprising different compatibilizer. For example, PO was mixed with styrene in the presence of an initiator that caused polymerization at temperatures below melting point of PO (Vestberg and Lehtiniemi 1994).

Interesting blends, having a broad range of properties, were prepared in two steps: (1) BR was grafted and cross-linked with either styrene or methylmethacrylate to produce a core-shell copolymer. (2) Next, it was blended with PO for improved processability, impact resistance, rigidity, etc. (Aoyama et al. 1993, 1994). Structural blends of styrene-grafted PP with either SBR, SBS, or an acrylic elastomer were developed (DeNicola and Conboy 1994).

Since the early 1990s, the constrained geometry metallocene catalysts have been used by Dow to produce either alternating or pseudo-random ethylene-co-styrene interpolymers (ESI) (Stevens et al. 1991). ESI with up to 50 wt% styrene is semicrystalline; it is known to compatibilized PE/PS blends since it forms domain structures into which the homopolymers can dissolve. ESI also has good melt strength, mechanical, impact, and damping characteristics (Ellebrach and Chum 1998). Flow and processing information on ESI were published (Karjala et al. 1998).

Himont (now Lyondell Basell) introduced a family of PP-based blends under the trade name of *Hivalloy*™. Some grades seem to be mechanical alloys of PP/PS, compatibilized and impact modified by incorporation of SEBS and EPR. Others are reactor made – here porous grains of PP serve as reaction beds for the polymerization and grafting of PS, SMA, acrylics, etc.

PS is one of the most frequently foamable thermoplastic resin. Blends that belong to this category are presented in Table 1.12. Blends containing $\geq$ 50 wt% PS (MW = 200 kg/mol) and acrylic copolymers were described as particularly useful for the manufacture of low-density foams. The acrylic copolymer contained methylmethacrylate and, e.g., 5 wt% of ethylacrylate. The presence of the copolymer facilitated foaming, but it reduced the foam compressive strength. The best balance was obtained using about 22 wt% of the copolymer. The foam had closed cells with cell diameter varying from 0.1 to 1 mm (Smith and Cross 1996).

1.5.1.2 PS/Engineering Resin Blends

The majority of PS blends that belong to this category are mixtures with PPE. Discovery of PPE miscibility with PS led to a family of *Noryl*™ blends, commercialized in 1965. Since that time, the PPE/PS blends were modified by the incorporation of a variety of additives. The PPE/PS blends show the glass transition temperature, T_g = 100–210 °C, continuously increasing with PPE content. The most often used compositions contain less than 30 wt% of PPE (PPE is about three times more expensive than PS).

PPE is the most "natural" additive that upgrades performance of PS to the required level. PS/PPE blends have been used as a replacement for PS in applications where higher HDT and/or impact strength is required. These alloys are easy to foam for the manufacture of, e.g., hot water piping insulation, in automotive applications, etc. Examples of PPE/PS blends are listed in Table 1.13.

Table 1.12 Foamable PS blends

Blend	Comment	References
PS with low concentration of siloxane-oxyalkylene copolymers	Reduced interface tension, easier bubble nucleation and growth, smaller cells	Granda et al. 1977
PS with radial teleblock SBS, PMS, naphthenic extender oil, formed at P = 1.4 MPa and then foamed using microwaves at 10–100 MHz	Molded articles had thin skin and uniformly foamed interior	Siedenstrang and Thorsrud 1984
PS with SAN, ABS, and 15–50 wt% of SMA	Chemical foaming ($NaHCO_3$) during injection molding	Sprenkle 1980
75–98 wt% of PS, 2–25 wt% of a BR (MW = 200–300 kg/mol)	Easy to foam due to fine dispersion of BR spheres	Henn et al. 1996
Mixtures of emulsion copolymers comprising acrylonitrile, butadiene, styrene, and acrylic or methacrylic acid	Low-density foams for non-wovens, carpets, fleece, or cardboard	Matner et al. 1977
SBR blends with 10–50 wt% of plastisol PVC	For foamed, flame-resistant carpet backing	Morgan and Ribaudo 1980
SBR, ABS, MABS, and/or SBS, with either PS, PO, PVC, PPE, PA, POM, PC, PSF, or PEST	For high impact strength moldings	Aoki et al. 1981
Polymer alloys of SMA and cellulose esters at a ratio varying from 1:100 to 100:1	Reaction between anhydride and cellulosic – OH facilitated foaming and gave good product performance	Heslinga and Greidanus 1982
5–35 wt% of SEBS, 65–90 wt% of PB-1, 5–30 wt% of EPR or EPDM, 2–15 wt% of LDPE	Foams had excellent bending capability, tear strength, stiffness, and HDT	Hwo 1996
Two SBR copolymers, (1) with of 53–75 wt% of styrene and (2) with 42–75 wt% of styrene	Cured foams for shoe soles with high shock absorption	Hashimoto and Ohashi 1985
ABS compositions	Foamed with supercritical CO_2 at $P \leq 5$ MPa	Kumar et al. 1995
45–90 wt% of PS or styrene-acrylic acid copolymer with 10–55 wt% of PVDC or vinylidenechloride-methyl acrylate copolymer	Physically foamed products had improved O_2 and H_2O permeability, toughness, and flame resistance	Romesberg 1991
PS, SMA, SAN, PMS, or HIPS blended with SBS and an extending oil and then incorporated into PA, PEST, PPS, SAN, ABS, ASA, PC, PPE, PO, their copolymers, or blends	A general method for the production of a variety of foamable injection moldings	Burnell 1993
75–97 wt% of either PS or HIPS and 3–25 wt% of an elastomeric (co) polymer having a $T_g < -20$ °C	Foamable materials with good performance characteristics	Blumenstein et al. 1994
Latex copolymers were blended, cross-linked, and foamed: (1) 20 wt% styrene, 20 wt% divinylbenzene, 60 wt% 2-ethylhexyl acrylate with (2) 80 wt% styrene, 20 wt% divinylbenzene	Pen-cell foams with great absorbency were prepared for baby dippers, for paint rollers, filters, etc.	Brownscombe et al. 1997

(*continued*)

Table 1.12 (continued)

Blend	Comment	References
ABS with ASA and two SAN copolymers were foamed with a physical foaming agent	Easy formability, excellent physical properties, and Freon resistance	Kim and Choi 1998
Blends of NR, SBR, BR, and SB copolymer that had 0–30 wt% of styrene and MW $\geq$ 30 kg/mol	Foamable rubber blend, suitable for tires or belts	Kawauzra et al. 1997

Table 1.13 Examples of PS/PPE blends

Modifier of PPE/PS blend	References
Elastomers such as PB, SBR, or NBR	Lauchlan and Shaw 1970
PB	Huels 1971
Poly(methylmethacrylate-co-styrene) and PO	Izawa et al. 1973a, b
Either SBR or ABS	Nishioka et al. 1973
Vinyl-terminated ethylene-propylene-styrene terpolymer (SEP)	Haaf 1979
PA-66	Mitsubishi Petrochemical 1982
Foaming with dry gases generated by the thermal decomposition of a dihydro-oxadiazinone + azodicarboxylic acid amide or ester	Kochanowski 1982
PPE-polyolefin graft copolymer and NBR	Mitsubishi Petrochemical 1983
Epoxy-terminated liquid PB, with either PP-MA or SEBS	Mitsubishi Petrochemical 1983
SBR and SBS copolymer	Mitsubishi Gas 1985
ABS and SAN	Japan Synthetic Rubber 1985
Hydroxynaphthoic acid	Tamura 1985
Ethylene glycol-propylene glycol copolymer (PEG-PPG)	Vaughan 1985
SBR and radial-SB copolymer	Sugio et al. 1987
PPE/PS closed-cell insulating foams, with high compressive strength	Allen et al. 1989; Weber et al. 1990
PPE/SAN with cross-linking and C3–C6 hydrocarbon blowing agents	Hahn et al. 1992
PPE with, e.g., PS, PMS, PES, PEI, PC, PA, PEST, PP, or PE and the blowing and nucleating agents	Bland and Conte 1993

Five *Caril*™ grades of expandable PPE/PS beads (diameter 0.3–0.5 mm) offer HDT up to 120 °C, thus are suitable for the production of microwavable and steam-cleanable packaging with the wall thickness $\geq$ 1 mm. The recommended density of molded product is $\rho = 60$ kg/m^3. Other foamable, flame-retardant PPE/PS blends, with good acoustic and thermal insulation properties, have been produced in suspension polymerization of a PPE solution in styrene and pentane. Resulting beads had diameter d = 0.5–1.0 mm and could be steam pre-foamed and compression molded in a standard equipment. The cited advantages are high HDT, non-flammability, dimensional stability, strength, stiffness, low molding cost, low density, easy lamination with decorative and weather-resistant ASA, and recyclability (Koetzing and Diebold 1995).

Table 1.14 Compatibilization of PS/PC blends by SAN

Additive to PC	Reason	References
Either SAN or styrene-allyl methacrylate-butyl acrylate-methyl methacrylate copolymer or with a *multilayered copolymer* from styrene, allyl methacrylate, benzyl acrylate, divinylbenzene	Toughening, high mechanical performance, solvent resistance	Kishida et al. 1978a, b
SAN and a styrene-grafted acrylic rubber	Improved mechanical properties	Kamata et al. 1979
PS and MBS	Higher modulus	Lee 1980

PS is antagonistically immiscible with all other engineering resins, viz., PA, PC, POM, and PEST. PS has been added to these polymers to improve processability and reduce cost without unduly affecting the performance (the so-called extension of the engineering performance).

Non-compatibilized blends of PS with either PEST or PEST and PMMA have been used for decorative applications or as the so-called plastic paper (Kamata et al. 1980). Similarly, PAr blends with either SAN (Brandstetter et al. 1983a, b, c) or high-performance blends of LCP with thermoplastic polymers (e.g., PP, PS, PC, PI) (Haghighat et al. 1992) showed adequate performance for the envisaged applications. However, most PS blends with engineering resins require compatibilization. Thus, for example, PS with PA-6 was compatibilized by addition of either methylmethacrylate-styrene copolymer (SMM) (Fayt et al. 1986b) or SMA (e.g., used in PARA/PS blends) (Lee and Char 1994). POM was blended with a small amount of either PS poly(α-methyl styrene) (MPS) or SAN and with particulate fillers (Tajima et al. 1991). PAr/PS blends were compatibilized with PAr-PS segmented copolymer (Unitika Ltd. 1983).

Several blends comprising PC and diverse styrenics, viz., ABS, SAN, SB, SBS, MBS, etc., are known (see Table 1.14). Similarly as for PVC blends (see Table 1.15), the strong interactions between AN and carbonyl groups of PC (in PVC it is the tertiary carbon) are responsible for the good performance. An interesting variation of the compatibilization procedure involved dispersing PC in water with vinyl monomer(s) that subsequently were polymerized. The in situ formed graft copolymers acted as a compatibilizer (Kanai et al. 1978; Kakizaki et al. 1979a). In 1974, polyphenylenesulfide, PPS, was blended with either PS or a styrene copolymer (Miyanishi 1976). Acid-base forces are responsible for strong molecular interactions. An understanding of specific forces is required if polymer blend systems are to be formulated, so as to satisfy steadily increasing demands on their performance and durability (Mukhopadhyay and Schreiber 1995).

Later, to provide a complete set of the required performance characteristics, multicomponent blends were promoted, for example, PC, PPE, ASA, SAN, PS, phosphate esters, PTFE, and SEBS (Niessner et al. 1993) or PC, PEST, ABS modified by incorporation of alkyl (meth)acrylates and glycidyl methacrylate, and PPE with either PS, HIPS, or SEBS and a polyalkyl(meth)acrylate (Laughner 1993).

Table 1.15 PVC/ABS-type blends

Additive to PVC	Reason	References
ABS	For either phonographic records or artificial leathers	Parker 1951; Schule 1952
5–30 wt% of either methylmethacrylate-acrylonitrile-butadiene-styrene(MABS)	High impact strength, mechanical properties	Himei et al. 1967
1–50 wt% ABS and post-chlorinated PVC	Improved processability, impact strength, and thermal stability	Kojima et al. 1970
ABS grafted with acrylonitrile-ethyl acrylate-styrene	Improved toughness	Tanaka et al. 1971a, b, c
ABS and SBS	Improved impact strength	Minekawa et al. 1971
MBS or MABS	Impact strength	Kumabe et al. 1973
Multilayer butadiene-styrene-divinylbenzene-butylacrylate-methyl methacrylate	Processability and high impact resistance	Usami and Ochiai 1976
Poly(2-cyano-5-norbornene) and ABS	Impact strength	Matsuura et al. 1978
PB grafted with styrene, methylmethacrylate, and maleic anhydride (ABSM-MA) or a mixture of ABS and SMM-MA	Processability, high impact strength, mechanical properties	Dufour 1982
Methylstyrene-styrene-acrylonitrile-grafted polybutadiene or with maleated styrene-methylmethacrylate-butadiene (ABS-MA)	Processability, high impact strength, mechanical properties	Dufour 1988
ABS and vinylchloride-ethylhexyl acrylate	Abrasion resistance	Greenlee et al. 1992
Core-shell copolymer: EPDM grafted with styrene-butadiene methacrylate or allyl cyanurate	Processability, high notched impact strength	Siol et al. 1993a, 1995
CPVC and PMMA, methylstyrene-acrylonitrile-methyl methacrylate, methylstyrene-acrylonitrile-styrene, imidized-PMMA, imidized-SMA, and SAN	Economy, high HDT and impact strength	Soby et al. 1994

1.5.2 Acrylonitrile-Butadiene-Styrene (ABS)

The first mechanical blends of NBR with SAN, known as “type-A ABS,” date from 1936. In the mid-1940s, Dow started emulsion polymerization of “ABS-type G.” By the late 1950s, the *high heat ABS* were invented, viz., interpolymers of α-methylstyrene and acrylonitrile (Irving 1961), a mixture of methylmethacrylate-α-methylstyrene either with styrene-grafted polybutadiene (SBR) or with an ABS (Kanegafuchi 1967, 1984), a mixture of SMA and ABS (Stafford and Adams 1972), a mixture of SMA with ABS and MBS (Tatuhiko and Akira 1982), a mixture of SMA-MMA with ABS, etc.

Acrylonitrile-styrene-acrylate terpolymers, known as either ASA or AAS, constitute another class of ABS resins, viz., *Centrex*™, *Luran*™ S, *Richform*™, *etc*. These materials may also contain reactive groups, viz., maleic anhydride or glycidyl methacrylate.

Weather-resistant ABS can be obtained either by the incorporation of EVAc (Fukushima and Mitarai 1971) or by replacing PB with EPDM to obtain AES (Wefer 1984, 1985, 1988). Alternatively, blends of SAN with maleated EPDM and CPE may be used (Kim et al. 1992). However, the non-weatherable styrenics are frequently prepared by dissolving an elastomer in methylmethacrylate and either styrene or α-methylstyrene, and then polymerizing them into methyl methacrylate-butadiene-styrene graft copolymers (MBS) (Ruffing et al. 1964; Schmitt et al. 1967). There is a great diversity of the MBS copolymers, viz., graft, core-shell, or multilayer type – lately also with acidic or epoxy groups (Lee and Trementozzi 1979, 1980, 1981, 1982; McKee et al. 1982; Keskkula et al. 1984).

1.5.2.1 ABS/SMA Blends

The ABS/SMA blends show excellent processability, high heat deflection temperature (HDT) low warpage, stiffness at high temperature, good impact strength, as well as solvent and chemical resistance. They successfully compete with PPE or PC alloys for the automotive applications (trim, instrument panels, roof linings, hubcaps, headlight housings), electronics, and electrical industry, houseware, appliances, power tools, industrial machinery, plumbing products, parts for washing machines and vacuum cleaners, etc. An example of commercial blends is *Cadon*™.

1.5.2.2 ABS/PVC Blends

There are several reasons for blending PVC with ABS-type copolymers, viz., to improve processability, mechanical properties, and low-temperature toughness. Good properties of these blends originate from the miscibility between PVC and SAN part of ABS. In some commercial blends, viz., *Geloy*™, ABS may be replaced by ASA to obtain improved miscibility and weatherability. For enhancement of HDT, SMA may also be added. The blends with more than 30 wt% PVC are self-extinguishing but are more difficult to process.

1.5.2.3 ABS/PC Blends

Blends of PC with 5–70 wt% ABS were developed in the early 1960s. The basic technology has been used to produce such alloys as *Bayblend*™, *Cycoloy*™, *Idemitsu*™ *PC/ABS*, *Iupilon*™, or *Triax*™ *2000*. The consumption of ABS/PC blends is increasing as the cost-to-performance ratio is low and properties are predictable (Khan et al. 2005). The alloys combine good processability of ABS with excellent mechanical properties, impact, and heat resistance of PC. The opaque blends show dimensional stability, low shrinkage and moisture absorption, high stiffness and hardness, good impact resistance at temperatures ($T \geq -50$ °C), excellent UV stability, processability, mechanical properties, heat resistance, flame retardancy, good chemical resistance, but poor to gasoline, aromatic hydrocarbons, esters, ketones, and some chlorinated hydrocarbon. The ABS/PC blends are being manufactured with either a dispersed or co-continuous morphology.

There are many similarities between ABS/PVC and ABS/PC blends. Both are immiscible, having three distinct phases of PVC or PC, SAN, and an elastomer

Table 1.16 PC/ABS-type blends

Reason	Additive to PC/ABS	References
Toughness	10–70 wt% ABS	Grabowski 1964a
HDT and stiffness	Styrene-α-methylstyrene-acrylonitrile, PSF	Grabowski 1970, 1971, 1972
HDT an impact resistance	MBS and PAES	Yamauchi et al. 1974
Processability, HDT, impact resistance	Polyethersulfone, PES	Weaver 1972
Flow, weatherability, thermal, and mechanical performance	EVAc	Hasegawa et al. 1974
Pearl-like iridescence, dyeability	PMMA	Ikura et al. 1974
Heat resistance, dimensional stability	PVC	Hardt et al. 1975
Mechanical performance	CPE grafted with SAN	Kabuki et al. 1973
Processability, impact strength	Skin-core graft copolymers of styrene and acrylonitrile on elastomeric latex particles	Sakano et al. 1978
Solvent and impact resistance	MBS and acrylic elastomer	Kitamura 1986

(Suarez and Barlow 1984). The blends are compatibilized by the dipole-dipole interactions between PC and SAN, particularly evident in SAN with ≥ 25 wt% AN (Kim and Burns 1988, 1990). ABS/PC blends can also be compatibilized by incorporation of either acrylic, acidic, or epoxy groups (see Table 1.16).

In the late 1970s, the reactive blending of PC/ABS began to dominate the technology. Initially, the PC blends with ABS modified by incorporation of the maleic anhydride moieties (ABS-MA), later ABS with acrylic acid groups (ABS-AA) were developed. The third generation blends comprise ABS modified by copolymerization with glycidyl methacrylate (ABS-GMA). Examples are listed in Table 1.17.

In 1983, Monsanto developed blends with co-continuous morphology, *Triax™ 2000*. These alloys comprised PC, ABS, and styrene-methylmethacrylate-maleic anhydride (SMMA-MA) (Jones and Mendelson 1985). One year later, PC was reactively blended with either ABS, SAN-GMA, or NBR or with graft copolymers of acrylonitrile-butadiene-α-methyl styrene-methyl-methacrylate (MeABS) and acrylonitrile-α-methyl styrene-methyl methacrylate copolymer (MeSAN) (Kress et al. 1986). The blends were commercialized by Bayer as *Bayblend*™.

In 1992, low gloss and moldable blends, with electrostatic discharge properties, were developed. They comprised PC, ABS, and either a graft copolymer of styrene, hydroxyethyl methacrylate, and acrylonitrile bonded onto a 1,3-butadiene rubber (ABS-HEMA), styrene-acrylonitrile-methacrylic acid copolymer (SAN-MAc), styrene-acrylonitrile-hydroxyethyl methacrylate (SAN-HEMA) or an acrylonitrile polymer containing gels (Vilasagar and Rawlings 1994). *Cycoloy*™ is the PC/ABS blend from General Electric Co (now SABIC).

Table 1.17 PC/ABS reactive blends

Composition	Reason	References
PC with ABS and rubber-modified SMA	Processability, impact strength, heat resistance	Henton 1980, 1982
PC with SAA and EMMA	Impact strength, mechanical properties	Thomas 1982
PC with ACM and SAA	Impact strength and HDT	Henton 1984
PC/ABS with EAA acidic compatibilizer	Processability and impact strength	Grigo et al. 1984
PC/ABS with SMA-AA	High HDT and impact strength	Brandstetter et al. 1982a, b, c; 1983a, b, c
PC/ABS with SMM-GMA	Processability, impact strength, and heat resistance	Daicel 1982, 1983, 1984
PC/MBS with SAN and PEST	Impact strength and thermal stability	Teijin Chem. 1980
PBT, PC, ABS, and PB grafted with acrylate esters and AN, ACM	Rigidity, flowability, solvent resistance, impact strength, dimensional stability	Bier and Indner 1982; Neuray et al. 1982
PC, PEST, polyester carbonate, etc., with 30–90 wt% of SMA + ABS and 2.5–20 wt% of a chemical blowing agent	Foamable engineering blends having excellent physical performance	White and Krishnan 1989
PC, PEST, or PEI with 1–50 wt% of ABS and a chemical foaming agent	Moldable blends for chemical foaming	Allen and Avakian 1987

1.5.2.4 ABS/PA Blends

ABS/PA mixtures are immiscible; hence, the standard three strategies are applicable: (i) addition of a small amount of ABS to improve PA toughness without a compatibilizer, (ii) generation of non-compatibilized blends with co-continuous morphology, and (iii) compatibilized blends in the full range of composition. ABS is an amorphous resin, while PAs are semicrystalline; hence, it is advantageous to incorporate ABS as either a dispersed or a co-continuous phase – the latter being preferred. However, addition of semicrystalline PA to ABS increases mold shrinkage, and thus, addition of filler is advised. Owing to high processing temperatures of PA, it is essential to use high heat ABS. For the adequate impact performance, at least 10 wt% of ABS should be added, but at this level, the compatibilization is required. The reactive compatibilization involves the use of ABS that has been modified by incorporation of either acrylic acid, maleic anhydride, or polyvinylphenol (PVPh).

The reason for blending ABS with PA is to reduce moisture sensitivity, improve toughness, and reduce shrinkage and warpage of the latter resin. The alloys show good processability; surface finish; high heat stability; a chemical, oil, wear, and abrasion resistance; dimensional stability; low-temperature impact strength; reduced moisture sensitivity; and economy. Synergistic properties have been reported. Examples of commercial alloys are *Stapron*™ *N*, *Novalloy*™-*A*, *Techniace*™ *TA*, *Triax*™ *1000*, *Ultramid*™, and *Macslloy*™ (Utracki 1994). Also, in a series of papers, Kitayama et al. (2000a, b, 2001) have described the blending of PA6 with SAN.

The first ABS/PA blends were announced in 1961 (Grabowski 1964b, 1966) and much later introduced as *Elemid*™. *Triax*™*-1000* is an alloy of PA-66 with ABS-MA, having the phase co-continuity (Lavengood et al. 1986, 1988). PA-6 was also blended with BR grafted with styrene and MA (SBMA) (Asahi-Dow Ltd. 1981). Later, transparent blends of copolyamide(s), PA, and ABS were developed (Fox et al. 1989). Blending either ABS-MA or EPR-MA, with amine-terminated PA or PEST, resulted in alloys with excellent performance (Akkapeddi et al. 1990, 1992a, 1993; Okada et al. 2004). Similarly, either ABS-MA or ABS-GMA copolymer was used to compatibilize and to toughen PA blends with other resins, viz., PC, PEST, or PAr (Yuichi and Suehiro 1989). Later the role of elastomer, its type, and location in the PA-66/SAN/Elastomer system was studied (Nair et al. 1997, 1998).

1.5.2.5 ABS/PEST Blends

The thermoplastic polyesters (PEST) are dominated by two resins: polyethylene terephthalate (PET) and polybutylene terephthalate (PBT). There are similarities between ABS/PA and ABS/PEST blends.

In blends with ABS, a part of PEST may be replaced by PC, and 10–20 wt% of an impact modifier may also be added, e.g., MBS, poly(methylmethacrylate-g-butadiene-co-styrene), poly(MMA-g-n-BuA), high rubber ABS ($\geq$ 50 wt% PB), or ASA with $\geq$ 50 wt% acrylate rubber, etc. Examples of commercial blends are *Alphaloy*™ *MPB*, *Cycolin*™, *Diaalloy*™ *B*, *Malecca*™ *B*, *Maxloy*™, *Lumax*™, *Triax*™ *4000*, and *Ultrablend*™ *S*. The alloys show excellent moldability, low post-molding shrinkage and warpage, stress-crack resistance, high gloss, high temperature stiffness, toughness and mechanical strength, high heat resistance at temperatures $T \leq 140\ ^{\circ}C$, low shrinkage, good dimensional stability, impact strength, good wear and abrasion resistance, good thermal and weathering resistance, as well as solvent (e.g., to gasoline and motor oils) and chemical resistance. An abbreviated evolution of the PEST/ABS technology is summarized in Table 1.18.

Table 1.18 PEST/ABS blends

Composition	Reason	References
PET with MBS	Notched impact strength and embrittlement resistance	Sauers and Barth 1970
PAr with ABS	Processability and impact strength	Koshimo 1973
PBT/ABS/SEBS	Stable morphology	Gergen and Davison 1978
PBT with carboxyl-modified ABS	Chemical, solvent, and impact resistance	Tanaka et al. 1979
PBT + PET or PC, with ABS or ACM (rubber particle diameters $d \cong 0.4$ μm)	Impact strength and balance of other properties	Bier and Indner 1982; Binsack et al. 1982
PBT with either ABS-MA or ABS-GMA	Heat, chemical, and impact resistance	Orikasa et al. 1989
PET or PBT with an AES-GMA (*Techniace*™)	Flowability and good balance of properties	Hirai et al. 1988, 1989, 1992

1.5.2.6 ABS/TPU Blends

Developed in the early 1960s, ABS/TPU blends combine TPU's toughness and paintability with ABS's low-temperature impact strength and adequate HDT. The main advantage is the excellent impact behavior at $T \geq -40$ °C. Furthermore, TPU improves antifriction properties, abrasion, and chemical resistance. Stiffness is also increased and the flowability of injection molding compounds is good. ABS is usually dispersed in the TPU matrix. TPU was also successfully blended with SBR grafted with acrylonitrile, acrylate, or methacrylate esters (MABS) (Abe et al. 1977), with SMM-MA copolymer (Gomez 1992), and with bulk-polymerized ABS (Henton et al. 1992). Depending on the type of TPU, compatibilization may be necessary. Examples of commercial alloys are *Prevail*™ and *Techniace*™ *TU*.

1.5.2.7 ABS/PSF Blends

In these blends, ABS's role is to improve flowability and reduce cost, while that of PSF is to improve the shape retention at high temperatures. ABS/PSF blends are compatibilized either by *phenoxy*, EVAc-GMA, or SMA copolymers. They have good processability, high notched Izod impact strength, plateability, hydrolytic stability, and economy. However, they may show poor surface and weld-line strength. *Arylon*™ and *Mindel*™ *A* are examples of the commercial ABS/PSF alloys, while *Ucardel*™ is an example of PSF blends with SAN. Evolution of ABS/PSF blends' technology is summarized in Table 1.19.

Table 1.19 PSF/ABS blends

Composition	Reason	References
PSF with 40–52 wt% ABS and poly (α-methyl styrene-co-AN)	Excellent flow, good impact resistance, non-flammability	Ingulli and Alter 1969, 1970
Polyarylethersulfone (PAES) with AES	Toughness and impact strength	Barth 1970
ABS with equal amount of PSF and PC	Processability, rigidity, and impact strength	Grabowski 1971, 1972
PAES with EVAc and/or MBS	Tensile, flexural, and impact strength	Lauchlan 1971
PAES with PC and either MBS or ABS	High HDT and impact resistance	Yamauchi et al. 1974
PSF with 10 wt% anhydride-terminated PSF and MABS	Excellent HDT and impact resistance	Aya et al. 1979
PSF with AES	Thermal stability and impact strength	Sumitomo 1982
PSF with cross-linked acrylate copolymer, cross-linked SAN, and uncross-linked SAN	Good tensile modulus, yield strength, impact resistance, and respectable HDT = 106 °C	Robeson 1985
PSF/ABS with EVAc-GMA	Processability, HDT, and impact strength	Orikasa and Sakazume 1990, 1992
PSF with 25–45 wt% semicrystalline PPS and 0–10 wt% MBS	resistance to impact, high temperatures, and adverse environmental conditions	Golovoy and Cheung 1994

1.5.3 SBS Block Copolymers

In 1961, using lithium catalyst, a series of styrene-isoprene (SI) and styrene-butadiene (SB) block copolymers were synthesized (Bull and Holden 1977). The resins had $T_g \approx -90$ to $+90$ °C. Full-scale production started in 1965. Since then, numerous two- and three-block copolymers have been developed, with hydrogenated and maleated block copolymers also being offered. With the world consumption of 330 kt/year, the block copolymers constitute the largest part of the commercial TPE market. Large quantity of SBS resin is used in blends. Commercial resins include *Elexar*™, *Collimate*™, *Finaclear*™, *Kraton*™, *Thermolastic*™, and *Tufprene*™.

1.5.3.1 SBS/SEBS Blends with Commodity Resins

SBS copolymers are used in blends as compatibilizers, impact modifiers, or stabilizers of morphology and performance. As shown in Table 1.20, they have been

Table 1.20 SBS blends with other styrenics

Composition	Reason	References
PVC with ABS and SBS	Toughness and performance	Minekawa et al. 1971
SBS with PS, EVAc, and other ingredients	For elastic films	Hinselmann et al. 1973
HIPS with 12.5 wt% PB and SBS	Excellent impact strength	Durst 1970, 1975
SIS with PS and/or IR	Optical and mechanical properties	Kawai et al. 1978
PS and/or HIPS with PP and SEBS	Impact and tensile strength, solvent resistance	Holden and Gouw 1979
Poly-*p*-methylstyrene (P*p*MS) with SBS	Impact strength and clarity	Sherman 1981, 1983
AN-grafted SEBS with SAN	Weatherability, impact strength	Paddock 1981
PS with $(SB)_n$ and SBR	Impact strength, transparency	Asahi Chemical 1982
SEBS dissolved in styrene, methacrylic acid, and isoprene and then polymerized	Thermoplastic IPN, with superior mechanical properties	Siegfried et al. 1984
SEBS-type IPN with carbon black, CB	Electrically conductive blends	Sorensen 1984
PS with AXBXA or $(AXB)_n$ (A = styrene, B = butadiene, X = AB tapered block)	Impact strength, and transparency, superior to that observed for SBS/PS blends	Toyama et al. 1985
SBS (acidic, amino, imido-terminated) and PA, PEST, TPU, POM, PVAl, PC, PSF, PPE, PPS, or PVC	Water-swelling materials for civil engineering, construction, etc.	Shiraki and Hattori 1986, 1994
SMMA, a tapered SB and ductile SBS, *Zylar*™	Transparent (extremely low haze), impact resistant	Blasius 1992, 1994
HIPS, PE, and either SBS or SIS; a co-continuous morphology	Chemical, solvent, and stress-cracking resistance	Hoenl et al. 1993; Seelert et al. 1993
SMMA and either a mixture of SBS and a tapered BSB triblock copolymer or SBR	Transparent, low haze, high impact, craze, and γ-radiation resistance	Hauser et al. 1993

Table 1.21 SBS Blends with polyolefins

Composition	Reason	References
PP with 20 wt% of either SBS or SIS	High impact strength, without adverse effect on other properties	Japan Synthetic Chemical Ind. 1971
PP blends with 6–8 wt% SEBS	Transparency and impact strength	Porter 1972
SBS with 20–30 wt% PO	Processability, mechanical properties	Tabana and Maki 1976
PS with HIPS, PP, and SEBS	Performance, co-continuous morphology	Holden and Gouw 1979
SEBS with diverse polymers, including PE	Dispersed drops of d = 200 nm	Davison and Gergen 1980
PP/PS with either SBS or $(SB)_n$	Moldability and mechanical properties	Grancio et al. 1981, 1983
HDPE with PS and SEBS	Superior performance over HDPE/PS	Lindsey et al. 1981
HIPS with HDPE SEBS	Impact strength	Castelein 1982
LLDPE with SEBS	Transparent, impact resistant	Holden and Hansen 1989
PS, LLDPE, and SEBS	Impact strength, lack of yellowing	Seelert et al. 1993
PP and PET reactively blended with maleated SEBS	Rigid blends with good impact strength and adhesion to solids	Tekkanat et al. 1993, 1994
PA/PO/SEBS compatibilized by SMA	Moldable, good impact strength	Chundury 1993, 1994
PO with PA, PET and styrenics	Recycled commingled scrap	Weber et al. 1994
SBS, EVAc, PS, and LLDPE or ULDPE	Elastomeric films	Djiauw 1994
PO with SEBS, SEPS, SEB grafted with maleic anhydride acrylic or sulfonic acid	Moldable resin with good impact strength, scratch, and abrasion resistance	O'Leary and Musgrave 1993
PP with either SBR, SBS, or an acrylic elastomer, and PP grafted with styrene	Stand-alone structural materials	DeNicola and Conboy 1994

frequently incorporated along other styrenics. There are many patents for mixtures of PO with SBS-type copolymers. Their history is outlined in Table 1.21.

1.5.3.2 SBS Blends with Engineering Resins

Since the anionically polymerized block copolymers are relatively expensive, they have been more frequently used in blends with engineering than commodity resins. Owing to miscibility of styrene blocks with PPE, the SBS and SEBS are "natural" tougheners for this polymer. However, for blending with PEST, PC, POM, or PA, the copolymer should be modified by incorporation of acidic, acid anhydride, or epoxy moieties.

SBS with Polyphenylene Ether (PPE)

Evolution of PPE blends with SBS-type block copolymers is summarized in Table 1.22. SBS or its derivatives have been frequently used to stabilize the morphology in more complex blends. In Table 1.23 examples of this type of system are presented.

Table 1.22 SBS Blends with polyphenylene ether

PPE modifiers	Reason	References
PPE with 10–90 wt% SBS	Processability and toughness	Kambour 1970
PPE with SEBS	Processability	Haaf 1979
SBS- or EPDM-modified PS and SEBS	Flow, impact, and thermal properties	Lee 1979, 1980, 1982, 1983, 1985
HIPS and SB di-block copolymer	Impact strength and solvent resistance	Brandstetter et al. 1982a, b, c
Styrene-phenyl-maleimide copolymer and either SB, SBS, or SEBS	HDT, chemical, solvent, and impact resistance	Fukuda and Kasahara 1982
HIPS, styrene-grafted EPDM and/or SB grafted with EGMA	Impact strength and processability	Ueno et al. 1982a, b
SBR, SBS, and EPR	Processability and impact strength	Mitsubishi Gas 1982
HIPS, SEBS, and PE	Processability and impact strength	Haaf 1983
Styrene-grafted PPE, PPE-S with SBR and SB	Processability, gloss, toughness, and tensile strength	Izawa et al. 1983
HIPS, SBS, SBR, EPR, and hydrogenated poly(bisphenol-A-phosphite)	Impact strength, processability, and flame retardancy	Sugio et al. 1984
ABS and SEBS	Moldability, toughness, strength	Ueda and Sasame 1986
PS, SBR, and SBS	Plateability and mechanical properties	Mitsubishi Gas Co. 1985
HIPS, SEBS, and LLDPE	High impact strength	Hambrecht et al. 1986
HIPS and either SB, SBS, or $(SB)_n$	Cracking and impact resistance	DeMunck and Lohmeijer 1986

SBS with Polyamides (PA)

SBS or SEBS has been used as an impact modifier in PPE/PA blends, with PA usually being the matrix and PPE an organic, low-density filler. The blends were developed in the early 1970s by the Asahi Chemical. By the end of the decade, the first reactive blends were announced by the Sumitomo Chemical (Ueno and Maruyama 1981) and General Electric (Van der Meer et al. 1989).

The simple, SBS/PA blends were in parallel development with the PPE/SBS/PA ones. Addition of SBS to PA improved the tensile and impact strength of the latter resin. The blends comprise either 1–25 wt% SBS as a dispersed or at higher concentration as co-continuous phase (see Table 1.24).

SBS with Thermoplastic Polyesters (PEST)

The development of PEST/SBS blends parallels that of the PA/SBS ones. First, blends of PBT, ABS, and SEBS were disclosed (Gergen and Davison 1978). Four years later, the reactive compatibilization was discovered – PBT was blended with SEBS and SMA (Durbin et al. 1983). By the end of 1970s, multicomponent blends comprising PBT, PET, PC, and either SEBS, $(SB)_n$, butadiene-caprolactone-styrene,

Table 1.23 SBS in PPE multicomponent blends

Additives	References
PPE with PA-66, PS, maleated PP, and SEBS	Fujii et al. 1987
PPE reactively blended with SBS and MA and then mixed with PA or PEST	Van der Meer and Yates 1987
Reactive blends of carboxylated PPE with PA-66 and SEBS	Grant and Jalbert 1987, 1989
PPE, PA, SBS, and a reactive mixture of styrene-glycidyl methacrylate with styrene and a peroxide	Mawatari et al. 1987
PPE, PBT, SEBS, and PC [PBT – matrix; PPE + SEBS – dispersed phase; PC at the interface]	Brown et al. 1987
PPE, HIPS, PEST, PS with reactive (2-oxazoline) groups, PC, and SBS	Avakian et al. 1988
PPE with PBT (or PET), SEBS, PC, and mica	Yates 1987, 1989
PPE grafted with fumaric acid, reactively blended with PC and SEBS	Ishihara 1989
Grafted PPE, blended with dimethylsiloxanes, PC, PBT, and SEBS	Brown 1992
PPE, with PBT, PC, SEBS, and/or acrylate copolymer	Yates and Lee 1990
PPE, HIPS, an ethylene-methacrylic acid copolymer, EMAA, SEBS, and SGMA	Fuji and Ting 1987
PPE with PVDF, SEBS, and poly(styrene-co-methyl-methacrylate)	Van der Meer et al. 1989
PPE with HIPS, PE, and SEBS	Ting 1990
PPE with PP and SEBS	Lee 1990
PPE/PET or PPE/PA reactively compatibilized with SEBS-GMA	Mayumi and Omori 1988
PPE/PET or PPE/PA reactively compatibilized with SEBS-MA	Modic and Gelles 1988
PPE/PBT, toughened by addition of urea-butylated resin and SEBS	Mizuno and Maruyama 1990
PPE with PC, PBT, and either SBS, SEBS, or a core-shell copolymer	Brown and Fewkes 1992, 1994
Epoxy- or phosphate-functionalized PPE, with PBT or PET, palmitamide, SEBS, and PC	Yates 1993
PPE with PA-66, SEBS, SB; a styrene-butadiene radial copolymer; citric acid; and either citric acid or chloro-epoxy triazine	Gianchandai et al. 1993
PPE with PA-6 or PA-66, MA and toughened with SB	Lee 1994
PPE-MA or PPE-GMA, with sPS, SEBS, and fillers	Okada and Masuyama 1994

or butadiene-caprolactone block copolymer were developed (Wambach and Dieck 1980). Reactive compatibilization of PEST/SEBS by addition of MA was disclosed in 1984. The method was general, applicable to polyamides as well as to polyesters (Shiraishi and Goto 1986).

SBS with Polycarbonates (PC)

Similarly to blends of SBS with PA or PEST, these with PC were first described in 1976. However, owing to the weak interactions between SBS and PC, these systems require compatibilization. Thus, either SBS must be acidified (e.g., with SEBS-MA) or acidified acrylate added, viz., MABS, MBS, SMA, etc. Selected examples are listed in Table 1.25.

Table 1.24 Evolution of the SBS/PA blends

Composition	Reason	References
PA-66, SEBS, *phenoxy*, and bisphenol-A-epichlorohydrin	Tensile and impact strength of PA	Freed 1975
PA-6 with SEBS	Toughness, balance of properties	Bull and Holden 1977
PA-6 or PA-66 with SBS	Improved toughness and reduced modulus	Cerny and Troncy 1981
PA-6 with SEBS-MA and/or LLDPE	Tensile and impact strength	Mitsubishi Chem. 1982
PA-6 and SEBS-MA	Processability, mechanical properties, impact strength	Asahi Chem. 1983, 1984, 1987
PA, or PEST with SEBS-MA	High notched Izod impact strength	Gelles et al. 1987
PA-66 with SEBS, SEBS-MA, PO	Moldable alloys with high impact strength	Gelles et al. 1988
COPO, with PA-6 and SEBS-MA	Good balance of strength and toughness	Machado 1992
PA + acidified SEBS, EPR, or EPDM; the adduct incorporated into PA	Processability, mechanical properties, and low-temperature toughness	Ohmae et al. 1991, 1992
PA-66 + 1:1 blend SEBS and SEBS-MA	Processability and toughness	Gelles et al. 1994

Table 1.25 SBS/PC blends

Composition	References
PC with 30 wt% SEBS for co-continuous morphology	Gergen and Davison 1977
PC with PE and hydrogenated and chlorosulfonated SBS	Bussink et al. 1978
PEST with PC, SEBS, and mineral filers	Dieck and Wambach 1980
PC/ABS/PP compatibilized and toughened by SEBS-MA	Gallucci and Bookbinder 1989
PC with SB-teleblock and SEBS	Lee 1983
PC with either SBS and MBA or SEBS, EEA, and LLDPE	Liu 1982, 1984
PC with PE and SEBS	Idemitsu Kosan 1983
PC with either SBS, EGMA, or MBS	Sumitomo Chemical 1982, 1983
PC with SMA and SBS	Daicel Chem. 1984
PC, COPO, PEST, SEBS + butylacrylate-methylmethacrylate grafted rubber	Laughner et al. 1992
PC, PPE, ASA, SAN, PS, phosphate esters, PTFE, and SEBS	Niessner et al. 1993
PC, modified SEBS, and hydroxyethyl acrylate-terminated ε-caprolactone	Wilkey 1994

1.5.3.3 SBS Blends with Specialty Resins

SEBS must be processed below 280 °C; thus, its use with specialty resins has been limited to polyphenylenesulfide (PPS) (Garcia and Martinovich 1984). Sometimes SBS and a specialty resin are parts of a multicomponent blend, viz., PPS, PPE, either PA- 6 or PA-12, SEBS (*Kraton*™ *G*), an acidified polyolefin (e.g., EPR-MA, PE-GMA, or EVAc-GMA), and reactive compatibilizer (citric, maleic, or agaric acid). Here, PPS was a matrix, and PA was the dispersed phase that contained PPE/SEBS and a filler (Ishida and Kabaya 1994).

1.5.4 Polyvinylchloride (PVC)

PVC was first synthesized by Regnault in 1835. The first patent on vinyl chloride monomer (VCM) polymerization was granted in 1912 to Ostromislensky. However, to make commercially viable articles, PVC must be stabilized and either plasticized or blended. In 1927, B. F. Goodrich started production of plasticized PVC, *Vinylite*™ (Semon 1933).

The first patented PVC alloys were prepared by latex blending with PVAc and poly(vinylchloride-co-vinylacetate) (PVCAc) (Voss, and Dickhäuser 1930, 1933, 1935, 1936). I. G. Farbenindustrie commercialized PVC extruder blended with polyacrylic ester – the so-called rigid formulation (Fikentscher and Heuce 1930; Fikentscher and Wolff 1931). *Troluloid*™ and *Astralon*™ were the first commercial thermoplastic polymer blends.

PVC blended with *Buna-N* produced excellent thermoplastic materials (Badum 1942). These blends were prepared either in a rubber mill, by latex blending, or powder blending and then extruding. The rigid PVC not only had higher heat HDT than the flexible one, but it was *permanently* plasticized. In 1940 also B. F. Goodrich patented the NBR/PVC blends. Many forms of PVC and its copolymers have been developed over the years to fit specific uses, viz., latex, plastisol, organosol, flexible, and mostly the rigid formulation. In 1991 world production of PVC was 22.0 Mt or 21.6 wt% of the thermoplastic resin market.

1.5.4.1 PVC/NBR Blends

The PVC/NBR blends were commercialized in 1936 by Bergisch-Gladbach. Nearly identical alloys, *Geon*™ *Polyblends*, were introduced by B.F. Goodrich 1947. To ascertain adequate interaction between PVC and NBR, the AN content in NBR should be at least 25 wt%. Most commercial blends contain 50–90 wt% NBR that acts as a solid plasticizer and processing aid. PVC blends with cross-linked NBR have been foamed since the 1940s, initially for the production of buoyancy vests, shock absorption and insulation (McCracken 1984), and later for shoe soles. Still later, acidification of NBR made it possible to incorporate the NBR/PVC blends into PA, PC, or PEST (Iwanaga et al. 1990). It was also found that NBR provides good compatibilization and toughening in blends of PVC with carbon monoxide-ethylene-vinylacetate copolymer (COPO-VAc) (Lund and Agren 1993). There are several commercial PVC/NBR blends, viz., *Geon*™, *JSR NV*, *Krynac*™ *NV*, *Nipol*™, *Paracril*™ *OZO*, or *Vynite*™.

1.5.4.2 PVC/Acrylics Blends

The most common acrylic, PMMA, shows limited miscibility with chlorinated hydrocarbons (e.g., PVDC, PVC, CPVC, or CPE). The miscibility depends on the type of chlorinated polymer, tacticity of PMMA, and molecular weights

Table 1.26 Toughened PVC/acrylic blends

Modifier	References
Butadiene-MMA-styrene copolymer (MBS, *Acryloid*™)	Fujii and Ohtsuka 1954
PMMA and poly(butadiene-g-MMA)	Jarrett and Williams 1960
Ethylene-ethylacrylate copolymer	Van Cleve and Mullins 1962
MBS with controlled size of the elastomeric particles, transparent	Saito 1975
Copolymer of vinylchloride, alkyl acrylate, and vinylidene chloride	Hoshi and Kaneko 1962, 1963, 1965
Butadiene-styrene-methylacrylate-ethylacrylate	Ichinoe 1967
Core-shell: cross-linked ABS with grafted onto it PMMA shell	Michel 1969
PB grafted with MMA, styrene, and vinyl acetate	Kakefuda and Ito 1971
Poly(butadiene-co-butyl acrylate-co-styrene)	Ide and Deguchi 1971
Core-shell: poly(AN-co-MMA) or poly(AN-co-ethylhexyl acrylate-co-MMA)	Tanaka et al. 1971a, b, c; 1972
Poly(styrene-co-AN-co-MMA-g-butyl acrylate-g-MMA)	Ide et al. 1972
5–20 phr of MMA-AN-butadiene-styrene (MABS) with 10–40 wt% AN and/or styrene, 50–80 wt% 1,3-butadiene, and 25–75 wt% MMA for foamed profiles, bottles, pipes, boards, moldings, etc.	Parks 1976
Core-shell: poly(butadiene-co-styrene-divinylbenzene-co-butylacrylate-co-MMA)	Usami and Ochiai 1976
$\leq$ 20 wt% of either poly(vinylchloride-co-vinyl acetate) or EVAc – the blends were though and easy to foam	Barth et al. 1976; Goswami 1977
CPE and poly(MMA-co-butyl acrylate)	Maruyama et al. 1977
MMA and styrene grafted onto an acrylic elastomer	Kishida et al. 1977
AN-b-MMA block copolymer	Iwata et al. 1979
PMMA with dehydrochlorinated PVC were found miscible and easy to foam for the cryogenic insulation in space vehicles	Jayabalan 1982; Jayabalan and Balakrishnan 1985
Copolymer of ethylene, 1–60 % acrylic ester and 1–30 % CO_2 or SO_2	Rys-Sikora 1983, 1984
Core, cross-linked silicone rubber; inner shell, cross-linked acrylate elastomer; outer shell, styrene-AN copolymers	Lindner et al. 1990

of the two polymers. The origin of miscibility is the interaction between the -CHCl- group of PVC and the carboxyl group of the acrylic (Jager et al. 1983). Acrylics have been incorporated into PVC blends quite early (Small and Small 1951). In spite of PVC miscibility with PMMA, blends of these two polymers are not commercially important. To be useful, the blends must be toughened, preferably by acrylic elastomers. Some of the toughening agents are listed in Table 1.26.

Examples of commercial PVC/acrylics blends are *Acrylivin*™, *Decoloy*™, *Enplex*™, *Hostalit*™, *Kane-ace*™, *Kydene* ™, *Metabulen*™, or *Vinidur*™. The blends have been used for industrial, commercial, and consumer goods; in medical, electrical, and chemical engineering equipment; for food or beverage; as aircraft or mass transit interior components; for power tool housings; etc.

Table 1.27 PVC toughening by non-acrylic elastomers

Modifier	References
PIB, NR, IR, or CR	Goodrich 1941
Thio-rubbers (TM)	Rittershausen 1949
CR and NBR	Signer and Beal 1953
Chlorinated polybutadiene (CPB)	Esso 1960
Polyisobutylene (PIB)	Lonza Ltd. 1964
Di-butyl fumarate and butadiene copolymer	Koenig et al. 1964
TM and CSR	Allied Chemicals 1965, 1966
BR and/or poly(ethylene-co- vinyl or acrylic monomer), e.g., EVAc	Kasuya et al. 1969
EPDM and polynorbornene having carboxylic and carboxylic ester groups	Mitsubishi Chem. 1983
PVC blends with cross-linked NBR for foamed floating devices	McCracken 1984
DOP plasticized PVC blended with TPU and EVAc	Shin et al. 1998

1.5.4.3 PVC/Elastomer Blends

These blends, usually with 30–60 wt% PVC, are represented by *Carloy*™, *OxyBlend*™, or *Vynaprene*™. They have been formulated for extrusion, calendering, injection, or blow molding, e.g., into bottles, sheets for exterior signs, window accessories, cables and hoses, printing plates and rollers, shoe soles, profiles, military coax jacketing, etc. PVC blends with ABS and modified ABS were already discussed. In Table 1.27 an abbreviated list of PVC blends comprising non-acrylic elastomer(s) is provided.

1.5.4.4 PVC/Polyolefin Blends

PVC is antagonistically immiscible with PO. Thus, the standard strategies are applicable: (i) addition of a small amount of PO to improve processing and impact strength, (ii) co-continuous morphology, (iii) incorporation of PO as part of a copolymer comprising miscible with PVC segments, and (iv) compatibilized blends. Owing to difficulties in compatibilization, the PVC/PO blends are not commercial (Liang et al. 1999). Evolution of these systems is outlined in Table 1.28.

1.5.4.5 PVC/CPE and PVC/CSR Blends

PVC blends with CPE were patented and commercialized in 1956 as *Hostalit*™. Blends with CSR soon followed. By the mid-1970s, the emphasis shifted toward blends with acrylic elastomers. Ternary alloys were developed, viz., of PVC with CPE and poly(methyl methacrylate-co-butyl acrylate) (MMBA) (Maruyama et al. 1977) or PVC, CPVC, and either MABS or a mixture of PMMA with imidized-PMMA or imidized-SMA (Soby et al. 1994). These blends have been used for outdoor applications, flame-retardant wall coverings, and automobile interiors. Injection molded components include gullies in sewage systems, caps for road reflector posts and bench slats, etc. Evolution of these blends is traced in Table 1.29.

Table 1.28 PVC blends with PO

Composition	Reason for blending	References
PO with PVC	For extrusion or milling	Rosenfelder and Rosen 1962
PVC with either PP, PE, PS, or SBR and ethylene-vinylchloride	HDT, flame resistance, impact, and tensile strength	Montgomery 1966
PVC with either PE or PP and MBS	Impact strength formulations for pipes or electrical insulation	Baer and Hankey 1967
PVC with either PE or PP and ABSM	Impact performance	Himei et al. 1967
PP with PVC and either PMMA or PC	Layered, wood-like materials	Yahata et al. 1971
PP and either EVAc-VC, EVAc, or HDPE	Low-temperature impact resistance	Kojima and Tanahashi 1972
PVC was copolymerized with PP	Flame retardancy	Unitika Ltd. 1984
PVC, HDPE, and CPE	Compatibilized blends	Nippon Zeon 1984
PVC/PO + poly(ethylene-co- alkyl, aryl, alkaryl or methylmethacrylate ester)	Mechanical and impact performance	Williams and Ilenda 1993

Table 1.29 PVC blends with either CPE or CSR

Composition	References
PVC with CPE	Frey 1958
PVC with CSR	Matsuda 1960
PVC with CPB	Esso 1960
Latex blending: PVC with CR	Nyori et al. 1962
PVC with PO, compatibilized by either CPE or MBS	Baer and Hankey 1963
Solution-blended PVC with CPE or CSR	Beer 1963
PVC with CPE and a diamine (an interfacial agent)	Hankey and Kianpour 1964
PVC with equal amount of CSR and SAN	Salyer and Holladay 1964
PVC with equal amount of CPE or CSR	Hedberg and Magner 1965
PVC with EVAc and CPE	Dow Chemical Co. 1965
PVC with chlorinated-SBR (C-SBR)	Takkosha Co. 1967
PVC with chlorinated EPDM (C-EPDM)	Watanabe et al. 1967
Powder blending: PVC and PE and then chlorinating and milling	Kato et al. 1967
PVC with two heterogeneously chlorinated LDPEs	Willott 1968
PVC with CPVC and ABS	Kojima et al. 1970
PVC with PS and C-SBR	Falk 1981
PVC/CPE with SMA	Bourland 1983
PVC with HDPE and C-SBR	Nippon Zeon 1984
PVC/CPE with glycidyl *p*-tert-butyl-benzoate	Sugiara and Takayama 1988
PVC/CPE with either SMMA or PS-VAc	Liou and Sun 1993

1.5.4.6 PVC/TPU (Mainly Polyester-Type) Blends

Initially, two-component, PVC/TPU blends were proposed (B. F. Goodrich Co. 1960), but soon, PVC/TPU blends with a modifier, e.g., ABS (Waugaman et al. 1963); NBR or PA (Képes 1959) were disclosed. Blending was also carried out by mixing PVC with polyols and isocyanates and then polymerizing these two (Dainichiseika Color & Chemicals 1982, 1983). Commercial PVC/TPU blends (with NBR) are represented by *Duralex*™. The materials are usually formulated for extrusion, e.g., for wire and cable insulation, hoses, and packaging.

Later, foamable, recyclable PVC blends were disclosed. They comprise PVC plasticized with DOP and/or epoxidized soybean oil, blended with either TPU and/or EVAc. The formulation could be foamed either during extrusion or injection molding. The material is used to produce anti-slip shoe soles with good abrasion resistance (Shin et al. 1998).

1.5.4.7 PVC/EVAc and PVC/EVAc-VC Blends

The miscibility of PVC with EVAc depends on the VAc content. Blends of PVC with PVAc were patented in 1938. PVC, or poly(vinylchloride-co-acetate) (PVCAc), was also blended with polyvinylacetal (PVA) (Lonza Elektrizitätswerke & Chem. 1948). In later patents, PVC instead of being mechanically blended with PVAc was copolymerized with vinyl acetate. The copolymer still required toughening; thus, it was emulsion polymerized in the presence of styrene-butadiene-vinylacetate latex (Farbwerke Hoechst 1970). Latex blending (followed by spray drying) was a simple and efficient mixing method (Hammer 1971). Similarly, PVC and/or PVCAc was blended with a variety of butadiene-butyl acrylate-styrene copolymers (Ide and Deguchi 1971). PVC blends with ethylene-vinyl acetate-carbon monoxide copolymer (EVAc-CO) and a methylmethacrylate graft copolymer, *Kane-Ace*™, are also commercially interesting (Mitsui Petrochemicals 1983).

Commercial PVC blends with either EVAc or PVC-VAc have been offered for outdoor applications since the 1970s as high impact strength, rigid formulations (e.g., *Denkovinyl*™, *Hostalit*™, *Vinidur*™, *Solvic*™, or *Trosiplast*™). The resins show good hardness, rigidity, adequate heat, chemical, and flame resistance.

1.5.4.8 PVC Blends with COPO

The first PVC/COPO blends were developed in 1960 (Mullins 1964). It was reported that PVC melt viscosity decreased by addition of COPO (Hammer 1973). Later, the compositions were modified – PVC was blended with ethylene-carbon monoxide-vinylacetate copolymer (COPO-VAc) and BMMM (Reardon 1982).

1.5.4.9 PVC Blends with Engineering Resins

Owing to poor thermal stability of PVC, the high temperature blending must be avoided. Thus, only few PVC/engineering resin blends are known. These are summarized in Table 1.30.

The first commercial blend of this type is *Cylon*™. Here PVC is the matrix, and PA (that melts below 215 °C!) the dispersed phase. The two resins were compatibilized using the well-known PVC plasticizer – *Elvaloy*™ (a terpolymer

Table 1.30 PVC blends with engineering resins

Composition	References
PVC with 5–25 wt% polypropylene terephthalate (PPT)	Hurwitz and DeWitt 1970
PVC + copolymer of PET with polybutyleneglycol, PBG, and 1,4-butanediol	Crawford and Witsiepe 1972
PVC with PC and ABS	Hardt et al. 1975
Low friction coefficient blends of PVC with POM	Doerffurt and Waeteraere 1977
Styrene-grafted PC with neat PC, PS and other styrenics, acrylics or PVC	Kakizaki et al. 1979b
PVC with polyethylene carbonate	Dixon and Ford 1979
High HDT blends: PVC, MBS, and polyimide (PI)	Kopchik 1981
PVC with poly(butanediol-terephthalate-adipate) and 30 wt% GF	Yang 1987
Vinylchloride polymerized in the presence of PI, blended with PVC and MBA	Clikeman et al. 1987
PVC with poly(methylmethacrylate-co-maleimide-co-vinyl cyanide) and styrene-cyclohexyl-maleimide-grafted butadiene	Ito et al. 1990
PVC with imidated polymethacrylate (polyglutarimide, PGI)	Fromuth et al. 1992
Plasticized PVC with an aliphatic polyester-b-aromatic polyester	Jean and Devauchelle 1993
Miscible blend: PVC/PC and a bishydroxyphenyl-hexafluoropropane (6F-PC)	Drzewinski 1993, 1994

of ethylene, carbon monoxide, and acrylics). These soft to semirigid alloys were commercialized for wire coating, automotive applications, and blow molding (Grande 1997; Hofmann 1998). They are flame, abrasion, and chemicals resistant, easy to process, and tough.

1.5.5 Polyvinylidenechloride (PVDC)

Polyvinylidenechloride, PVDC, was discovered in 1838 by Regnault but commercialized 100 years later as *Saran*™. The commercial PVDC is modified by the incorporation of either 15–20 wt% vinyl chloride or 13 wt% vinyl chloride and 2 wt% acrylonitrile. PVDC blends are summarized in Table 1.31.

1.5.6 Polyvinylidenefluoride (PVDF)

PVDF was patented in 1948 and commercialized by Pennsalt in 1962. It is a semicrystalline polymer with $T_g = -56$ to -35 °C, 50 % crystallinity, and $T_m = 160$–180 °C. PVDF has been blended mainly with PMMA (Lin and Burks 1993). The blends are suitable for the use as stable electrets or weather-resistant architectural coatings. Nearly 25 wt% of PVDF consumption is in weather-resistant architectural spray finishing or coating to metals, roofing, curtain walls, wall panels,

Table 1.31 Examples of PVDC blends

Composition: PVDC with	References
NBR and CR	Signer and Beal 1951
Polyurethanes	McCready 1976
Ethylene-carbon monoxide-vinyl chloride copolymer, *Alcryn*™ blends	Loomis and Statz 1984, 1986
PO and ethylene-methylacrylate compatibilizing ionomer	Burgert 1987
PA-6, PA-1212, or PARA and poly(ethylene-co-alkyl (meth)acrylate-co-vinyl acetate-co-CO-co-maleic anhydride)	Hofmann 1994
PVDC-VC with vinylidene chloride-methyl acrylate copolymer (PVDC-MeA)	Paleari and Fornasiero 1994

Table 1.32 Examples of PVDF blends

Composition: PVDF with	References
PCTFE for wire coating	Kaufman 1963
30 wt% PMMA for outdoor films with good clarity, chemical, and UV stability	Koblitz et al. 1966
PMMA and polyethylacrylate	Schmitt and Miller 1970
Solution blended with PA-610 to lower PA’s water absorption	Saito 1975
PC and acrylic copolymer for clear, yellowish films with single $T_g \approx 120$ °C	Leibler and Ringenberg 1986
PPE/SEBS and SMMA for weatherability, chemical, and solvent resistance	Van der Meer et al. 1989
Compatibilized PA for impact resistance and gas barrier properties	Hizasumi et al. 1989
COPO, PVP, PSF, polyester rubbers, or poly-2-oxazoline	Gergen and Lutz 1989
POM for resistance to frictional wear, heat, and UV stability	Shibata et al. 1992

window frames, doors, hand rails, fascias, awnings, louvers, and canopies. PMMA/PVDF blends are commercially available, e.g., *Polycast*™ from Royalite. PVDF blends are summarized in Table 1.32.

1.5.7 Acrylic Blends

Polymethylacrylate (PMA) and polymethylmethacrylate (PMMA) were discovered, respectively, in 1880 and 1930. The resins have been used for the production of transparent plastic sheets, viz., *Plexiglas*™ or *Perspex*™, and used for the military aircraft cockpit canopies, gunner’s turrets, and the like (Riddle 1954). Acrylic elastomers (ACM or ANM) were developed by Röhm in 1901 and commercialized in 1948 as *Hycar*™ vulcanizable copolymers of ethyl acrylate, allyl maleated lactones, chloroethyl vinyl ether, butadiene, isoprene, acrylonitrile, etc. (Mast et al. 1944). Since the 1950s, a wide variety of acrylic compatibilizers and impact modifiers have been developed.

Table 1.33 Acrylic compatibilizers-*cum*-impact modifiers, MBA and MBS

Composition	References
Methylmethacrylate-butadiene-styrene terpolymer (MBS)	Fujii and Ohtsuka 1954
methylmethacrylate-butadiene-styrene-α-methylstyrene, for weather resistance	Ruffing et al. 1964
Butadiene-styrene-methylacrylate-ethylacrylate (ASA)	Ichinoe 1967
Partially cross-linked ABS core and PMMA shell (a MABS)	Michel 1969
Copolymers of styrenics (e.g., PS, SAN, SMMA, etc.) with, e.g., 0.1 wt% of hydroxyethyl acrylate	Rubens 1986

1.5.7.1 Co-poly(meth)acrylates (MBA and MBS)

In the 1950s, the core-shell, emulsion-type methylmethacrylate-butadiene-styrene terpolymer (MBS) was developed to toughen PVC or PC. These blends could also contain other polymers, viz., SAA (Murdock et al. 1960), SMM and PS (Murdock et al. 1962), SMM-AN (Schmitt et al. 1967), *high heat* ABS (Kanegafuchi Chemical Industry 1967), HIPS (Ward 1970), MMVAc-AA (Holland et al. 1970), SMMA (Blasius 1992), etc. Table 1.33 traces the evolution of these systems. Later, these multipolymers were modified by incorporation of MA, AA, or GMA units to serve as reactive compatibilizers and toughening agents for PA, PEST, or PC blends.

1.5.7.2 Impact modification of PMMA

PMMA, like PS, is brittle and requires toughening. These efforts are summarized in Table 1.34.

1.5.7.3 PO Blends with Acrylic Polymers

PMMA is antagonistically immiscible with polyolefins – blends of this type have been used in non-critical applications, viz., PP/PMMA blends with EVAc were used as plastic paper (Yamamoto et al. 1971), while those with PVC (or CA) as wood-like materials (Yahata et al. 1971). For more demanding applications, either PO should be blended with an acrylic copolymer comprising a PO block, or PO should be grafted with acrylic moieties. Examples of the PO/Acrylics blends are listed in Table 1.35.

Blends of a PO (PE, PP, PB, P4MP, their blends, and copolymers, e.g., with 1-alkenes, vinyl esters, vinyl chloride, methacrylic esters, and methacrylic acid) with 0.2–50 wt% of a graft copolymer showed high tensile modulus and high sag resistance without increased melt viscosity. The blends could be shaped into foamed profiles at T = 200–230 °C.

To prepare the graft copolymer, a PO (MW = 50–1,000 kg/mol) was either dissolved or swollen in an inert hydrocarbon, monomers (≥80 wt% of a methacrylic ester, $CH_2 = C(CH_3)COOR$), and an initiator was added to the heated mixture while stirring. As a result, acrylic branches of a relatively high molecular weight (MW = 20–200 kg/mol) were grafted onto the PO macromolecules. The graft copolymer could be used as a compatibilizer-cum-impact modifier in a variety

Table 1.34 Impact modification of PMMA

PMMA impact modifier	References
PVAc	E. I. du Pont de Nemours 1942
Copolymers of methacrylonitrile, ethylacrylate, and/or α-methylstyrene	Coover and Wooten 1962
Ethylene-vinyl acetate-vinyl chloride copolymer (EVAc-VC)	Kishikawa et al. 1971
SMA and methylmethacrylate-methylacrylate copolymer (MMMA)	Bronstert et al. 1971
MBA: copolymer of butadiene, butylacrylate, and methylmethacrylate	Kotama 1972
Styrene-acrylonitrile copolymer (SAN)	Sugimura et al. 1972
SAN, PS, and poly(methyl norbornene-2-carboxylate)	Ikeda et al. 1976
IPN: cross-linked PBA, cross-linked and uncross-linked SAN	Silberberg 1982
Poly(*p*-hydroxy styrene), PVPh, and EVAl	La Fleur et al. 1992, 1994
Acrylic core-shell copolymer and either PBT or PET	Bright et al. 1993
Poly(allyl methacrylate-co-butyl acrylate-co-butanediol dimethacrylate-co-styrene-co-methyl methacrylate) or poly(acrylonitrile-co-butyl acrylate-co-tricyclodecenyl acrylate-co-styrene)	Farwerck et al. 1993
Poly(acrylate-*N*-cyclohexyl maleimide), PMI, and a copolymer: PMMA – core, cross-linked butyl acrylate-styrene copolymer – middle layer and PMMA shell, $d = 200\text{–}300\ nm$	Shen 1994
PEG/atactic PMMA blends were characterized by PVT at T = 20–200 °C and P = 0–200 MPa. Free-volume fraction was calculated from an equation of state	Schmidt and Maurer 1998

Table 1.35 Polyolefin/acrylic blends

PMMA impact modifier	References
40–90 wt% of ethylene-co-acrylic or methacrylic acid with ethylene-co-vinylacetate or ethyl acrylate for foam production	Park 1978, 1980
Ionomer with (1) a terpolymer of ethylene, vinylacetate and CO or SO_2, and (2) an elastomer (e.g., NR, IR, PU)	Enderle 1984
PE with EVAc, CPE, BR, etc., have been chemically foamed at T = 150–210 °C	Kuhnel and Spielau 1981
5 to 95 wt% of LDPE or LLDPE with EAA	Park 1985, 1986d
PE with either poly(ethylene-co-vinylcarboxylate) or an acrylate	Broadhed 1987
PP with an ionomer and EBA-GMA	Saltman 1988, 1989, 1992
PP with an ionomer, EBA-GMA, and EPDM	Dawson 1993
PO with a core-shell graft copolymer MBS type	Aoyama et al. 1993, 1994
PP with acidified PP, or a carboxylic acid-modified EPR, SMM-MA, and either EMMA-GMA or EVAc-GMA	Abe et al. 1994
LLDPE, PMMA and SEBS, EPR, or ethylene-styrene block copolymer (ES)	Dobreski and Donaldson 1994
At least two elastomers and an ethylene-methacrylate-acrylic acid ionomer	Arjunan 1994, 1995
PE with alkyl acrylate or alkyl methacrylate	Godfrey 1995

of polymers selected from between PO, acrylic polymers, SAN, EVAc, PA, PEST, PC, POM, PAr, PVC, ABS, PVDC, cellulosics, polyester-polyether block copolymers, PEA, PEEK, PEI, PES, CPVC, PVDF, PPE, PPS, PSF, TPU, PAI, PCL, polyglutarimide, and blends of PEST with PC or PVC (Ilendra et al. 1992, 1993).

1.5.7.4 PC Blends with Acrylic Polymers

PMMA has been blended with PC since 1971. Two types of PMMA/PC systems are of interest: (i) impact-modified alloys and (ii) miscible blends. To the first category belong *Meta-marble*™ blends of PMMA/PC with ABS (Ikura et al. 1974) or with ASA (Giles and Sasserath 1986). Blends of PC with two acrylic copolymers showed good processability, notched impact strength, and HDT (Eckel et al. 1993).

Acrylic polymers are recognized for their miscibility with a variety of polymers, viz., miscibility of PMA with PVAc (Kern 1957). PMMA is miscible with standard PC at $T < LCST \approx 140$ °C. The miscibility range can be greatly increased by modifying the PC chain ends ($LCST \leq 300$ °C) (Kambour 1988). Demixing PMMA/PC blends by the spinodal decomposition mechanism generated alloys with excellent mechanical properties (Kyu 1990).

PMMA is also miscible with fluorinated PC (Drzewinski 1993, 1994).

1.5.7.5 PEST Blends with Acrylic Polymers

Blends of PEST with acrylic polymers are limited to systems with acrylic elastomers. Examples are listed in Table 1.36. PBT and PET were reported to form miscible blends with either a poly-*p*-methoxyphenyl methacrylate or poly(phenyl methacrylate) (Siol et al. 1993b, 1994).

1.5.7.6 PPE Blends with Acrylic Polymers

Poly(2,6-dimethyl-*p*-phenylene ether) (PPE) was rarely blended with acrylics, viz., with styrene-methylmethacrylate-co-*cis*-polyisoprene (Abolins and Reinhardt 1976) and PMMA (Izawa and Nakanishi 1973; Matsunaga et al. 1974).

Table 1.36 Polyester/acrylic blends

1. Acrylic impact modifiers for PEST	**References**
Ethylene-methylmethacrylate copolymer (EMMA)	Dijkstra and Jones 1969
Graft copolymer: acrylonitrile-butadiene-styrene-methylmethacrylate, ABSM, and PDMS	Sauers and Barth 1970
Ethylene-hydroxyethyl methacrylate (EHEMA)	Jones et al. 1971
Ethylene-vinylacetate (EVAc)	Jones et al. 1971
methylmethacrylate-methyl acrylate copolymer (MMMA)	Kamata et al. 1974
Ethylene-vinylacetate-methacrylic acid copolymer	Gander et al. 1977
2. Blends of PMMA with	
1,4-butanediol terephthalate-co-polybutylene glycol (PBT-PBG)	Charles and Gasman 1979
PET and PS	Kamata et al. 1980
PBT and CH_3NH_2 (to convert PMMA into polyglutarimide)	Toray Ind. 1984

1.5.7.7 PA Blends with Acrylic Polymers

Polyamides, PA, can be impact modified by addition of acrylic multipolymers, e.g., methylmethacrylate-co-methacrylic acid-co-ethylacrylate (Halliwell 1965, 1966), ethylene-2-hydroxy ethyl methacrylate-methylmethacrylate (Hepworth et al. 1970), or ethylene-ethylacrylate-acrylic acid ionomer (Meyer and Tacke 1978).

1.5.7.8 POM Blends with Acrylic Polymers

These systems are not of industrial importance. However, addition of an acrylic was reported to improve processability, abrasion resistance, and weatherability of POM. For example, to improve weatherability, POM was blended with polythioisocyanate, TPU, PMMA, and benzotriazole (Endo et al. 1990). POM/TPU with EMMA and benzotriazole show enhanced performance (Okuda 1990). POM was also blended with EGMA (Takahashi and Kobayashi 1992), EGMA/AS, EGMA/PMMA, or their mixture (Kobayashi and Shinohara 1993).

1.5.8 Polyethylenes (PE)

1.5.8.1 Homopolymers

Properties of PE depend on molecular weight (MW), molecular weight distribution (MWD), as well as on the degree and type of branching (Peacock 2000). The density and modulus of PEs increase with crystallinity. As shown in Table 1.37, seven principal categories of PE are recognized. Commercial polyethylenes are generally copolymers of ethylene with varying amounts of α-olefins, and the comonomer has the effect of reducing crystallinity and density.

The first polymethylene was obtained in 1897 by the thermal decomposition of diazomethane. In 1931, about half a gram of PE was obtained in a free radical polymerization at high T and P. In 1937, *Telcothene*™, a blend of PE and polyisobutylene (PIB) was produced for submarine cables, and in 1939, the first LDPE, *Alketh*™, plant with 100 t/year capacity went into operation (Kennedy 1986). In 1951, HDPE was polymerized using the Z-N catalyst (Zletz 1954).

Table 1.37 Polyethylenes

No.	Type	Code	Density (kg/m^3)	Characteristics
1.	Ultra-high MW	UHMWPE	$\rho \approx 969$	MW > 3,000 kg/mol
2.	High density	HDPE	941–969	High MW and crystallinity
3.	Medium density	MDPE	926–940	
4.	Low density	LDPE	910–925	Long-chain branching, $T_m = 115$ °C
5.	Linear low density	LLDPE	910–925	Ziegler Natta type with short branching, $T_m = 120$–135 °C
6.	Very low density	VLDPE	900–910	
7.	Ultra low density	ULDPE	855–900	$T_m = 40$–85 °C

In 1957, Du Pont Canada developed LLDPE, *Sclairtech*™ (Lank and Williams 1982). In the 1980s, new catalysts made it possible to polymerize VLDPE and ULDPE, commercialized in 1986. The newest PEs (*Tafmer*™ was introduced by Mitsui Petrochemicals in 1975) are prepared using the single-site metallocene catalysts (Choi and Soares 2012). These new resins have controlled MW, MWD, comonomer placement, and density. Their melting point, $T_m = 70–120$ °C, increases linearly with density, $\rho = 880–930$ kg/m^3. Details of the different catalysts used for olefin polymerization and the resulting molecular structures and attendant properties may be found in the recent review by Posch (2011). We note that Exxon Mobil has developed a grade for tough, high clarity films called Enable™ mPE 35-05HH resin that can extend downgauging opportunities on LLDPE and LDPE film equipment. This resin and its blends are useful for making compression packaging film, lamination film, stand-up pouch film, and medium- and heavy-duty bag film.

1.5.8.2 PE Blends

As much as 30% of all polyolefin products involve blends (Robeson 2007). It has been found, for example, that blending metallocene-catalyzed linear low-density polyethylenes (mLDPEs) with HDPE improves the Izod impact strength and some tensile properties of HDPE. Adding mLLDPE to LDPE increases the ductility of LDPE (Cran and Bigger 2009). In general, PE blends can be divided into three categories: (1) PE lots blended to meet standard specifications for density and melt flow, (2) PE modified with $\leq$ 15 wt% of other polymer(s), and (3) PE bends with other thermoplastics or thermoplastic elastomers.

PEs are immiscible with nearly all polymers; thus the standard strategies are applicable: (i) non-compatibilized blends with low concentration of the dispersed phase, e.g., blends of either PP or PE with 2 wt% PVAl; (ii) non-compatibilized blends for the use in noncritical applications; (iii) non-compatibilized blends having co-continuous morphology, e.g., PE, blended with neoprene rubber at a ratio 1:1 and then irradiated by electron beam; and (iv) compatibilized blends.

PE/Elastomer Blends

Polyolefins have been modified by the incorporation of elastomers to improve low-temperature impact strength and elongation. Table 1.38 provides examples of these systems.

PE/EPR or EPDM Blends

The first patent on PE/EPR blends was deposited before commercialization of EPR (Corbellini 1962). Several similar inventions were disclosed, viz., HDPE blends with EPR (Crawford and Oakes 1963, 1966), PE with EPDM (Prillieux et al. 1962), PE/EPDM blends with either PP or PB (Schreiber 1966), PE with EPR and ethylene-acetoxybicycloheptene copolymer (Shirayama and Iketa 1971), or VLDPE with EPR, EPDM, or their mixtures (Nishio et al. 1992). To improve PE/EPDM adhesion to polar materials, PE was first grafted with MA and then blended with EPDM (Honkanen et al. 1983).

Table 1.38 PE/elastomer blends

Modifier	Reason	References
Rubber	Impact modification	Standard Oil 1937
Cyclo-rubber	Adhesion to metal	Child et al. 1942
PIB	Transparent, impermeable, shrink-wrap films	Briggs et al. 1958;
CSR	For films or coatings	Boger and Thomas 1958
BR	Improve elongation	Cole 1959
Poly-1-butene	Processability and ESCR	Rudin and Schreiber 1964
BR and EVAc	Improved extensional behavior	Ceresa et al. 1968
An ionomer, with or without EVAc	Films with good tear and yield strength	Willott 1968
0.1–5 wt% aPP	Blown or stretched packaging films	Nakamura et al. 1973
EVAc and EVAl	Transparency and impact strength	Pritchett 1980, 1981
Polytransoctanamer (PTO)	Impact modification	Kita and Hashimoto 1987
Poly(ethylene-co-vinylcarboxylate)	High impact strength	Broadhed 1987
ULDPE/CSR or CPE, dynamically vulcanized and then dispersed into fresh CSR or CPE	Processability, hot-weld strength, adhesion and crack resistance for single-ply roofing membranes	Ainsworth 1990, 1994
Starch and at least one ionic compound	High-frequency sealable packagings	Dehennau et al. 1994

The first reactor-type thermoplastic polyolefin (R-TPO) was LLDPE/PP (Yamazaki and Fujimaki 1970, 1972). The three-component R-TPOs (PE with PP and EPR) soon followed (Strametz et al. 1975). PE was also polymerized in the presence of active catalyst and an olefinic copolymer (Morita and Kashiwa 1981). Blending amorphous co-polyolefins with crystalline POs (HDPE, LLDPE, PP) and a filler resulted in moldable blends, characterized by excellent sets of properties (Davis and Valaitis 1993, 1994). Blends of polycycloolefin (PCO) with a block copolymer (both polymerized in metallocene-catalyzed process) and PE were reported to show outstanding properties, viz., strength, modulus, heat resistance, and toughness (Epple and Brekner 1994).

Later, blends of a partially cross-linked thermoplastic elastomer with 5–40 parts of a PO (viz., LLDPE, PP, EPR, or PB-1) were developed for low-density, foamable alloys (Okada et al. 1998a). The density was reduced at least by a factor of two. In the following patent, 1–17 wt% of a long-chain branched PP was also added (Okada et al. 1998b). The extruded foam was free of surface roughness caused by defoaming, was soft to the touch, and showed excellent heat and weathering resistance.

For the power distribution cable industries, insulation compounds are selected primarily to obtain required electrical properties for their intended service and anticipated conditions of use. PE insulation is very sensitive to partial discharges, while XLPE insulation is better where temperature stability is concerned. PE can be cross-linked either by chemical reaction (such as peroxides) or by γ-ray or by high-energy electron beam irradiation. However, in cable fabrication, chemical cross-linking of PE is used almost exclusively. Cross-linking of PE decreases modulus and elongation but increases ultimate tensile strength. However, enhanced thermal characteristics and excellent electrical properties coupled with mechanical toughness and good resistance to chemicals make XLPE an ideal insulant for applications in many types of electrical cables. Blends of various synthetic elastomers (EPM, EPDM, EVAc, Butyls, Silicones) with XLPE have been studied (Blodgett 1979; Mukhopadhyay and Das 1989, 1991). The effects of ethylene to propylene ratio (E/P) on the flow behavior, structure, mechanical properties, and failure mechanisms of XLPE and EPDM blends have also been studied (Mukhopadhyay et al. 1989; Mukhopadhyay and Das 1990).

PE/PE Blends

Molten polyethylenes of different type chain structures usually are immiscible (see ► Chap. 2, "Thermodynamics of Polymer Blends"). Upon crystallization the spherulites of one PE (having higher T_m) are encapsulated by those of the other PEs. Co-crystallization of two PEs into a single-type isomorphic cell is rare (Utracki 1989a). However, due to low interfacial tension coefficient, the phase coarsening is slow.

Alloys of different PEs constitute a large and important part of the PO technology. For example, in some countries, 70 wt% of PE is sold after blending (e.g., LLDPE with LDPE). As the technology evolves, these blends are prepared from resins of widely different rheological character, giving the viscosity ratios $\lambda \geq 10{,}000$. Usually, they do not require compatibilization, but owing to such a large value of the viscosity ratio, blending in shear flow is inefficient. Mixing in the extensional flow field is the potential solution (Luciani and Utracki 1996; Utracki and Luciani 1996a). Once cooled below the crystallization point of one component, the blend's morphology is fixed by crystalline cross-links. Blending of different grades and types of PE improves processability and mechanical performance. Blending, as it will be evident from the examples in Table 1.39, also may lead to transparency, improved abrasion resistance, stress-crack resistance, etc.

PE/PP Blends

PE has been used to improve the low-temperature impact strength of PP (see Table 1.40). The blends are mostly immiscible, compatibilized either by addition of EPR, EPDM, by reactive blending, or by post-blending co-cross-linking, e.g., by electron beam or γ-radiation (Utracki and Dumoulin 1995). Recently, Sonnier et al. (2008) showed that the use of 5wt% metallocene random copolymers of ethylene-olefin (mPE) as a compatibilizer increased the elongation at break of an 80/20 blend of high impact PP/HDPE from 60 % to 340 %. This was due to better interfacial adhesion. The comonomer content in mPE ranged from 8.3 % to 19.2% and the comonomer was either butene or octene.

Table 1.39 PE/PE blends

Blend	Advantage	References
LDPE with LLDPE	Processability, stiffness, abrasion resistance, H_2O vapor permeability	Wissbrun et al. 1962; 1965; Golike 1962
LDPE, HDPE, and EPDM or aPP	Soft, thin films	Sakane et al. 1979
Two types of LLDPE	Processability, impact strength, mechanical performance	Larsen 1982
LLDPE with LDPE, PP, TPOs, rubbers, EVAc, PP-MA, EPR	Improved processability	Haas and Raviola 1982; Cowan 1983; Fukui et al. 1983
HDPE with LLDPE	Improved strength, toughness, and transparency	Showa Denko 1983; Ogah 2012
LDPE with HDPE, PP, and EP-block	Modulus, strength, no sagging	Shin-Kobe Electric Machinery 1984
LLDPE, LDPE, and PP or EPR	High stiffness and film clarity	Bahl et al. 1985
HDPE with either LLDPE or LDPE	High stress-crack resistance	Boehm et al. 1992
VLDPE and LLDPE	Processability	Godbey and Martin 1993, 1994
Metallocene LLDPE and ionomer	Heat shrinkable films	Babrowicz et al. 1994
High and low molecular weight PE	Processability and physical properties	Coutant 1994
Reactor blends of LLDPE	Improved MD/TD tear balance	Ali et al. 1994
100 parts of LDPE ($\rho = 890$–925 kg/m^3), 1–110 parts of a HDPE	Expandable compositions for a small diameter electric wire insulation	Sakamoto et al. 1994
LLDPE with EVAc (10–20 % VAc)	Processability, tear strength, transparency	Benham and McDaniel 1994
LDPE with LLDPE	Improved tear strength and haze	Benham et al. 1995
70–98 wt% of LDPE (with ≤ 60 wt% LLDPE) and 2–30 wt% HDPE	For physical foaming of recycled HDPE	Lee 1995, 1996
Bimodal PEs (LCB = 0.01–3; $M_{n1}/M_{n2} > 7$) was lightly cross-linked. The PE-1 was prepared in the first reactor, and PE-2 was prepared in the presence of 15–65 wt% of PE-1 in the second reactor. The reaction could be carried out in the slurry, solution, or gas phase	Blends ($\rho \leq 885$ kg/m^3) were used for wire/cable coating; weather stripping; seals; foamed articles with closed, open, or mixed cells; containers; medical appliances; drapes and coverings; fibers; tapes; tubes; pipes and hoses: bellows: boots; gaiters; footwear; etc.	Cree et al. 1998

PE/Other Commodity Polymer Blends

The PEs are frequently used as impact modifiers for a variety of other thermoplastics. For example, addition of either PE, CPE, or CSR to PVC improved its moldability, stability, impact strength, and chemical resistance (Matsuda et al. 1960). Blends of PO/PVAl were developed to improve the antistatic properties (Minekawa et al. 1969). LDPE was blended with poly(2-ethyl-2-oxazoline) (PEOX) for improved adhesion, e.g., to PET (Hoenig et al. 1984). Blends of PE, PP, PS, or their copolymers with ethylene-fluorinated vinyl ether copolymer were

Table 1.40 PE/PP blends

Composition	Reason	References
PP/LLDPE	Mechanical properties at low temperature	Holzer and Mehnert 1963, 1966
PP/LLDPE	Impact resistance and low-T brittleness	Martinovitch and March 1963
PP/LDPE	Impact strength and low brittle temperature	Sun Oil 1964
PE/PP compatibilized with EPR	Low-T brittleness and Izod impact strength	Rayner et al. 1964
PE/PP compatibilized with PIB	Low-temperature impact strength	Lehane 1964
Isotactic PP with sPP	Low-temperature impact strength	Emrick 1966
PE/PP compatibilized with EPDM	Improved impact properties of PEs	Schreiber 1966
PE grafted with methacrylic acid and PP with dimethylaminoethylmethacrylate	Blended at a ratio 1:1 showed excellent mechanical properties	Langworth 1967
PE/PP compatibilized with EPR	High impact strength	Sumitomo Chem. 1968
Isotactic PP with aPP	Impact strength at low temperature	Tanahashi and Kojima 1970
PE/PP compatibilized with EP-block copolymers	Mechanical, low-temperature impact, and optical properties	Leugering and Schaum 1970
Reactor blends: PE with PP and EPR	Reactor-*thermoplastic polyolefin*, R-TPO	Yamazaki and Fujimaki 1970
PP/EPR and 5–30 wt% of hexene- or octene-type LLDPE	Improvement of mechanical properties	Shirayama et al. 1972
PP/HDPE = 1:1	Processability, weld-line strength, low-T impact strength	Moorwessel et al. 1974
PP with 5–20 wt% LDPE and EPR	Transparency and mechanical performance	Oita et al. 1978
PP with EPR and then with PE	Co-continuous morphology – impact and mechanical properties	Huff 1978
Blending PP with EPR and then with PE	Co-continuous morphology, high performance	Huff 1980
PP, LDPE, HDPE, and an EP-block copolymer	Films with good modulus, tear strength, and sagging properties	Shin-Kobe Electric Machinery 1984
PP, LLDPE, LDPE, and/or EPR	High modulus and clarity	Bahl et al. 1985
PP, LLDPE, and a *Plastomer*™ (a metallocene ethylene-co-butene)	For melt-spun or melt-blown fibers or fabrics	Bartz et al. 1993a
EPR with *Plastomer*™	Packaging films, tubes, and trays	Mehta and Chen 1994
HDPE with PP autoclave-foamed with CO_2	Foam with $\geq 10^9$ cells/mL and cell diameter, $d \leq 10$ μm. High impact strength	Dorudiani et al. 1998

Table 1.41 PE/PA blends

Composition	Reason	References
LDPE or PP with either PA-6 or PA-66	For sheets, films, fibers, or bottles	Mesrobian and Ammondson 1962
PE with a PE-PA-6 copolymer	Transparency and low permeability	Craubner et al. 1962
PE mixed with a lactam and then polymerized	Low water absorption, strength	Hill et al. 1970
PA-6/LDPE or PIB/N-stearyl stearamide	Low-temperature impact, tenacity	Gilch and Michael 1970
PA-66, PE, PBT, and PC with SEBS	Co-continuous morphology	Gergen and Davison 1978
Aromatic polyamide (PARA) compounded with PE	Processability, elongation at break, tensile, and impact strength	Paschke et al. 1983
PA with carboxylated EPDM and PE	For improved impact resistance	Unitika Ltd. 1983
PA blended with a mixture of PP, HDPE, and EPR	Processability, mechanical properties even after water immersion	Hasuo et al. 1985
PA with HDPE, EPR, and maleated PP	Rigidity and low-T impact strength	Kondo and Tominari 1987
PARA with PE or PP-MA and hydrazine	Resistance to thermal degradation	Yoshihara 1990
PO-g-GMA, acrylamide, vinylpyrrolidone, acrylic, and/or methacrylic acid ester and then blended with either PA or PEST	Adhesion to fillers, excellent performance of filled compositions	Teraya et al. 1994

used for the electrical insulation of high-voltage, submarine cables (Barraud et al. 1993). Blends of LLDPE with EVAc or EEA have comparable physical properties and cost to plasticized PVC (Rifi 1994).

PE/PA Blends

The reasons for blending PE with PA are (1) a desire to improve the impact strength and moisture absorption of PA and (2) to improve rigidity and barrier properties (to oxygen and solvents) of PE. Films and containers manufactured from the latter blends show overlapping lamellar structures that cause high tortuosity for molecular diffusion and significant reduction of oxygen or solvent (e.g., gasoline) permeability. The technology became particularly attractive after the reactive grafting of PO with either maleic anhydride, acrylic acid, or glycidyl methacrylate was invented (Steinkamp and Grail 1976). These modified POs could be directly used in blends with either PA or PEST (Davis 1975). In Table 1.41 examples of PE/PA blends are given.

PE/PC Blends

To increase rigidity of PE, the resin has been blended with about 5 wt% of a high-modulus polymer, e.g., PC (Peters and Schuelde 1963). PC also stabilized PO against the thermal degradation (Schutze et al. 1972). Addition of 3–5 wt% PO

Table 1.42 Compatibilized PE/PC blends

Compatibilizer/impact modifier	References
0.01–2 wt% ABS	O'Connell 1974
Hydrogenated chlorosulfonated butadiene-styrene block copolymer	Bussink et al. 1978
Maleated LLDPE	Mitsubishi Chemical Ind. 1980
Ethylene-glycidyl methacrylate copolymer (EGMA)	Sumitomo Chem. 1982, 1983
Methyl-phenyl siloxane	Rosenquist 1982
Acrylic *and* hydrocarbon elastomers (viz., BR, EPR, EPDM, IR, IIR)	Teijin Chem. 1982, 1983, 1984
EPR or EPDM	D'Orazio et al. 1982
1–5 wt% SEBS	Idemitsu Kosan 1983
Acrylic rubber or maleated PO	Idemitsu Petrochem. 1983, 1984
4 wt% poly(butylacrylate-co-methylmethacrylate) copolymer	O'Connell 1983
ABS with polysiloxanes containing Si-H bonds	Liu 1983, 1984
Ethylene-ethyl acrylate copolymer (EEA) and SEBS	Overton and Liu 1984, 1985
0.2–15 wt% acrylic impact modifier (MBA, *Acryloid*™ *KM*)	Endo and Ishii 1984
TPE (acrylic rubber, butyl rubber, EPDM, or SBS)	Kozakura et al. 1992, 1994

Table 1.43 PPE/styrenics blends with PE

Composition	References
PPE with LDPE	General Electric 1966
PPE with either SBR or HIPS and LDPE	Summers et al. 1972
PPE was blended with SEBS and PE	Yonemitsu et al. 1976
PPE with HIPS, SEBS, and PE	Haff and Lee 1978
PPE with PS, SEBS, and PE	Haaf 1979
PE with 0–35 wt% PP, PDMS, and 5–35 wt% PPE, PC, PET, or PA	Plochocki et al. 1979
PPE with hydrogenated SB block copolymer and LDPE	General Electric 1984
PPE with HIPS, SEBS, and LLDPE	Hambrecht et al. 1986
PPE with styrenics and high molecular weight HDPE	Bopp and Balfour 1993

toughened PC (Yamada 1963). For good dispersion, the blending should be carried out at $T > 290\,^{\circ}C$, using PE grades with the viscosity ratio $\eta(PE)/\eta(PC) \leq 0.3$–$0.9$. Several impact-modified grades of PC (viz., *Lexan*™ *EM*) comprise PE (Freitag et al. 1991). However, as Table 1.42 illustrates, most PE/PC blends also contain a polymeric compatibilizer-*cum*-impact modifier.

PE/PPE Blends

The PPE/PE blends are not commercial, but a small amount of PE is frequently added to PPE/HIPS or PPE/SBR blends to improve processability and solvent resistance (see Table 1.43).

To enhanced rigidity of PO, 5–35 wt% of modified PPE was added. In this application, PPE can be considered a low-density filler. Similar effects can be obtained adding a small quantity of other polymers, viz., PC, POM, PPS, etc.

Table 1.44 PEST/PE blends

Composition	References
PET with 0.5–50 wt% PE, for impact strength	Glanzstoff 1967
PET with poly(ethylene-co-acrylic acid) ionomer	Cope 1969
PET with oxidized and carboxylated PE and glass fibers	Segal 1973
Poly(ethylene-2,6-naphthalene dicarboxylate) (PEN) with MDPE and/or PP	Tokai and Sakai 1973
PBT (or PET) with PC and LLDPE	Boutni and Liu 1983
PBT (or PET) with PC and PB	Dieck and Kostelnik 1983
PET with LLDPE	Smith and Wilson 1984
PET with either PE, PP, PO-GMA, vinyl- or acrylic-grafted PO, and GF	Mukohyama 1993
PBT with PC, and PE, PP, and/or EPR grafted with GMA or MA	Fujie 1993
HDPE and copolymer of n-butylterephthalate with ethylene- and propylene glycol	Abu-Isa and Graham 1993
PET with 30–70 wt% LDPE, HDPE, or LDPE and EEA-GMA	Natarajan et al. 1993, 1994

Table 1.45 POM/PE blends

Composition	References
POM was blended with 1–5 wt% of either PE, EVAc, or PEG	Burg et al. 1972
POM was blended with 90–99 wt% of LDPE	Rudin and Schreiber 1964b
PE or PP with EVAc and either POM, PMMA, PS, or SMM	Yamamoto et al. 1971
POM was blended with EVAc and HDPE	Ishida and Masamoto 1974
POM was first blended with TPU and then with either PA, LLDPE, PP, PBT, or PET	Flexman 1992

PE/PEST Blends

Addition of PE to PEST is known to improve impact strength, processability, solvent resistance, and weatherability. When more than 5 wt% of PE is required, compatibilization is advisable. Examples of these systems are listed in Table 1.44.

PE/POM Blends

POM is difficult to compatibilize, and without compatibilization only $\leq$ 10 wt% of POM in PE, or vice versa PE in POM, can be used. For example, addition of a small amount of PE to POM improves its processability, impact and abrasion resistance, hardness, surface finish, and rigidity, while addition of POM to PE improved its modulus and abrasion resistance – see Table 1.45.

PE/Specialty Resin Blends

Most specialty resins are processed at temperatures that limit the possibility of blending them with PE. The PE/specialty resin blends usually contain low concentration, $\leq$ 5 wt%, of either component. Addition of PE improves the processability, surface finish, chemical, solvent, and impact resistance. Addition of specialty polymer to PE may improve rigidity and processability (viz. PE/LCP). Examples are given in Table 1.46.

Table 1.46 Specialty polymer blends with PE or PP

Composition	References
Polyarylene polyether sulfone (PAES) with $\leq$ 5 wt% of PE or PP	Gowan 1969
Polysulfone (PSF) with either PE, PP, BR, EPR, or EPDM	Hart 1971
Polyarylamideimide (PAI) with a small amount of PE	Toray Ind. 1981
Polysulfide (PPS) blends with PDMS and either PE or PP	Liang 1987
PPS/PE compatibilized by addition of an aromatic nitro compound	Köhler et al. 1992
Polyoxycyanoarylene (POCA) with PO, compatibilized by EGMA	Hashimoto et al. 1990
PE blends with liquid crystal polyester (LCP)	Alder et al. 1993

1.5.9 Polypropylene (PP)

1.5.9.1 Homopolymers

There are three types of polypropylene: amorphous (aPP), isotactic (PP), and syndiotactic (sPP) (Karian 2003). Performance of these resins depends on the tacticity content. PP was commercialized in 1957 by Hoechst. The slurry process in hexane used the Ziegler-Natta ($AlEt_2Cl + TiAlCl_6$) catalyst (Sailors and Hogan 1982). The new metallocene catalysis leads to isomer purity in excess of 96 % (see, for example, Posch 2011). It is also possible to produce branched, *high melt strength PP*, with extensional stress hardening, similar to that of LDPE (Phillips et al. 1992). The new PPs show the melting point, $T_m = 120–164$ °C. To enhance the performance, PP is usually blended (in the reactor or outside the reactor) with much more viscous PP-copolymers. As a consequence, one of the most serious industrial problem is homogenization of these materials (Luciani and Utracki 1996; Utracki and Luciani 1996b).

Most industrial polypropylenes are isotactic, but a few syndiotactic polypropylenes are available (De Rosa and Auriemma 2006). The advantage of sPP over PP is that impact strength and tensile modulus of sPP are significantly higher. While PP has a planar zigzag helical structure, the sPP has a three-dimensional one that leads to lower crystallinity and melting point: $T_m(\text{PP}) \approx 165$ vs. $T_m(\text{sPP}) \approx 133$ °C.

1.5.9.2 PP Blends

PP is brittle, especially at $T \leq T_g \approx 0$ °C. The resin fractures by the crazing-cracking mechanism (Friedrich 1983). The discovery of PP immediately followed by search for methods of improvement the low-T impact behavior. PP was blended with EPR or EPDM (Hogan and Banks 1953, 1955), PE (Holzer and Mehnert 1963), sPP (Emrick 1966), aPP (Tanahashi and Kojima 1970), etc.

PP/Other Polyolefin Blends

PP is often made using two reactors in series: the first reactor makes isotactic PP, while the second reactor makes a random copolymer of PP and PE. The copolymer is amorphous, and it is blended with the PP homopolymer to enhance impact resistance (Tan et al. 2005). PP blends with elastomers will be discussed in the following parts. In Table 1.47 few examples of PP blends with other POs are given.

Table 1.47 PP/PO blends

Elastomer added to PP	Comment	References
PP/PIB miscible (?) blends	Low-temperature impact properties	Ranalli 1958
PP miscible with aPP or polybutene-1	Reduction of T_g by up to 20 °C	Romankevich and Frenkel 1980
10–60 wt% PP or LLDPE with EPDM and $\leq$ 95 wt% PIB or butyl rubber	Soft, easy foamable blends (due to strain hardening)	Matsuda et al. 1981, 1988
PP with polytransoctanamer (PTO)	Fivefold increased impact strength	Kita and Hashimoto 1987
PP with polyoctadecene (POD)	Temperature sensitive transparency	Tanaka et al. 1988
PP/PB and *Plastomer*™	Impact and mechanical properties	Bartz et al. 1993b
PP/PB and a poly(*1*-butene-co-ethylene)	Processability, impact strength, and optical properties	Hwo 1994
High MW aPP blended with high MW of either PP or sPP	aPP was immiscible with PP and partially miscible with sPP	Silvestri and Sgarzi 1998
Addition of EPR to PP	To strengthen spherulites boundary	Lustiger et al. 1998

PP/Elastomer Blends

These blends constitute a large, commercially important group. Usually 5–20 wt% of elastomer have been used. Alloying improves processability (e.g., in blow molding) and impact strength at low temperature. Diverse elastomers have been used, e.g., EPR, BP, PIB, BR, uncured PB, and SBR; *dynamically co-vulcanized* CBR; and BR, CSM, and EPDM (Reid and Conrad 1960, 1962; Dow Chem. 1963; Gessler and Haslett 1962; Esso R&E 1962; Coran and Patel 1978). Blends with amorphous CSR showed good mechanical properties (Shikata et al. 1973). Partially vulcanized blends of CSR with PP and/or ULDPE had good processability, hot-weld strength, interplay adhesion, and crack resistance (Ainsworth 1990, 1994). Addition of CPE improved PP's processability and properties (Newe et al. 1984).

Many EPR and EPDM elastomers show a block copolymer behavior. When blended with PP, they form emulsion-like dispersions. For the ease of compounding, a small amount of PE may also be added. Furthermore, if the elastomeric phase is lightly cross-linked, the morphology is more stable. The PP/EPR blends can be processed by all methods used for PP. They are characterized by good processability, dimensional stability, low shrinkage, high stiffness, tear strength and softening temperature, good mechanical properties (at T = −40 °C to 150 °C), ozone resistance, fatigue, and abrasion resistance (see Table 1.48). These materials have been used in more than 200 applications, in automotive industry, appliances, hardware and plumbing, medical, shoe industry, sports equipment, toys, etc. Examples of commercial PP/EPR blends are *Buna*™, *Dutral*™, *Epcar*™, *Epichlomer*™, *Epsin*™ and *Santoprene*™, *Esprene*™, *Ferrocline*™, *Gafply*™, *Intolan*™, *Kelburon*™, *Larflex*™, *Milastomer*™, *Nordel*™, *Royaltherm*™, *Trilene*™, and *Vistalon*™.

Table 1.48 PP/EPR blends

Elastomer(S) added to PP	Reason	References
0.1–60 wt% EPR, containing 2–25 % ethylene – the earliest patents	Increased impact and tensile strength, superior mechanical properties	Schilling 1964, 1966; Short 1967; Shirayama et al. 1971
EPDM (EPR with dicyclopentadiene or ethylidene-norbornene), partially cross-linked with peroxides	Alloys could be shaped into articles with good properties without further vulcanization	Fischer 1972
EPDM	Unexpectedly high tensile strength	Stricharczuk 1977
Dynamic vulcanization of PP with either EPR or EPDM; *Santoprene*™	A range of Shore hardness, toughness, elongation, impact strength	Coran and Patel 1978
Dynamically blended PP/EPR and a peroxide-containing co-polyolefin	A masterbatch that subsequently was blended with EPDM into TPO	Yamamoto and Shimizu 1979
Sequential compounding of PP, first with EPR and then with PE	Co-continuous morphology, good impact and mechanical properties	Huff 1980
Amorphous EPR + crystalline EPR	Balance of properties, impact strength	Galli and Spataro 1983
Bimodal EPR	Impact strength and mechanical properties	Makino et al. 1986
PP/PE, EPR, EPDM, SBS, ionomers, EVAc, EEA, or ESI. Styrene-grafted PP added and "visbreaking"	Blends foamed with isopentane; good dimensional stability	Fudge 1987
Reactive preblend of PP with either EPR or EPDM (in a ratio from 1:0.01 to 1:0.5) added to PP	Improved homogeneity, heat resistance, impact resistance, and greater flowability	Yeo et al. 1989
Dynamically vulcanized BR or CBR and EPDM	High tensile strength	Puydak et al. 1990, 1992
PP, PE, PS, PMMA, or PVC was blended with either EPR or EPDM	Sequentially cured and foamed blends	Cakmak and Dutta 1992; Dutta and Cakmak 1992
EPR blends with sPP	Transparent, low-T impact resistance	Asanuma et al. 1992
EPR, EPDM, or their mixtures, with a metallocene-type VLDPE, PP, and talc	Moldability, surface appearance, hardness, and impact resistance	Nishio et al. 1992
Ethylene-α-olefin copolymers, stereo-block polypropylene, or EPR	Enhanced inter-spherulitic and interlamellar strength	Lustiger 1993
Isotactic EPR, $T_g < -20$ °C	Modulus, low-T impact strength	Winter et al. 1993
Random crystalline terpolymers – EPR	For fibers with high resiliency and shrinkage, for pile fabrics	Clementini et al. 1993
EPDM with ethylene-methacrylate-zinc, glycidyl methacrylate-acrylate or epoxy	To improve the scuff resistance	Dawson 1993

(*continued*)

Table 1.48 (continued)

Elastomer(S) added to PP	Reason	References
Dynamically vulcanized blends of PP with EPDM, mineral oil, and PDMS	For slush molding large plastic parts	Hikasa et al. 1994
Poly(4-methyl-1-pentene) with PIB	For food overwrap films	Nagase et al. 1994
Olefinic, partially cross-linked elastomer: EPDM, EPR, BR, NR, IR, CBR, etc.	For manufacturing automotive components	Ellul 1994
Metallocene PP was alloyed with EPR	For low-temperature heat sealability	Shichijo 1994
PP blended with EPR and EPDM and then irradiated in the presence of O_2	Easily foamed blends with high strain hardening	DeNicola et al. 1995, 1997
Long branch containing PP with partially cross-linked EPR and a foaming agent	Reduction of density by ≥ 2, smooth surface, heat and weathering resistance	Okada et al. 1998

PP/EVAc blends are immiscible; thus, in two-component systems, only a small amount of EVAc can be used, e.g., to improve dyeability, flexibility, electrostatic dissipation, or barrier properties. The hydrolyzed EVAc (EVAl) was also used (Minekawa et al. 1969). In most cases, the PP/EVAc blends are part of more a complex, multicomponent system comprising a reactive compatibilizer (see Table 1.49).

1.5.10 Thermoplastic Olefin Elastomers (TPO)

Ziegler-Natta catalyst makes it possible to polymerize α-olefins into elastomers with controlled degree of crystallinity and cross-likability. The first EPR's were manufactured in 1960, 3 years later, the first EPDM. It is advantageous to produce block copolymers with PP being the rigid and PE the soft block. A direct sequential polymerization of propylene and ethylene-propylene mixture leads to the reactor blends (R-TPO) (Cecchin and Guglielmi 1990).

EPR may be cross-linked by peroxides, while EPDM by the standard methods of the rubber industry. By varying the composition and process variables, a wide range of properties can be obtained. The resin with vulcanized, dispersed phase has CUT $\approx$ 125 °C, higher than standard TPO, and they are known as the *thermoplastic vulcanizates*, *TPV* (Fritz and Anderlik 1993). Diverse TPOs with properties that range from flexible to rigid (but tough) are manufactured by the large resin producers, as well as by the compounding houses (Utracki and Dumoulin 1995).

Polytransoctanamer (PTO) has been used as a high-performance elastomer and in blends with commodity and engineering resins. Polyoctadecene (POD) blends with PP are thermochromic. The most interesting are the metallocene-type polycyclic polyolefins, e.g., polycyclopentene or polynorbornene, either syndiotactic or isotactic with $T_m = 400\text{–}600$ °C.

Table 1.49 PP/EVAc blends

Elastomer added To PP	Comment	References
PP with 18–32 wt% EVAc and/or ethylene-ethylacrylate copolymer (EEA)	Impact strength, elongation, and low-T brittleness	Miller and Reddeman 1962
PP with EVAc	Dyeability, flexibility, barrier properties, and toughness	Sakata et al. 1968
PP/EVAc and POM, PMMA, PS, or SMM	For paperlike films	Yamamoto et al. 1971
70 wt% PP and EVAc, PVCAc, HDPE	Low-temperature impact resistance	Kojima and Tanahashi 1972
PP/EVAc with maleated LDPE	Melt strength and rigidity	Idemitsu Petrochem. 1983
35 wt% PP, 50% PIB, and 15% EVAc	For films, moldings, and extrusions	Shulman 1984
PP/PC with 2–35 wt% EVAc	Excellent solvent resistance	Giles and Hirt 1986
10–90 wt% PP, 5–60 wt% EVAc, and 5–50 wt% PEOX	Miscible (?) alloy for intermediate layer in recyclable barrier films	Sanchez et al. 1991
PP/EVAc with PP-MA	Low permeability by gases or liquids	Kamal et al. 1992
PP/EVAc with EAA and polybutene	Tough, radiation resistant, heat sealable	Wilfong and Rolando 1993

1.5.11 PP/Engineering Resin Blends

1.5.11.1 PP/PA Blends

There are three types of PP/PA blends: (1) with a small percentage of PO, either acidified or not, (2) alloys with high component ratio where PA is a matrix, (3) and blends with a small amount of dispersed PA to increase rigidity. Table 1.50 gives some examples of these systems.

To toughen PA, 2–5 wt% of either PO, elastomer, *ionomer*, acidified, or epoxidized copolymer may be added. PA/PO blends of type (2) were developed to improve dimensional stability and to reduce water absorbency of PA. Alloying PA with PO reduces the *rate* of water migration to and from the blend, but not the inherent water absorption of PA (Utracki and Sammut 1991, 1992). The alloying is either a two- or three-step reactive process: (1°) acidification of PO, (2°) preparation of a compatibilizer, and (3°) compounding PP, PA, and the compatibilizer. Usually, the reactive blending is carried out in a twin-screw extruder (Nishio et al. 1990; Hu and Cartier 1998). Since it may cause reduction of the blend crystallinity (thus performance), the extent must be optimized. The rigid PA/PP blends usually comprise PA:PP = 3:2 with 12 wt% of a compatibilizing copolymer. Finally, in type (3), incorporation of PA improves processability, solvent resistance, CUT, HDT, and surface finish. For enhanced performance, the blends should be compatibilized.

Table 1.50 PP/PA blends

Composition	Comment	References
1. Toughened PA		
PA, PP, and 0.5 wt% of PP-MA	Compatibilized blends	Davis 1975
PA/PO and ionomer	*Surlyn*™ as a compatibilizer	Toyobo 1981
PA/PO and PO grafted with MA or a compound containing two epoxy groups	High impact strength	Subramanian 1980, 1983, 1984
PO grafted with glycidyl methacrylate, acrylamide, vinylpyrrolidone, acrylic acid esters, and/or methacrylic acid esters and then blended with PA or PEST	Two-stage, reactive impact modification: preparation of reactive compatibilizer and then blending	Teraya et al. 1994
2. Rigid PA/PP blends		
Non-compatibilized PP/PA blends	For films, sheets, or bottles with good printability and low liquid permeability	Mesrobian and Ammondson 1962
PP with PA-6 or PA-66 and GF	Rigid, non-compatibilized blends	Asahi Fiber Glass 1981
PP/PA-6 compatibilized by EPR-MA	Impact-resistant blends	Katsura 1986
PP was maleated and then reactively blended with PA to obtain 12 wt% of PP-co-PA	Two-step blending: maleation of PP, incorporation of PA	Glotin et al. 1989
PA was blended with acidified PP and GF	Moldability, water resistance, HDT, low-T impact strength	Iwanami et al. 1989
Reactive blending of PP/PA-6 with either EPR-MA or SEBS-MA	SEBS-MA gave better impact strength, yield stress, toughness, and modulus	Rösch and Mülhaupt 1994
3. PA/Elastomer blends		
PP, PA-6-co-PA-66, PP-MA with NBR and EPDM	Impact strength, high stress at break, high elongation, good ductility, and high gloss	Tokas 1981
PP, EPR, PA, and SMA, SEBS-MA, EPR-MA, MBA, ASA, etc.	For automotive, electrical, electronics, building, furniture, small appliances, etc.	Chundury and Scheibelhoffer 1994
PP, EPR, PA, and 2 compatibilizers from between SEBS, SEBS-MA, and poly(ethylene-co-acrylic ester-co-MA)	Recyclable high impact strength blends	Chundury 1994
PP-MA was blended with PB	Adhesive to metals and polar polymers: PA, PET, or PC	Lee et al. 1994

1.5.11.2 PP/PC Blends

PP and PC are immiscible; thus, excepting the exploratory use as a “plastic paper,” only the two ends of the concentration range have been explored, viz., addition of 5 wt% PP to PC (to improve processability of PC) (Dobkowski 1980) or addition of $\leq$ 10 wt% of PC (to improve PP processability, enhance crystallinity and crystallization temperature, the appearance, modulus, and impact strength) (Liang and Williams 1991). For concentrations $\geq$ 10 wt%, compatibilization is necessary.

Table 1.51 PP/PEST blends

Composition	Comment	References
PAr with low concentration of PO, elastomer, or EVAc	Uncompatibilized blends	Koshimo et al. 1973
PBT with PP	Improved moldability of PBT	Seydl and Strickle 1976
PET, PO, and either glycidyl methacrylate-modified PO or vinyl-grafted PO	High heat and moisture absorption resistance	Mukohyama 1993
PBT/PC with PE, PP, or EPR modified with 0.05–15 wt% glycidyl methacrylate and/or 0.1–2 wt% MA	Processability, toughness, rigidity, strength, dimensional stability, and flexural modulus	Fujie 1993
PPE, PA, or PEST with EPDM, SBS, SEBS, or EPR, and PP grafted with styrene and a glycidyl moiety	Flexural and tensile strength	Okamoto et al. 1993, 1994
Recycled PET/PP = 2:3–3:2 and SEBS-MA	For molding battery containers	Tekkanat et al. 1993, 1994
PP with PET or PBT and a polyolefin-polyester graft copolymer	Compatibilized	Fujita et al. 1994
PEST, PA, PP-MA, and either PET or PBT with sodium dimethyl 5-sulfoisophthalate	High tensile and impact strength	Tajima et al. 1994

This is accomplished using ethylene-acrylic copolymer, cellulosics, PA, PVAc, or TPU (Goldblum 1963, 1964); an acrylic elastomer, acrylic elastomer with PP-MA, and either butyl rubber or isobutene-isoprene rubber (Teijin Chem. 1982, 1983); SBR and EEA (Liu 1984); MBS (Overton and Liu 1984); or EVAc (Giles and Hirt 1986).

1.5.11.3 PP/PEST Blends

PP is antagonistically immiscible with PEST, and when the concentration of the dispersed phase exceeds 5–10 wt%, compatibilization is necessary. Initially, the uncompatibilized blends were formulated within the low concentration region of the dispersed phase. By the end of 1980s, reactive compatibilization started to dominate the technology. Examples of PP/PEST blends are listed in Table 1.51.

1.5.11.4 PP/PPE Blends

Two-component blends of PP with PPE are unknown. To get a reasonable performance out of a PP/PPE mixture, first PPE must be toughened using a styrenic resin, and then the blend compatibilized. Thus (see Table 1.52), PP is only one ingredient in multicomponent PPE blends.

1.5.11.5 PP/POM Blends

PP/POM blends are antagonistically immiscible, not available on the market. The early blends contained a small amount of one resin in another, viz., either PP or LDPE, with 1–10 wt% POM showed improved processability, good appearance,

Table 1.52 PP/PPE Blends

Composition	Comment	References
PPE-MA with PP-MA, SBR, glycidyl methacrylate copolymer, and/or phenylenediamine binder	Solvent resistance, moldability, impact, and mechanical properties	Togo et al. 1988
PPE dispersed in PP, PE, PA, PEST, POM, PPS, or PEEK, compatibilized by EPR-MA, EVAc-GMA, and either maleic anhydride or bis(4-phenyl isocyanate)	Processability, heat resistance, and mechanical properties	Nishio et al. 1988, 1994
PPE, PP, and SEBS	Modulus, rigidity, tensile strength, and HDT	Lee 1990
PPE with PP grafted with styrene and MA and EVAc-GMA, styrene-grafted EPDM	Rigidity as well as high heat, chemical, and impact resistance	Furuta and Maruyama 1990
PPE, PP, and PPS with hydrogenated styrene-isoprene block copolymers	Heat, impact, and solvent resistance	Maruyama and Mizuno 1990
PPE modified by glycidol or epichlorohydrin with PP-MA or PP-GMA and PA or PEST	Moldability and mechanical strength	Nakano et al. 1992
PPE with PP, compatibilized with styrene-grafted propylene-methyloctadiene (or hexadiene)	Stiffness and impact strength	Tanaka et al. 1992
PPE/PS, styrene-grafted polypropylene (PP-PS), SEBS and PP	Processability, HDT, impact and tensile strength, stiffness solvent resistance, gloss	DeNicola and Giroux 1994
PPE/PP compatibilized with PO grafted with ethylenically unsaturated *t*-alkylcarbamate	Copolymers used as decomposable compatibilizing agents	Campbell and Presley 1995

and improved performance (Rudin and Schreiber 1964a). However, blends containing higher concentration of ingredients must be compatibilized, viz., by addition of muconic acid-grafted PP (Chen et al. 1991) or by TPU and EBA-GMA (Subramanian 1992).

1.5.12 PP/Specialty Polymer Blends

Most specialty resins require high processing temperatures, while PP usually has $T_{proc} < 250\ °C$. Thus, only few blends of this type are known. For example, addition of PP enhanced throughput of PAES (Gowan 1968, 1969), PEI, PC/PEST blends, etc.

Linear, aromatic polyamides (PARA) are either liquid crystalline, semicrystalline, or amorphous. Mainly the latter resins are used in blends with PP, viz., PARA with PP-MA (Iwanami et al. 1990), PARA with PE-MA, or PP and hydrazine (Yoshihara 1990). Blends of copolyphthalamide (PPA) with PP were compatibilized using either PP-MA (Paschke et al. 1993, 1994) or PP grafted with acrylic acid (Brooks et al. 1993, 1994).

Table 1.53 PP/LCP blends

Composition	Comment	References
Low concentration of LCP in a resin	To improve processability	Cogswell et al. 1981
10 wt% of LCP was blended with, e.g., PP, PS, PC, or PI	Molecular orientation imposed by extrusion through a rotating die	Haghighat et al. 1992
LCP and PP, PET, PA, PC, PE, PVC, PVDC, PPS, PVDF, PVF, or PMMA	To produce oriented films with protrusions that resulted in low friction	Wong 1990, 1994
PP was blended with LCP	2 extruders with a static mixer, to stretch LCP into microfibrils	Sukhadia et al. 1991, 1992
PP/LCP compatibilized with PP-MA	(Processing as described above)	Baird and Datta 1992
LCP with either PP, PPE, PPE/PS, PC, or PEI	(1) Prepregs from an extruder, mixer, and rolls; (2) prepregs consolidated at $T < T_m$	Isayev 1991, 1993

PP blends with a small amount of LCP are of industrial interest for two reasons: (i) to improve processability or (ii) to improve the mechanical performance. The second effect depends on the blend's morphology, i.e., on the orientation of LCP domains. The latter depends on the concentration, viscosity and elasticity ratios, interfacial tension coefficient, flow type and intensity, total strain, drawdown ratio, etc. Three stages of orientation are (1) drop deformation, (2) fibrillation of the domains, and (3) stretching of the LCP chains (Champagne et al. 1996). Only the latter provides a reasonable cost-to-performance ratio. Examples of PP/LCP systems are listed in Table 1.53.

1.6 Engineering Resins and Their Blends

The term *engineering polymer* is applied to a processable resin, capable of being formed to precise and stable dimensions, having high performance at CUT $\geq 100\,°C$, and the tensile strength of $\sigma \geq 40$ MPa (Utracki 1989a). Five polymer families belong to this category: PA, PEST, PC, POM, and PPE. While the relative size of the engineering resin market varies from country to country, these polymers constitute about 13 % by volume and 34 % by value of the total plastic's consumption. Since the blends of engineering/commodity resins have already been discussed, here only engineering/engineering and engineering/specialty resins will be considered.

Engineering resins and their blends have been foamed using mainly chemical foaming agents, e.g., hydrazodicarboxylates, benzazimides, or 5-phenyltetrazole. However, products of decomposition of these agents (e.g., alcohol, ammonia, water, etc.) were found to hydrolyze PC, PA PC/ABS, or PEST, reducing the performance of foamed products. For this reason, dihydro-oxadiazinones were proposed as the preferred chemical foaming agents for the engineering resins, their compositions, and blends (including PPE/HIPS) (Nizik 1978, 1979). Another method for foaming high temperature polymers profits from thermal

Table 1.54 Comparative properties of PAs

Property	PA-6	PA-66	PA-11	PA-12	PA-46	PA-610	PA-63T
Tensile modulus (MPa)	1,400	2,000	1,000	1,600	1,700	1,500	$\geq$ 2,000
Tensile stress (MPa)	40	65	50	45	59	40	$\geq$ 75
Maximum elongation (%)	200	150	500	300	60	500	50–150
Density (kg/m^3)	1,130	1,140	1,040	1,020	1,100	1,080	1,060–1,120
T_g(°C),	57	57	46	37	295	50	145
T_m (°C)	220	255	185	180		215	240
HDT (°C)	80	105	55	140	90	95	150

instability of polypropylene carbonate (PPCO, MW = 1–1,000 kg/mol) (Kuphal et al. 1990). The process involves blending PPCO with a resin or its blend that is to be foamed. The blend is then heated to T > 300 °C, sufficient to melt the principal resin and to decompose PPCO. Talc, wollastonite, clay, $CaCO_3$, or citric acid can be used as a nucleating agent. The densities of the molded articles were reduced by at least 50 %. Today foaming of the engineering resins with supercritical CO_2 is practiced.

1.6.1 Polyamides (PA)

Polyamides are abbreviated as PA, followed by the number of carbons in a diamine and dicarboxylic acid, viz., PA-66 has six carbons in each component, etc. Poly-ε-caprolactam or polyamide-6 (PA-6) was first studied by Von Brown in 1905–1910, and 30 years later commercialized as *Perlon*™. In the year 1936, PA-66 and several other aliphatic and semi-aromatic polyamides were disclosed (Carothers 1937). Two years later, du Pont introduced *Nylon*™. PA-11 was commercialized in 1955, PA-12 in 1966, PA-612 in 1970, and PA-46 in 1987. In 1976 du Pont started production of the *super tough* PA blends (Damm and Matthies 1990). In 1991 consumption of the thermoplastic PAs was estimated at 1.2 Mt. Comparative properties of the better-known PAs are listed in Table 1.54.

Liquid crystal aromatic polyamides (PARA), poly(*meta*-phenylene isophthalamide), *Nomex*™, and poly(*para*-phenylene terephthalamide), *Kevlar*™-49, were commercialized in 1961 and 1965, respectively. Amorphous aromatic polyamide, *Trogamid*™, was introduced in 1969, and polyphthalamide *Amodel*™ in 1991.

PA started to be blended with other engineering resins at the end of the 1960s, viz., PA with POM (Moncure 1969; Asahi Chem. 1969), PA with POM and PET (Fujiwara 1971), PA-6 reactively compatibilized with PET (Reimschussel and Dege 1969), PA-6-co-diisocyanate copolymer with PET (Illing 1970), etc. By the year 1970, the number of PA blends rapidly started to increase. The main efforts were directed toward improvement of toughness and processability of PA. Reactive compatibilization and impact modification became an integral part of the PA-blends technology.

Table 1.55 PA(1)/PA(2) blends

PA(1)	PA(2)	Comment	References
PA-66	PA-6 or PA-610	Reduced residual stresses in moldings	Stott and Hervey 1958
X-linked PA-66	PA-6 or PA-11	Excellent impact resistance	Uniroyal 1968
PARA	PA-6, PA-66, PA-610, PA-11, or PA-12	To improve the impact strength	Dynamit Nobel 1969
PA(1)	PA(2)	Miscibility/immiscibility studies	Zimmerman et al. 1973
PA-6I6T	Another PA at 1:1	Tough and strong fibers or films	Unitika 1982
PA-6	PA-11	Toughened by sulfonated EPDM	Weaver 1983, 1985
PA-66	Either PA-6, PA-612, PA-11, or PA-12	Printability, clarity, barrier, and dimensional stability	Mollison 1984
PA-6	Poly(trimethyl hexamethylene terephthalamide)	Resistant to cracking when exposed to metal halides	Ube Ind., 1984, 1985
PA-66	PA-6	SMM-MA and mineral filler	Asahi Chemical Industry 1985
PA-66	PA-6	With aminosilane-treated GF	Toray Ind., 1985
PA-mXD6	PA-66 and PBT, or PA-6	Tough, high-T, films; good barrier against O_2 permeation	Mitsubishi Gas Chem. 1985
PA-12	PARA	Transparent blends	Maj and Blondel 1993
PA-6I6T	PA-612 or PA-666, with PA-6, PA-11, or PA-12	At least 5 % shrinkage at 90 °C in at least one direction	Vicik 1994
PA-6 or PA-66	Semi-aromatic copolyamide	Compatibilized with either SMA, maleated EPDM, or MBA	Schmid and Thullen 1994
PA-66	PARA	Maleated elastomer and filler; low-T impact strength and HDT	Heger and Oeller 1994

1.6.1.1 PA(1)/PA(2) Blends

These blends are commercially available, e.g., *Zytel 3100*™ and *Grilon*™ *BT*. They show improved processability, solvent resistance, elongation, low-temperature impact and tensile strength, as well as enhanced barrier properties (see Table 1.55). They have been also incorporated into more complex, multicomponent systems, e.g., PA/PARA = 1:1, PPE, PCL, *ionomer*, EPR, a monomeric mixture of oxide and/or carbonate (e.g., ethylene carbonate, ethylene oxide, etc.), and a polyhydric alcohol (e.g., ethylene glycol or trimethylene glycol). The alloys were used to mold parts for the automotive, electrical, or electronic industries (Hamada et al. 1994).

1.6.1.2 PA/PPE Blends

PAs are excellent candidates for blending with PPE – each ingredient compensates for deficiency of the other. Since the resins are immiscible and brittle, they must be compatibilized and toughened. In consequence, PA/PPE blends comprise minimum four polymeric components: PA, PPE, a styrenic modifier, and an acidic compatibilizer. Usually PA is the matrix in which PPE/styrenic resin domains are dispersed. As time progresses, these blends are getting more complex – examples are shown in Table 1.56. Commercial blends are *Artley*, *Dimension*™, *Luranyl*™, *Lynex*™ *A* and *Xyron*™, *Noryl*™ *GT*, *Remarry*™, *Ultranyl*™, *Vestoblend*™, etc.

1.6.1.3 PA Blends with POM, PEST, or PC

The immiscible blends with $\leq$ 5 wt% of either component were introduced first (e.g., POM with PA or PARA) before adequate methods of compatibilization were developed. Owing to the crystalline nature of these resins, the blends should also be impact modified. It is noteworthy that in blends of semicrystalline resins, the total crystallinity tends to increase (Nadkarni and Jog 1991). The compatibilization and impact modification are often accomplished using a multipolymer. For example, POM/PA-66 blends have been modified by adding either an ethylene-methylacrylate copolymer (EMAC), PEG (Kohan 1982), or a melamine-derivative "dispersant" (Tsukahara and Niino 1992, 1994).

In PA/PEST blends, PA improves the processability, mechanical properties, and solvent resistance of PEST. Examples of the developed PA/PEST blends are listed in Tables 1.57–1.58. PA blends with PC are similar to those with PEST. Since addition of PA to PC may lead to crystallization of the latter resin, also these blends should be compatibilized *and* impact modified (see Table 1.59).

1.6.1.4 PA/Specialty Polymer Blends

Addition of a small amount of PA improves processability of the specialty resin and is beneficial to performance of the GF-reinforced systems. Addition of specialty resin to PA enhances the thermal behavior and rigidity of the latter resin. For higher concentration of these ingredients, compatibilization and impact modification are required. Since PA is sensitive to heat, oxygen, and moisture, the compounding requires a special care. Examples are listed in Table 1.60.

1.6.2 Thermoplastic Polyesters (PEST)

Aromatic polyesters show good performance and have high T_m and HDT (see Table 1.61). Polyethylene terephthalate (PET) was invented in 1941 and commercialized as *Terylene*™ fibers. The catalytic transesterification also lead to PPT, PBT, PHMT, PEN, etc. Polybutylene terephthalate (PBT) has better processability than PET and lower T_m. Poly(ethylene-2,6-naphthalene dicarboxylate) (PEN) has high modulus, strength, HDT, and excellent barrier properties. Polypropylene terephthalate (PPT) is a resin from shell. It combines the high crystallization rate of PBT with performance of PET. Polyarylates $[\text{-O-}\phi\text{-C(CH}_3)_2\text{-}\phi\text{-CO}_2\text{-}\phi\text{-CO-}]_n$ (PAr) are linear amorphous polyesters, usually of bisphenol-A with isophthalic and terephthalic acids – they show intermediate performance between that of PC and PEST – high strength, stiffness, excellent impact strength, and HDT. Polyethyleneterephthalateglycol (PETG) is an amorphous copolymer of ethylene glycol and 1,4-cyclohexanedimethanol, with terephthalic and isophthalic acids. The block copolymers, having hard PBT segments and soft polyetherglycol ones, are versatile elastomers (e.g., *Hytrel*™ from du Pont).

Table 1.56 PA/PPE blends

Composition	Comment	References
PPE/PA-12	Processability and performance	Komoto 1972
PPE/PA-66 = 1:1 with SBR-MA	First reactive compatibilization	Ueno and Maruyama 1981, 1982
PPE/PA and a compatibilizer	Compatibilized by SMA	Kasahara et al. 1982
PPE/PA and a compatibilizer	Polycarboxylic acid derivatives	Abolins et al. 1985
PPE/PA and a compatibilizer	With citric acid	Gallucci et al. 1985
PPE/PA and a compatibilizer	With oxalic dihydrazide	Lohmeijer et al. 1986
PPE/PA and a compatibilizer	Acid chloride of trimellitic, terephthalic, or 1-acetoxyacetyl-3,4-dibenzoic acid	Aycock and Ting 1986, 1987, 1994
PPE blended with PTO and MA and then compounded with PA-12	Processability, impact strength, solvent resistance, and HDT = 156 °C	Droescher et al. 1986
PPE/PA and a compatibilizer	Core butylacrylate-MMA; shell SMA	Van der Meer and Yates 1987
Amino-terminated PPE with PA-MA	Mechanical properties, low-T ductility	Fujii et al. 1987
PPE/PA and a compatibilizer	Addition of SEBS-MA	Modic and Gelles 1988
PPE-MA with bis-2-hydroxy ethyl fumaramide, PA, and functionalized ethylene-α-olefin elastomer	*Dimension*™ commercial blends with high elongation, impact strength, HDT, and dimensional stability	Akkapeddi et al. 1988, 1992b
PPE/PA and a compatibilizer	Either EPR-MA, EVAc-GMA, MA, or bis(4-phenyl isocyanate)	Nishio et al. 1988, 1994
PPE functionalized with trimellitic anhydride acid chloride and dimethyl-*n*-butyl amine, PA and PDMDPhS	PDMDPhS with carboxylic acid, amine, epoxy, anhydride, or ester groups	Smith et al. 1990, 1994
PPE/PA and a compatibilizer	Compatibilized by organic diisocyanates	Pernice et al. 1992
PPE/PA and a compatibilizer	By aromatic nitro-derivative	Bencini and Ghidoni 1993
The above blends were modified with styrene-butadiene radial copolymer	Threefold increase of the Izod impact strength	Gianchandai et al. 1993
The above blends were modified with tapered block copolymer	Further improvement of the impact strength	Yates 1993
PPE capped with trimellitic anhydride acid chloride and blended with PA-66	Toughened by addition of SEBS	Aycock and Ting 1994
PPE/PA and a compatibilizer	Either EPR-MA, E/GMA, or E/VAc/GMA, citric, malic, or agaric acid	Ishida and Kabaya 1994
Modified PPE with PA and SEBS	Moldability and mechanical properties	Kodaira et al. 1994
PPE modified with glycidol or epichlorohydrin, with PA or PEST	Either PP-MA, PP-GMA, *ionomers*, or EVAl was added	Arashiro et al. 1994

(*continued*)

Table 1.56 (continued)

Composition	Comment	References
PPE-MA with PA and SEB	Selectively hydrogenated S-B di-block	Lee 1994
PPE capped with salicylic ester and SBS dispersed in PS, PA, PEST, or PEI	Resistance to loss of impact strength after recycling	Richards and White 1994
PPE, PA, POM, and a Lewis acid (e.g., trialkylboran or borate, boric acid or halogenated boron)	For automotive applications	Takayanagi et al. 1994
PPE dissolved in lactam(s) and then compatibilized and polymerized	The compatibilizer was either PPE-MA, SAA, or SMA	Samuels 1994

PESTs and PCs are known to have low melt strength and are difficult to process in operations involving elongational flows, viz., blow molding, stretching, or foaming. During foaming the cell size distribution is broad, the wall thickness variable and the mechanical properties are poor. To improve the melt strength, a diacid anhydride and a metal compound may be added during extrusion (Hirai and Amano 1993). These additives induce branching, increase MW, and strain hardening. Alternatively, linear and branched resins may be blended.

The branched macromolecules can be produced in reactions with polyols having 3–6 hydroxyl groups. This approach has been successful even for recycling post-consumer PET. For example, $\geq$ 25 wt% of a bPET with recycled PET were extruder blended with $\leq$ 20 wt% of a chain extender (e.g., partially neutralized ethylene-methacrylic acid ionomers, copolymers of maleic anhydride or glycidyl methacrylate, etc.). Downstream up to 5 wt% of a chemical or physical blowing agent was incorporated. The blends were used to produce rigid insulation, trays, food packaging, microwave cookware, oxygen and moisture barrier films, etc. (Muschiatti and Smillie 1995).

1.6.2.1 Polyester Blends

The largest group comprises the impact-modified PESTs – these were summarized while discussing commodity resin blends. The commercial blends with, e.g., SMA or acrylic rubber show good processability, rigidity, impact and tensile strength, as well as excellent weatherability, viz., *Arloy*™ 2000, *Bexloy*™, *Celanex*™, *Pibiter*™ *HI*, *Rynite*™, and *Ultradur*™ *KR*.

The second largest group comprises different combinations of PEST, for example, PET/PBT, PBT/PAr, or PET/PEN. These have been mainly developed for improved processability, good surface properties, HDT, impact strength, and dimensional stability, viz., *Celanex*™, *EMC*™, *Valox*™, etc. Examples of their formulations and performances are given in Table 1.62.

1.6.2.2 PEST Blends with PC

The PEST/PC blends are immiscible (T_g of PC is depressed by ca. 20 °C) and brittle, requiring toughening. Usually, PC blends with PEST contain 10–20 wt% of ABS, ASA, or MBS. In most commercial blends, PC is the matrix, but blends

Table 1.57 PA/PET blends

Composition	Comment	References
PA/PET blends		
PET/PA-6	With α,α-dimethylol-propionic acid	Reimschussel and Dege 1969
PET with PA-6-co-diisocyanate	Compatibilized and toughened blends	Illing 1970, 1973
PET with PA-66	Crystallization rates and mechanical properties	Nakamura and Neki 1981
Reactive PA/PEST blends	Direct coupling	Mitsubishi Petrochem. 1984
Reactive PA/PEST blends	Catalyst, *p*-toluenosulfonic acid	Pillon and Utracki 1984, 1986
Reactive PA/PEST blends	With *phenoxy*	Robeson 1988
PA/PET blends	Polyamide-polyester block copolymer	Maresca and Shafer 1988
Reactive PA/PET blends	Butylacrylate-methyl-acrylate block copolymer	Tsumiyama et al. 1988
Reactive PA/PET blends	Phosphoryl azide reactive coupler	Bhattacharje et al. 1990
Reactive PA/PET blends	PET containing toluenosulfonic acid groups	Van Sluijs et al. 1992
PA blends with PBT or PAr		
Non-compatibilized PA/PBT	To enhance PBT crystallinity	Toray Ind. 1983
Reactive PA/PBT blends	Acidified ethylene copolymer	Sheer 1982
Reactive PA/PBT blends	Maleated PS	Mitsubishi Petrochem. 1985
Reactive PA/PBT blends	Epoxy compounds	Urabe and Ikuhara 1989
Reactive PA/PBT blends	Either SGMA or SMA	Watanabe and Inozuka 1991
Compatibilized PA/PBT	Low molecular weight PBT	Goetz et al. 1993
1:1 PAr with PA, PET, or PBT	Transparent, impact resistant	Asahara et al. 1977a, b
PAr with PA-6 and Si-compounds or PET	Processability, high gloss, chemical, mechanical, electrical properties, and HDT	Unitika 1982, 1983, 1984
PAr with PA or PARA	PA-co-PAr added; single T_g	Dean 1990, 1992

formulated for low-T impact strength (down to −40 °C) have co-continuous morphology and are reinforced by addition of $\leq$ 30 wt% of GF. It is vital to avoid reduction of PET crystallinity during blending or processing. The main advantage of the PC/PEST alloys is the increased stiffness, reduced susceptibility to stress cracking on contact with fuels, and an improved resistance to chemicals and fuels. The blends show good processability, heat resistance, ductility, HDT, high modulus at high temperature, good electrical properties, thermal stability, impact, tensile and flexural strength over a wide temperature range, low shrinkage,

Table 1.58 Multicomponent PA/PEST blends

Composition	Compatibilizer	References
Amorphous PA or PARA, with either PEST, PC, PEC, or PAr	A polyamide-polyester block copolymer, PA-b-PEST	Maresca and Shafer 1988
PA blends with either PAr or PC	EGMA	Yuichi and Suehiro 1989
PAr/PA	Either ABS-MA or ABS-GMA	Yasue et al. 1989
PET, PA-6, and PO	EEA-GMA	Natarajan et al. 1994
PEST, EVAl, PA, and PEST (with Na- dimethyl 5-sulfoisophthalate groups)	An *ionomer* and PP-MA	Tajima et al. 1994
PEST/PA	Reactively blended in solid state	Al Ghatta 1994

Table 1.59 PA/PC blends

Composition	Comment	References
PA-12/PC	For electrical insulation	Okuzono and Kifune 1975
PA-12/PC with PSF, PPE, or PET	Moldability and mechanical performance	Okuzono and Kifune 1976
PA/PC	Toughened with SEBS	Gergen and Davison 1978
PARA/PC	Pearly looking, resistance to oils and water, good mechanical properties	Mitsubishi Chem. 1980
Polyestercarbonate (PEC) with PA	Compatibilized and toughened by MABS	Sakano et al. 1981, 1982
PC/PA-6	Compatibilized by addition of SMA	Dainippon Ink. 1983
PA/PC commercial alloys *Dexcarb™*	Polyesteramide, an elastomer, and either PP-MA or EPR-MA	Perron 1984, 1988
PC end-capped with trimellitic anhydride acid chloride and then reactively blended with PA-6 and MBS	Moldability, excellent Izod impact strength, and elongation	Hathaway and Pyles 1988, 1989
PA-6I with PC	High impact and tensile strength	Gambale et al. 1988, 1994
PC/PA-6; compatibilized	Polyethyloxazoline, PEOX, added	Thill 1989
PA blends with, either PAr or PC	Compatibilized and modified by EGMA	Yuichi and Suehiro 1989
PA blends with, either PAr or PC	With ABS-MA or ABS-GMA	Yasue et al. 1989
PA with, PAr or PC and PA-co-PC	With glycidyl isocyanurate	Derudder 1990
Branched, bPC, and $\geq$ 1 polymer from: PEST, styrenics, PA, PO, and TPE	Processability, solvent and impact resistance, mechanical properties	Kozakura et al. 1992, 1994
PC and/or PEC with PA-6	With acrylic elastomer	Heger et al. 1992
PC/PA-6/ABS	With imidized polyacrylates	Leitz et al. 1992
PC/PA-6 with PEI and/or TPU	With butyl glycidyl ether, EPR-MA, or EPDM-MA	Perron et al. 1993
PA-6/PC/SEBS/SEBS-MA	20-fold increase of impact strength, 50-fold increase of elongation	Industrial Technology Institute, Japan 1996

Table 1.60 PA specialty polymer blends

Composition	Comment	References
1. PA/PSF blends		
PSF with PA-11	For improved impact properties	Nield 1971
PA/PSF with poly(sulfone-g-lactam)	Processability and mechanical properties	McGrath and Matzner 1972
PA-6/PSF	Processability, thermal and mechanical properties	Kyo and Asai 1978
PARA/PES	HDT = 172 °C and mechanical properties	Hub et al. 1986
PA-46/PES	Mechanical and thermal properties	Koning and Vroomans 1992
PARA/PES	Mechanical and thermal performance	Bapat et al. 1992
PAES or PES blended with PA-6T6	High heat resistance and stiffness	Weber and Muehlbach 1993
2. PA/PPS blends		
PARA with a small amount of PPS	Moldability, HDT, and impact strength	Shue and Scoggins 1981
PA-46 with PPS	Impact and mechanical properties, HDT, heat, and chemical resistance	Chiba et al. 1978
PPS with polyphthalamide (PPA)_	Heat and chemical resistance, HDT, mechanical properties	Chen and Sinclair 1990
PPS with PPA and GF	Mechanical properties	Davies 1990
PPS/PA with EPDM and MA	Compatibilized-*cum*-impact modified	Yu and Beever 1992
PPSS with either PA or PEST	Mechanical properties, HDT, dimensional and chemical stability	Ishio and Kobayashi 1992
PPS, either PA-66 or PA-MXD6 and $Mg(OH)_2$	Tensile strength, arc tracking, and heat resistance	Dubois et al. 1993
3. PA/*phenoxy* blends		
PA-6 with *phenoxy*	Excellent ESCR	Schober 1973
PA-66 with *phenoxy* and SEBS	Tensile and impact strength	Freed 1975
PA with PEST, *phenoxy*, and MBS	Tensile and impact properties	Robeson 1988
4. PA/PEA blends		
PA-12 with PEA	Tough, flexible, heat and hot oil resistant	Sumitomo Chem. 1984
PEBA/PA (ABS, MBS, NBR, SBR, or EPDM)	Impact strength at low-T, *Rilsan*™	Arraou 1986
5. PA/PAI blends		
PAI with PA-66 or PARA and inorganic filler	Moldings with high mechanical performance	Toray Ind. 1979
PI, PA, PAI, or PI + PA and aromatic PI	Miscible blends for selective permeation	Ekiner and Simmons 1993
6. PA/PEI blends		
PEI with PA or PEST	Processability	Giles and White 1983

(*continued*)

Table 1.60 (continued)

Composition	Comment	References
PEI with PA-6 and PEI-b-PA	Impact strength	Robeson and Matzner 1984
PEI with PA-6 or PA-66	Compatibilized by nonyl-phenolic	Gallucci 1988
PEI with PA-12	Reduced shrinkage and water absorption	Giles 1987
Copolyesteretherimide, PEEI *Lomod*™, blended with either PA or PARA	Thermal aging behavior	Angeli 1992

Table 1.61 Comparative properties of PEST's

Property	PC	PET	PPT	PBT	PEN	PETG	PAr
Tensile modulus (MPa)	2,300	2,800	2,500	2,600	2,400	6,700	2,200
Tensile strength (MPa)	62	81	68	52	82	34	60–70
Maximum elongation (%)	120	70	–	200	100	110	7–100
Density (kg/m^3)	1,200	1,375	1,350	1,300		1,250	1,190–1,210
T_g (°C)	149	98	80	60	117	88	> 180
T_m (°C)	220	255	225	223	337	–	–
HDT (°C)	280	167	149	136	109	70	120–175

and good dimensional stability, but they may have poor weatherability, and their solvent resistance (while superior to that of PC) is moderate. The commercial blends include *Alphaloy*™ *MPB*, *Baitaloy*™ *VL*, *Cycolin*™, *Dialoy*™, *Ektar*™, *Hyperlite*™, *Eastalloy*™, *Idemitsu*™ *S*, *Impact*™, *Lumax*™, *Malecca*™ *B*, *Makroblend*™, *Maxloy*™, *Novadol*™, *Novaloy*™ *B*, *Petsar*™, *Pocan*™, *Sabre*™, *Stapron*™, *Techniace*™ *TB*, *Triax*™ *400*, *Ultrablend*™, *Valox*™, and *Xenoy*™. The blends are mainly used for automotive body panels, in outdoor power or recreational equipment, appliance housings, telecommunications, etc.

The PC/PEST blends were first described in 1966. The first, three-component blends were disclosed in 1972 (see Table 1.63). Many multicomponent alloys comprise PC and PEST. From between them, these with PPE are particularly important – see the following part.

1.6.2.3 PEST Blends with PPE

Blending PPE with either PEST or PC poses similar problems – the polymers are immiscible and brittle, hence require compatibilization and toughening. The PEST/PPE blends are multicomponent systems, with $\geq$ 5 components: PEST, PPE, styrenic copolymer, compatibilizer, and impact modifier. Examples of commercial blends are *Dialoy*™ *X*, *Gemax*™, or *Iupi-ace*™. For improved modulus and dimensional stability, they are usually reinforced with GF. These alloys are known for excellent processability, high solvent resistance, and dimensional stability. Evolution of these systems is outlined in Table 1.64.

Table 1.62 Examples of PEST blends

Composition	Comment	References
First PET/PBT blends	Enhanced crystallizability, miscibility	Heywang 1966
PBT with 40 wt% PAr	For electrical insulation, films, moldings	Wiener 1969
First modified PET/PBT blends	Toughening with butyl rubber	Hiri and Kotama 1971
PET with PA	For good frictional resistance	Fujiwara 1971
PAr with either PC or PEST	Moldability and impact strength	Koshimo et al. 1973
PBT with PET or PHT	High elongation and impact strength	Tsunawaki et al. 1973
PBT with PC	Impact resistance and elongation	Matsukane and Azo 1973
PBT with PPE	Processability and mechanical properties	Nakamura and Toyomoto 1974
PET with PC	High stress corrosion resistance	Horiuchi and Kamiya 1974
PAr with PEST and PA-6 or PPS	Further enhancement properties	Asahara et al. 1977a, b
PET/PBT blends	Modified by of acrylic elastomers	Kamata et al. 1978a
PAr with acetate-capped POM	Processability of POM	Gale 1978
PAr with either PET or PBT	Transparency, HDT, and impact strength	Fukushima et al. 1979
PET/PBT/SEBS	Impact, heat, and tensile strength	Wambach and Dieck 1980
PBT/PET/PC	Impact strength, rigidity, strain at break	Goedde et al. 1980
PBT/PET/*phenoxy* and a toughener	Butylacrylate-glycidyl methacrylate-MMA	Charles and Coleman 1981
PAr with PCT	Processability, weatherability, impact	Robeson 1981
PAr/PEST with TPU	High modulus while retaining strength	Robeson et al. 1981
PAr, PET, and EEA, TPU, etc.	To improve impact resistance and HDT	Robeson 1981, 1982
PET/PBT or PEST/PC, toughened	Toughener: MBS, ACM, or ABS, etc.	Bier and Indner 1982
PBT with either POM or PA	Impact modified by an ionomer	Sheer 1982
PET/PBT and, e.g., EGMA	Processability and performance	Memon and Myers 1983
PBT reactively blended with PAr	High impact strength	Toga and Okamoto 1983
PET with PAr and PA-6	Processability, gloss, HDT, transparency	Unitika Ltd. 1983
PAr with PEST and PC, ABS, PA	Processability blends, set of properties	Robeson 1985
PAr/PEST with EGMA or EPR grafted with glycidyl oxybenzyl acrylamide	Excellent processability and performance	Toyoda et al. 1986
PET/PC/PCT, EPR, and/or MBA	High impact resistance	Romance 1990

(*continued*)

Table 1.62 (continued)

Composition	Comment	References
POM, POM-copolymer, aliphatic polyester and polyether	Processability, crystallization, low shrinkage, HDT, and mechanical prop.	Makabe et al. 1991
POM/TPU/EBA-GMA/PA or PEST	Processability and mechanical properties	Subramanian 1992
PEST/POM and isocyanate or isothiocyanate coupling agent	Processability, mechanical properties, and low gloss	Katsumata and Matsunaga 1992, 1993, 1995
Solution-prepared PAr/PET	Immiscible: two Tgs and $\chi > 0$	Chung and Akkapeddi 1993
Blend of linear and branched PET	For high-quality mineral water bottles	Greaves et al. 1993
PET with PCT	High impact strength at low-T	Stewart and Bell 1995
PET with PEN	Transesterification reducing crystallinity	Wu and Cuculo 1998

1.6.2.4 PEST Blends with Specialty Resins

PESTs are immiscible with polyphenyl sulfides (PPS) or polyphenylenesulphidesulfone (PPSS). The customary three types of uncompatibilized blends are known, with 5–10 wt% of the dispersed (either PPS or PEST) phase and the phase co-continuity. The compatibilized blends (with a copolymer containing either epoxy or acid anhydride groups) show high tensile and impact strength (Nishiyama et al. 1990, 1991a, b) that can further be improved by addition of a TPE (Nishiyama and Nakakita 1991). PPS/PEST blends were also compatibilized by addition of a PPS-PEST copolymer (Suenaga and Ishikuwa 1991). The alloys could be reinforced with GF, talc, mica, wollastonite, or clay (Gary 1993).

Polyarylethersulfone (PAES) $(\text{-[O-}\phi\text{-O-}\phi\text{-SO}_2\text{-}\phi\text{-]}_{0.25n}\text{-[-O-}\phi\text{-SO}_2\text{-}\phi\text{-]}_{0.75n}\text{-})$ blended with either PAr, PEST, PC, or their mixtures showed well-balanced mechanical properties and good environmental stress-cracking resistance (Robeson and Harris 1985, 1986). For improvement HDT, mechanical properties, and flame retardancy, PET was blended with a PAES: $(\text{-[-}\phi\text{-SO}_2\text{-}\phi\text{-O-}\phi\text{-C(CH}_3\text{)-}\phi\text{-O]}_n\text{-})$ (El-Hibiri et al. 1992). Blends of this type PAES with PC, PET, $ZnBO_3$, and PTFE had high flame retardancy (Jack et al. 1993).

Polyetherimide (PEI) was blended with PAr for improved moldability and mechanical properties (Holub and Mellinger 1981). Similarly, polyestercarbonate (PEC) was blended with either PEI, PA, PI, PAI, or their mixtures, to give alloys characterized by high HDT and tensile strength (Quinn 1984). Blends of PEI, PAr, and PC showed good moldability, flexural strength, and modulus (Holub 1990). Also PEI, PET, and PEC blends had good processability and impact strength similar to PEI (Quinn and Holub 1986). Adding ABS to PEI/PEST blends enhanced the impact resistance (Gaafar 1990). PEI was also blended with PBT and a cross-linking triallyl cyanurate and triallyl isocyanurate (Hosoi 1991). To produce soft, flexible, dimensional stable, and water-resistant materials, polyesteramide (PEA) was blended with PET (and/or PA-6) (Toray Industries, Inc. 1982).

Table 1.63 PEST/PC blends

Composition	Comment	References
PBT with PC and MBS	Processability, chemical resistance, impact	Nakamura and Toyomoto 1974
PET/PC with a compatibilizer-impact modifier	Butylacrylate-styrene-triallyl isocyanurate, grafted with MMA and styrene	Kamata et al. 1978b
PCT with PC and branched PC	Good clarity, tensile strength, and notched Izod impact strength	Mohn et al. 1979
PBT/PC with *Acryloid*™	Moldability and high impact strength	Motz 1980
PBT/PC and PEC	High impact strength and strain at break	Dieck and Cohen 1980
PEST/PC, SEBS, PVAc, or $(SB)_n$ and butadiene-caprolactone-styrene	*Xenoy*™ alloys, with mineral filers or not	Dieck and Wambach 1980
PEST/PC, BR, and an impact modifier; *Makroblend*™	With (meth)acrylic esters (and acrylonitrile, acrylate rubber, ACM, EVAc, and/or ABS)	Cohen 1980, 1982; Bier and Indner 1982
PET/PC, butyl rubber (BR)	Good overall performance	Teijin Chem. 1983
PEST, PC, PO, and MBA	High impact strength alloys	Boutni and Liu 1983
PEST, PC, BR, an acrylic elastomer, *HIA-15*, and PMP	Good sets of mechanical properties	Teijin Chem. 1983
Reactively blended PEST, PC, and an acidified elastomer	Tensile strength, impact resistance, and electrical conductivity; *Tafmer*™	Mitsubishi Chem. 1983
PEST/PC/ styrene-α-methylstyrene-acrylonitrile-butadiene	Good moldability, mechanical properties, and heat resistance	Biglione and Fasulo 1983
PEST/PC/2-methyl-1,3-propanediol	Improved HDT, elongation, and impact strength	Yoga et al. 1983
PBT/PC with AES	Greatly improved impact strength	Sumitomo Naug 1983
PC/PEST with EVAc	For uniaxially drawn shrink films	Weyer et al. 1984
PET/PC and 10–15 wt% *Acryloid*™	High impact resistance	Hepp 1984
PEST, PC, and an ethylene-acrylic acid-butylacrylate	High impact strength moldable compositions	Portugall et al. 1984
PC/PEST/elastomer/*phenoxy*	Impact-modified blends	Liu and Giles 1986
PC/PET, or PETG, EEA, and an impact modifier	Extrusion-blended, foamed, and then injection molded; $\rho = 900$ kg/m^3, good performance	Avakian and Jodice 1986
PEST, PC, and MBS-AA or GMA	High impact strength; *Ultrablend*™	Lausberg et al. 1987
PC/PEST and siloxane copolymer	Chemical, weather, impact resistance; *Dialoy*™	Hongo et al. 1987
PC/PET with $\geq$ 90 wt% PES	PES foamed by degradation of PET/PC	Haggard 1987
PC/PEST with acrylic elastomer	Improved impact strength	Sakai et al. 1989
PC/PEST and PE-MA wax	Improved impact strength	Liang 1989

(*continued*)

Table 1.63 (continued)

Composition	Comment	References
PET/PC/EPDM/PCL/EEA-MA	Chemically resistant, impact properties	Natarajan and Mininni 1991
PBT/PC, PO-GMA, or PO-MA	Moldability, toughness, strength, and stability	Fujie 1993
PBT/PC/ABS/PE-GMA or -MA, vinyl, styrene or (meth)acrylate	Impact strength conditions	Steendam et al. 1993

Table 1.64 PEST blends with PPE

Composition	Comment	References
Blends with unmodified PPE		
PPE/PBT/SBS	Processability, impact, and tensile strength	Lee 1978
PPE, PC, SEBS, and either PBT or PET	Stable morphology, processability, high impact strength, and solvent resistance	Brown et al. 1987
PPE/PET/PC/EGMA	For automotive applications	Yonetani et al. 1987
PPE/PET with SEBS-GMA	Excellent solvent resistance, moldability, impact and mechanical properties	Mayumi and Omori 1988
PPE/PET, EPR-MA, EVAc-GMA, MA or bis(4-phenyl isocyanate)	Processability, heat resistance, and mechanical properties	Nishio et al. 1988, 1994
PPE, PEST, PS, PC, SEBS, and/or acrylic modifier	High impact strength PPE alloys; *Gemax*™	Yates and Lee 1990
PPE/PBT with PC-b-PS-b-PC, PC, and either SEBS or MBS	Processability, tensile elongation and strength, as well as chemical and impact resistance	Brown and Fewkes 1992, 1994
PPE, PEST or TMPC, PS-VPh, HIPS	PEST is miscible with PVPh, thus PS-VPh is an efficient compatibilizer	Colby et al. 1993, 1994
PPE, PEST, PC-PBT, and SEBS	Excellent rigidity and impact strength	Chambers et al. 1995
Blends with modified PPE		
PPE modified with unsaturated dicarboxylate, e.g., fumaric acid	Reactively blended with PBT, PC, and SEBS for improved mechanical performance	Ishihara 1989
PPE modified with dimethylsiloxanes,	Blends with PPE, PEST, and SEBS for enhanced solvent and impact resistance	Brown 1989
PPE modified with an epoxy-compound	Blended with PPE, PEST, and hydrogenated poly-α-olefin for processability and impact resistance	Hasson and Yates 1993
PPE modified with end-capped with salicylic acid ester	Blended with SEBS and then dispersed in either PA, PEST, PEI, or PS; for processability, resistance to loss of impact strength after recycling	Richards and White 1994
PPE modified with either glycidol or epichlorohydrin	Blended with PP-MA, PP-GMA, *ionomers*, EVAl, PA, and PEST; for moldability, solvent and heat resistance, mechanical strength	Arashiro et al. 1994

The low-temperature phosphate glasses (LTG: -[-Zn-O-P(O_2Na)-O-P(O_2Li)-O-Zn-O-P(O_2Na)-O]-) have been blended with PET, PBT, PEK, PEEK, PPS, PEI, LCP, PC, etc. (Bahn et al. 1991). The blends containing up to 65 vol.% of LTG were reported to have good mechanical properties (Frayer 1993, 1994). The technology makes it possible to generate controlled morphology of the dispersed LTG phase as well as to ascertain its good bonding to the organic matrix.

1.6.3 Polyurethanes (TPU)

The polyester-type thermoset polyurethanes were commercialized in 1942, and the linear thermoplastic ones (TPU) 10 years later. Polyester-type TPUs, *Texin*™ resins for extrusion and injection molding, were introduced in 1961, whereas polyether-type, *Roylar*™, in 1971. Owing to great diversity of the ingredients, the TPU performance can be readily modified. For this reason, as well as because of the cost, TPUs are seldom blended. Their use can be divided into three groups: (i) blends with POM, (ii) blends in which TPU is used as a compatibilizer and impact modifier, and (iii) others.

1.6.3.1 POM/TPU Blends

The oldest and most common method of POM toughening is by incorporation of TPU. *Delrin*™ POM/TPU blends were commercialized in 1960. The others followed, e.g., *Celcon*™, *Duraloy*™, *Formaldafil*™, *Fulton*™ *KL*, *Hostaform*™, *RTP 800*, *TC*, or *Ultraform*™. These alloys have high impact strength and elastic recovery that depend on composition, morphology, as well as on the compounding and processing methods. Examples of these blends are listed in Table 1.65.

1.6.3.2 PC/TPU Blends

TPU has been used to toughen PC, to enhance its mechanical behavior and ESCR. The blends have been used in industrial and medical applications (De Boer and Heuschen 1988; Pinchuck 1991). Blends of PC/PET/TPU with EVAc-GMA and optionally MBS or ABS have good flexural modulus, strength, weld-line strength, solvent resistance, and impact behavior (Laughner 1994). PC blends with a polycaprolactone-polyurethane resin, TPU *Pellethane*™, and either MBS or MBA showed similar behavior (Henton et al. 1993).

Texin™ *3000* and *Texin*™ *4000* are the commercial blends. In the first TPU is the matrix, while in the second PC plays this role. The resins are used for the production of gears, tubings, housings, top-lifts, extruded profiles, and for the automotive industry and consumer goods.

1.6.4 Polycarbonate (PC)

Polycarbonates are polyesters of polyhydric phenols and carboxylic acid. Except for the lack of crystallinity, their properties resemble those of PEST. The most

Table 1.65 POM/TPU blends

Composition	Comment	References
POM with OH- NCO- or NCS-terminated TPU	To improve POM elasticity	McAndrew 1971
POM/TPU with mineral fillers	For enhanced stiffness	Reske and Wolters 1984
POM/TPU and polycarbodiimide and ethylene-*bis*-stearamide	Moldability and impact strength (POM was acetate end-capped)	Richardson 1984
POM/TPU	High impact strength at low-T	Drzal et al. 1986
POM, PC and TPU	High impact strength	Silvis et al. 1990
POM with polythioisocyanate-TPU	Impact and flexural strength	Sugiyama and Mochizuki 1990
POM/TPU and acrylics	Abrasion resistance and weatherability	Endo et al. 1990
POM/TPU and ABS	Processability, thermal and dimensional stability, chemical and creep resistance	Guest et al. 1991
POM/TPU, with SAN, ABS, AES, PC, PA, PAr, PPE, HIPS, acrylics, imidized acrylics, or SMA	For lower mold shrinkage, good stiffness, elongation, toughness, etc.	Flexman 1992
POM/TPU and EBA-GMA, with PA-612, PA-6, PP, or PET	Good modulus, impact strength, and processability	Subramanian 1992
POM/TPU and di-glycerin, pentaerythritol, *phenoxy*, or PVAl	Tensile strength and elongation at break, impact resistance, etc.	Nagai et al. 1993, 1994

common polycarbonate is that of bisphenol-A (PC), which was commercialized in 1956. PC is tough, transparent, self-extinguished, dimensionally stable, resistant to salts and oxidation, but susceptible to abrasion, stress cracking, and attacks by solvent, acids, and alkali. It is $T_g = 149$ °C, but the ductile-brittle transition is at 0–10 °C. The resin ought to be toughened, for example, by addition of ABS, MBA, or MBS. The annual consumption and its growth rate of PC are, respectively, 700 kt and 5 %. About 40 % of PC is used in blends.

Originally, the commercial PC resins were linear polymers with high shear viscosity and low melt strength, thus difficult to process in operation involving extensional flows, viz., blow-molding stretching and foaming. Several years ago, branched PC (bPC) became available. The resin is usually blended with linear PC at the ratio that on the one hand is economically viable and on another that provides sufficient melt strength for the required process. For example, 60–95 wt% bPC (MW = 32–45 kg/mol) was blended with 5–40 wt% PC (MW = 15–27 kg/mol). The blends with MFR = 2–8 g/10 min were suitable for extrusion, injection molding, blow molding, and/or foaming at $T_{process} = 250$–310 °C (Van Nuffel et al. 1998).

1.6.4.1 PC Blends with PPE

Blends of PPE with PC are immiscible and brittle; thus, they must to be compatibilized and toughened (see Table 1.66).

Table 1.66 Examples of PPE/PC blends

PPE/PC and	Comment	References
PS or SMMA and PEST	Compatibilizer: acrylic elastomer, *phenoxy*; or Cl-SBR	Izawa and Nakanishi 1973
PBT and SEBS	Processability, impact strength, solvent resistance	Brown et al. 1987
HIPS/PEST/SBS and PS grafted with 2-oxazoline (PSOX)	Advantageous set of performance characteristics	Avakian et al. 1988
Fumaric acid-grafted PPE and SEBS	Mechanical properties and low gloss	Ishihara 1989
PS, PEST, SEBS, and/or MBA	High impact strength	Yates and Lee 1990
PBT, PC-PS-PC block copolymer, and impact modifier	Excellent rigidity and impact strength	Brown and Fewkes 1992, 1994
SAN/PS – compatibilized	Poly(butylacrylate-co-styrene-co-acrylonitrile)	Niessner et al. 1993
PEST/ABS with PS, HIPS, SEBS, PA, PC, and/or PEST	Multicomponent blends prepared by reactive processing	Laughner 1993, 1994
PEST, PC-PBT copolymer, and SEBS	Good rigidity and impact strength	Chambers et al. 1995

1.6.4.2 PC/POM Blends

These blends are immiscible, thus should be compatibilized and toughened. Addition of POM to PC improves the solvent and chemical resistance (Miller 1972). PC blends with POM and TPU were easy to mold into articles having high impact strength (Silvis et al. 1990). POM-b-PC was used either as a compatibilizer or as a modifier of performance for such polymers as PES, PEEK, PA, and PAN (Dhein et al. 1993).

1.6.4.3 PC Blends with Specialty Resins

There is a great diversity of polyimides (PI) having $T_g = 180–420\ ^\circ C$. Several were blended with PC to improve its stiffness, HDT, and strength. PEI/PC blends were commercialized in 1992 as *Ultem*™ *LTX*, for injection molding or extrusion. They show higher impact resistance than PEI and higher heat resistance than PC, as well as they retain the strength, chemical resistance, and the hydrolytic stability of PEI.

Fluoropolymers are notoriously immiscible with any other polymer. Usually, they are dispersed in blends of engineering and specialty polymers either to improve processability or to induce lubricity and abrasion resistance. Examples of the PC/specialty resin blends are listed in Table 1.67.

1.6.5 Polyoxymethylene (POM)

Polycondensation of formaldehyde was reported by Butlerov in 1859, but only in 1950 du Pont developed end-capping that prevented unzipping. POM is crystalline, thus rigid, brittle, and chemically nonreactive. Production of *Delrin*™ and *Celcon*™ started in 1959 and 1962, respectively. The world consumption of POM and its annual growth rate are 500 kt and 5 %.

Table 1.67 PC blends with specialty polymers

Composition	Comment	References
1. PC/Siloxane resin blends		
PC with PDMS	Solution cast films with good properties	Caird 1961
PC and/or PEST with siloxane-based vinyl copolymer	For chemical, weather, and low-temperature impact resistance	Hongo et al. 1987
PC with poly(dimethyl siloxy biphenylene oxide)	Transparent, flame, and impact-resistant alloys	Jordan and Webb 1992
PC with siloxane/vinyl-based copolymer	Thermal stability, ductility at low-T, and impact resistance	Derudder and Wang 1993
PC, or polyestercarbonate with PC-b-PDMS	Low-flammability, impact strength over a wide T	Hoover 1993
PC/PArSi and SBS	Excellent mechanical properties	Jordan and Webb 1994
2. PC/PSF blends		
PAES: $[-\phi-C(CH_3)_2-\phi-O-\phi-SO_2-\phi-O-]_n$, with PC	Impact, tensile strength, elongation at break	Union Carbide Corp. 1966
PC with PAES and MBS or AES	Impact and tensile strength, HDT	Grabowski 1971
PC with PAES and CHR	Good impact and fire resistance	Lauchlan and Snodgrass 1973
PSF with linear *and* branched PC	Improved solvent resistance	Binsack et al. 1979
PSF with PEC	Impact strength and flame retardancy	Quinn and Rosenquist 1982
PC and polycarbonate-sulfone grafted with ethylhexyl acrylate	High impact strength	Tyrell et al. 1984
PAES with PC, PAr or PEST	Well-balanced mechanical properties	Robeson and Harris 1985, 1986
PSF/PC with PET or PBT and GF	Performance, solvent, and chemical resistance	Militskova et al. 1993
PC/PAES with MBA	BR grafted with MMA, styrene, and/or AN; then (shell) MMA, styrene, AN	Weber and Muehlbach 1993
3. PC/Fluoropolymer blends		
PC with ETFE	Processability, lubricity, and abrasion	Kawai and Miyauchi 1974
PC with PP and with PTFE	Improved performance	Kishimoto 1976
PC/PVDF with co-polyacrylics	Miscible, yellowish films, $T_g = 120$ °C	Leibler and Ringenberg 1986
PC with PTFE	Processability, lubricity, and abrasion	Akega 1991
PC with PTFE, ABS, and cresol novolak phosphate oligomers	Improved performance, flame resistance	Fuhr et al. 1992
4. PC/Polyimide blends		
PC with SMI	Improved stiffness, HDT, and strength	Fava 1979, 1981
PC with PEI	Processability, flexural and impact strength	Giles 1983, 1984

(*continued*)

Table 1.67 (continued)

Composition	Comment	References
PEI/PAr, PC, and phenyl phosphate	Improved melt stability	Peters and Rock 1989
PEI with PAr, PC and HIPS	Flexibility and impact resistance	Holub and Rock 1989
PEI with PAr and PC	HDT, flame, and impact resistance	Holub 1990
PC with PAI	Mechanical and antistatic properties	Shimamura and Suzuki 1991
PC with a carbodiimide: $(X)_m$-(-N = C = N-Y-$)_p$-(-N = C = N-X$)_m$	For sheath optical fibers	Kamps et al. 1994

The most common POM blends are homologous mixtures of POMs having different molecular structures (linear, branched, cross-linked) (Matsuzaki 1991), different molecular weights (Ishida and Sato 1970), or with different end groups (Nagasaki et al. 1991; Hanezawa and Ono 1991). On the second place are blends of POM with TPU, preferably polyester type. POMs are also blended with core-shell acrylic elastomers, MBS or MBA. Commercial blends of POM with PEST are available. To improve weatherability of POM, the resin was blended with PMMA and a fluoropolymer (viz. PTFE, PVF, PVDF) (Katsumata 1991).

For the manufacture of sliding parts, POM blends were developed with PTFE (Ishioka 1991); with PVDF (Shibata et al. 1992); with either wax, PTFE, silicone oil, or PEG; and with EBA-GMA (Takahashi and Kobayashi 1993). Later blending technology of POM involved introduction of the reactive end groups – it makes compatibilization with other polymers relatively simple.

Addition of PPE/PS to POM was used to improve processability, HDT, and mechanical properties (Ishida and Masamoto 1974). Then, POM with a Lewis acid was incorporated into PPE/PA blends to improve compatibilization and induce high heat and impact resistance (Takayanagi et al. 1994). POM blends with specialty polymers are formulated either to take advantage of POM (the resistance to abrasion) or of the specialty resin (e.g., to improve stiffness and wear resistance by incorporation of PEEK or PEI) (Suzuki and Nagahama 1987). POM is miscible with polyvinylphenol, PVPh; thus addition of PVPh to blends of POM with COPO compatibilizes the system (Machado 1993).

1.6.6 Polyphenylene Ether (PPE)

In 1956, by oxidative coupling of *2,6*-dimethyl phenol, poly(2,6-dimethylphenyl ether) was obtained (PPE) (Hay 1959, 1964, 1967, 1968). The resin was commercialized in 1964. PPE is amorphous (T_g = 210 °C), but it can crystallize (T_m = 257 °C). It is thermally stable only to $T \leq 150$ °C (CUT = 125 °C). It has good rigidity, creep resistance, dimensional stability, and high electrical, chemical, moisture, and flame resistance. The main disadvantages are processability, oxidative degradation, low-impact strength, and weatherability. The resin is usually "plasticized" by blending with styrenics. The annual production and growth rate of PPE are, respectively, 300 kt and 9 %.

1.6.6.1 PPE Blends

The first PPE blends with PS and polydiphenylsiloxane (PDPS) were reported to be transparent, colorless solids that turn into liquid at 85 °C (Boldebuck 1962). Since then PPE has been modified by blending (e.g., with HIPS, ASA, MBA, SBS or SEBS, etc.), by grafting (Brown 1989), or by reacting its end groups (Richards and White 1994).

Modified PPE is mainly blended with other engineering resins – most of these were already discussed. The principal types of PPE blends are with styrenics, with PA, and with PEST. Owing to miscibility of PPE with PS, the compatibilization is relatively simple. However, blending PPE with either PA or PEST is more challenging, since these systems require reactive compatibilization. Development of PPE grafted with acidic functionality was motivated by this need.

PPE has been blended with most specialty resins – the latter usually as a minor component. Exceptions are the PPE/PPS alloys. Their performance depends on the level of PPS crystallinity. The commercial blends, *DIC PPS* (introduced in 1982), were developed for the electrical, electronic, and mechanical industry. These show good processability, reduced flash in injection molding, toughness, high heat, and chemical resistance.

Several blends of PPE with specialty resins are parts of multicomponent systems. For example, PI was blended with PPE and then cured. The alloys were used as rigid and stable matrices for manufacturing fiber-reinforced composites (Camargo et al. 1986). Similarly, end-capped PPE was blended with SEBS and then dispersed in either PEI, PA, PEST, or PS, to give improved resistance to loss of impact strength after thermal recycling (Richards and White 1994). Blends of PAI with PPS and at least one of either PA, PEST, PC, PPE, PSF, PES, PEI, PEK, PEEK, PPS, PEST, PA, PEA, or siloxanes were compatibilized with aromatic polyisocyanates. The systems showed excellent flowability, high heat resistance, and mechanical strength (Kawaki et al. 1995). Examples of PPE/specialty polymer blends are listed in Table 1.68.

1.6.6.2 Miscible PPE Blends

Miscibility of PPE with PS has been known since 1960. Later, two other PPE blends were announced miscible. PPE blends with polytransoctanylene (PTO) can be processed at 260 °C and have HDT $\geq$ 194 °C. The patents suggested that PTO is miscible with PPE (Jadamus et al. 1986, 1987). The PPE blends with polyphenyl methacrylate, poly(p-methoxy phenyl methacrylate), poly(benzyl methacrylate), or poly(3-phenyl propyl methacrylate) were reported to have the lower critical solution temperature, LCST = 105–150 °C (Fischer and Siol 1993, 1995).

Immiscible, but transparent, are blends of PPE with a copolymer of cyclohexanedimethanol, ethylene glycol, and terephthalic acid (PCTG) – the clarity was achieved by closely matching the refractive indices at the use temperature. The alloys also show good processability, thermal dimensional stability, and economy (Stewart and Massa 1993).

Table 1.68 PPE specialty polymer blends

Composition	Comments	References
1. PPS/PPE blends		
PPS with PPE/PSF and/or PC, GF	The first, reactively compatibilized blends	Bailey 1977
PPS with a styrene-grafted PPE and polyetherester rubber	Good toughness, impact, and tensile strength	Dainippon Ink and Chem., Inc. 1982
PPS/PPE with EPR-MA, EBA-MA, SGMA, EVAc-GMA, etc.	Reactive blending, yielded reinforcing spherical PPE particles $d = 0.01–10\ \mu m$	Nishio et al. 1988, 1994
PPS/PPE/core-shell graft copolymer	Toughened by silicone elastomer particles	Sasaki et al. 1989
PPS/PPE with SEBS and PP	Tough blends	Maruyama and Mizuno 1990
PPS + ABS, PPE, PC, PA, PEST	Presence of macromers with epoxy group	Tsuda and Azuma 1991
PPSS with PPE, PC, PA, or POM	Impact strength, mechanical properties	Ono et al. 1991
PPE/PPS and polymethylene-phenylene-isocyanate with GF	Mechanical and welding properties, solvent resistance	Gotoh and Nagaoka 1993
PPE/PPS/core-shell MBS or SEBS	PPE reacted with trimellitic anhydride acid chloride and dimethyl-*n*-butylamine	Dekkers 1994
PPS/PPE/EBA-GMA blends with particle size $d = 0.001–10\ \mu m$	Impact resistance, stiffness, heat resistance, moldability, appearance	Orikasa and Sakazume 1994
PPE with co-poly(arylene sulfide), $[(\text{-}\phi\text{-S-})_{1-x}(\text{-}\phi\text{-S-S-})_x]_n$	Processability, good mechanical properties	Bagrodia et al. 1994a
2. PSF/PPE blends		
PSF, POM with PPE	High HDT	Ikeguchi and Nagata 1974
PC/PA-12 and PPE/PSF	Moldability and mechanical performance	Okuzono and Kifune 1975, 1976
3. PI/PPE blends		
PPE/SBR grafted (SBMI)	Improved performance	Fava and Doak 1980
PPE/SBS, styrene-phenyl-maleimide	HDT, impact, and solvent resistance	Fukuda and Kasahara 1982
PI with PPE, PPS, PEI, or PSF	Moldability, stability, mechanical strength	Ohta et al. 1988
PEI with PPE-MA	Mechanical performance	White and van der Meer 1989
Two PPEs with polyetherimide-silane copolymer	Processability, flame-retardant properties, and impact strength	Haaf 1992
4. PEBA/PPE blends		
PEBA with PPE and triglycidylisocyanurate	Non-delaminating behavior, good rigidity, and strength	Brown et al. 1992

(*continued*)

Table 1.68 (continued)

Composition	Comments	References
5. PPE/fluoropolymer blends		
PPE with poly (hexafluoropropylene-co-vinylidene fluoride)	Thermoformable, high HDT, and flame resistance	Snodgrass and Lauchlan 1972
PPE with PVDF, SMMA, and SEBS	Improved impact strength and elongation	Van der Meer et al. 1989

1.7 Specialty Polymers and Their Blends

The *specialty* resins are expensive, produced in relatively small volumes either for a specific application or looking for a market niche. Their $T_g > 200$ °C and modulus > 3 GPa. In 1991 the total world consumption of polysulfones (PSF) and polyethersulfones (PES) was 8.5 kt. Blends of the following polymers are known: polyfluorocarbons, polysiloxanes, sulfur-containing polymers (PPS, PPSS, PES, and PSF), polyetherketones (PEK, PEEK, PEKK), polyimides (PI, PEI, and PAI), PAr, COPO, polyphosphazene (PHZ), and LCP.

1.7.1 Fluorocarbon Polymers

Known in Germany since 1933, polytetrafluoroethylene (PTFE) is a semicrystalline resin (92–98 % crystallinity), with $T_m = 342$ °C and melt viscosity of $\eta \approx 10$ GPas. Other more common fluoropolymers are polychlorotrifluoroethylene (PCTFE), *Hostaflon*™ commercialized in 1934, fluorinated ethylene-propylene (FEP), *Teflon*™*-FEP* introduced in 1972, and numerous copolymers with $T_m = 260–304$ °C, processable at $T_{process} = 315–425$ °C and having the degradation temperature $T_{deg} = 425–440$ °C. The fluoropolymers are characterized by stability at high temperatures; toughness and flexibility at low temperatures; low friction, insolubility, and inertness to chemicals; low dielectric losses; and high dielectric strength. The world consumption of fluoropolymers in 1991 was 72 kt.

In blends, fluoropolymers are used in small quantities to enhance throughput, reduce the frictional properties, and increase the wear resistance. Blends comprising 0.3–50 wt% of a low molecular weight PTFE ($T_m \leq 350$ °C) with engineering resin showed improved antifriction properties (Asai et al. 1991). LLDPE generally exhibits sharkskin melt fracture, but the use of fluoropolymer additives, such as the copolymer of vinylidene fluoride and hexafluoropropylene, can help to eliminate the extrusion instability (Hatzikiriakos and Migler 2005).

PPS and PEEK which blended with fluoro(co)polymers and reinforced with either CF or GF were wear resistant with a short break-in period for forming a self-lubricating film (Davies and Hatton 1994). Many commercial blends contain fluoropolymers (primarily PTFE) for the improved weatherability and wear and solvent resistance: *SUPEC*™ – "self-lubricating" blend of crystalline PPS with

PTFE and 30 wt% GF, *Lubricomp*™ blends from LNP and similar *RTP*™ blends from RTP Co. (e.g., 15 wt% PTFE, 30 wt% GF, and any of the following resins: ABS, PA, PEST, PC, PE, PEI, POM, PP, PPE, PPS, PS, PSF, PVDF, SAN, TPU, PEEK, PES, etc.), *Sumiploy*™ from Sumitomo Chem. Co., etc. (Utracki 1994).

1.7.2 Siloxane Polymers

Polysiloxanes, [-O-Si(RR′)-], are linear resins that can be branched or cross-linked into elastomers. They have high compressibility, permeability to gases, low T_g and viscosity, exceptional weatherability, low surface tension coefficient, and are relatively expensive. Siloxane polymers or copolymers have been incorporated into engineering or specialty resins to improve processability, toughness, HDT, and solvent and weather resistance.

The main polymers of this type are polydimethylsiloxane (PDMS) and polymethylphenylsiloxane (PMPhS). Their $T_g = -127$ and -86 °C, respectively. They start oxidizing at 290 °C and 375 °C and undergo structural rearrangement at 435 °C and 410 °C. Polysiloxanes have been used as high temperature impact modifiers that improve the flame resistance, processability, and optical properties. Several commercial blends are on the market, viz., *Rimplast*™ (high tensile, flexural, and Izod impact strength PAs), *Dialoy*™ (PC/PET blends with good chemical, weather, and low-T impact resistance), etc. Evolution of polysiloxane blends with engineering and specialty resins is summarized in Table 1.69.

1.7.3 Polyarylene Sulfide (PPS)

Polyarylene sulfides (PPS), $(\text{-}\phi\text{-S-})_n$, was commercialized in 1971 as *Rayton*™ *R*. The resin is semicrystalline with $T_g = 194$ °C and $T_m = 288$ °C; thus $T_{process} \geq 290$ °C. PPS is difficult to mold – it tends to adhere to the mold surface and to flow into mold crevices. It has also relatively poor impact resistance. Blends have been developed to alleviate these problems, e.g., with 25 wt% of either PSF, PPE, or PC (Bailey 1977). Commercial PPS blends are available with PPE (e.g., *DIC PPS* commercialized in 1982, *Noryl*™ *APS*), PARA (*RTP 1300*), or PTFE (*Lubricomp*™ *PPS*). They show good processability with reduced flash, are tough, excellent wear, as well as high heat, solvent, chemical, and oxidation resistance.

PPS has been frequently blended with PSFs. The latter resins are mainly amorphous, frequently transparent, with $T_g = 196–288$ °C, able to maintain high-performance characteristics over a wide temperature range, but poor weatherability, notched impact strength, and ESCR. The PPS/PSF blends have been developed to improve PPS processability and/or the mechanical performance over a wide range of temperatures, to improve PSF weatherability, impact, and ESCR characteristics. Evolution of these blends is outlined in Table 1.70.

PArs are aromatic amorphous polyesters, viz., *U-polymer*™, *Ardel*™ *D-100*, *Durel*™, *Arylon*™, etc. Their $T_g \approx 188$ °C and HDT = 120–175 °C. Blends with

Table 1.69 Polysiloxane blends

Composition	Comments	References
1. PA blends		
PA, vinyl-terminated PDMS, siloxane with Si-H groups and Pt	Tensile, flexural, and notched Izod impact strength	Arkles 1983, 1985
Acidified PPE, PA, PDMDPhS	Flame resistance	Smith et al. 1990, 1994
2. PEST blends		
PET with PDMS and MABS	Impact and embrittlement resistance	Sauers and Barth 1970
PEST and/or PC with siloxane-based vinyl-grafted copolymer	Chemical, weather, and low-temperature impact resistance	Hongo et al. 1987
PEST/PC/PPE/star-block copolymer	Impact-modified engineering resins	Hoxmeier 1994
PEST and siloxane-acrylic elastomer	Impact strength at low temperature	Yamamoto et al. 1992, 1994
3. PC blends		
PC with PDMS	Solution cast films	Caird 1961
PC with siloxane and elastomer	Impact resistance	De Boer and Heuschen 1988
PC with PArSi	Transparent, flame and impact resistant	Jordan and Webb 1992, 1994
PC or PEC with PC-b-PDMS	Low flammability and good impact strength,	Hoover 1993
PC with elastomeric polysiloxane/polyvinyl-based graft copolymer	thermally stable, low-T ductility, impact, and heat resistance	Derudder and Wang 1993
4. POM blends		
POM/PDMS adsorbed on silicone	For sliding parts with high wear resistance	Takayama et al. 1991
5. PPE blends		
PPE, PS, and PDPS	Clear, transparent, colorless solids at 65 °C	Boldebuck 1962
PPE-g-siloxane and SEBS	Enhanced solvent and impact resistance	Brown 1989
Poly(bisphenol-A dimethylsiloxane) with PPE, PAr, PI, PEST, or PC	HDT, reduced melt viscosity	Herrmann-Schoenherr and Land 1993, 1994
PArSi with PPE and SBS	Flame retardancy	Jordan and Webb 1994
6. PEI blends		
PEI with poly(carbonate-b-siloxane) and EPDM, ABS, MBS, or MMBA	Processability, impact strength	Giles and White 1983
PEI with PArSi	Processability, flame retardancy	Jordan and Webb 1994
PArSi with PPE and SBS	Flame retardancy	Jordan and Webb 1994
7. PPS blends		
PPS/PDMS, trialcoxysilane, and PO	Processability and impact strength	Liang 1987
PPS/PBT, silane, and GF	Chemical resistance and toughness	Serizawa et al. 1992

(*continued*)

Table 1.69 (continued)

Composition	Comments	References
PPS with silicone and acrylate elastomer lattices	Improved heat and impact resistance	Koshirai et al. 1992, 1994
PPS-g-amine with PDMS-g-epoxy	Improved tensile elongation and strength	Han 1994
8. PHZ blends		
PHZ or its copolymer with a siloxane polymer and/or elastomer	Bisazoformamide (foaming agent) gave semirigid, highly flame-retardant foams	Dieck and Quinn 1977

PPS have been developed to improve the performance of PAr – processability, rigidity, and hydrolytic stability.

To the category of amorphous, aromatic polyamides (PARA) belong polyphthalamides (PPhA), e.g., *Amodel*™ (T_g = 127 °C, T_m = 310 °C, HDT = 285 °C, CUT = 180 °C). PPS/PARA blends were formulated to increase the reinforcing effects of GF on PPS. They show good processability, mechanical performance, and resistance to thermal degradation.

Polyimides (PI) were introduced in 1962 as thermally non-processable *Kapton*™. To improve processability, the main-chain flexibility was enhanced by incorporating segments with higher mobility, viz., polyamide-imide (PAI), polyetherimide (PEI), polyimide-sulfone (PISO), etc. These polymers are characterized by high T_g = 150–420 °C and thermal resistance. They are blended with PPS to enhance its moldability, thermal stability, and mechanical performance.

Polyaryletherketone (PEEK), $[\text{-}\phi\text{-CO-}\phi\text{-O-}\phi\text{-O}]_n$, was commercialized in 1980 as *Victrex*™. It is a tough resin with T_g = 143 °C and T_m = 334 °C. Blends of PEEK with PPS show synergistic effects toward tensile and flexural strength as well as the impact resistance.

The inorganic low-temperature glasses (LTG) with $T_g \leq 300$ °C are durable and water resistant. LTG was blended with either PPS, PET, PBT, PEK, PEEK, PEI, LCP, PC, or fluorinated polymers (Frayer 1993, 1994).

Oxidation of PPS by addition of N_2O_4 in a sulfuric acid solution results in the incorporation of surfoxide groups, leading to either polyphenylenesulfidesulfoxide or polyphenylenesulfoxide. Their blends with high temperature resins (viz., PSF, PES, PPS, PEI, PAr, PEEK, PC, PI, PAI, LCP, fluoropolymers, cycloolefins, and their alloys or composites) produced high temperature-resistant foams by heating for 5–60 min at T = 300–470 °C (Scheckenbach et al. 1998). The process reduced the moldings' density by at least 50 %.

1.7.4 Polysulfone (PSF)

Polyarylsulfones (PSF or PSU), or polyarylethersulfones (PAES), have the chain structure $(\text{-}\phi\text{-SO}_2\text{-})_n$. The commercial resins include *Udel*™ PSF,

Table 1.70 PPS blends

Composition	Comments	References
1. PPS/PSF		
PSF/PPS with 45 parts of a styrene-butadiene rubber (SBR)	The first PPS/PSF blends – to improve the impact strength	Asahi Chem. Ind. Co., Ltd. 1981
PPS with PSF and 5–40 wt% PTFE	Processability and resistance to corrosives	Bailleux et al. 1984
PSF/PPS/PSF-b-PPS copolymer	Impact strength, uniformity, and cohesion	Hashimoto 1986
PPS/PPSS {PPE, PC, PA, POM}	Impact strength and mechanical properties	Ono et al. 1991
PPS with either PSF or PPSS	Improved interfacial adhesion and moldability	Bagrodia et al. 1993, 1994a, b
45–60 wt% PSF, 25–45 wt% PPS, and 0–10 wt% MBS	Resistance to impact, high-T performance, weatherability – for car body panels	Golovoy and Cheung 1994
2. PPS/PAr		
PAr with 40 wt% PET and PPS	Enhancement of properties	Kyo et al. 1978
PAr with 1–99 wt% PPS	Processability, impact, fire, and abrasion resistance	Matsunaga et al. 1978
PAr/PPS and chloro-hydro-dimethano-di-benzocyclo octene	good hydrolytic stability, moldability, and flame retardancy	Salee 1980, 1981
PAr/PPS, ABS, or acrylic elastomer	Excellent hydrolytic stability	Salee, 1982
3. PPS/PARA		
PARA with a small amount of PPS	Moldability, HDT, and impact strength	Shue and Scoggins 1981
PPS with a small amount of PPhA and GF	Mechanical properties, adhesion (NH_2 with GF), and aromatic parts of PPhA with PPS	Davies 1990
Reinforced blends of PPS with PPhA and POCA	High degradation temperature, chemical resistance, HDT, mechanical properties	Chen and Sinclair 1990
95–5 wt% PARA with PPS	High resistance to heat and thermal aging; improved melt flow	Yamamoto and Toyota 1992
PPS with 25–95 parts of either PA-66 or PA-MXD6 and $Mg(OH)_2$	Excellent tensile strength as well as arc, tracking, and heat resistance	Dubois et al. 1993
4. PPS/PI		
PPS with 60 wt% PI	To improve moldability at 310 °C	Alvarez 1977
PI with PPS, PPE, PEI, or PSF	To improve the moldability of PI	Ohta et al. 1988
PPS, 20–65 wt% PAI, and 4,4′-diphenyl methane diisocyanate	Processability, heat, chemical, and solvent resistance, mechanical strength	Kawaki et al. 1992, 1994, 1995
5. PPS with PEEK and LTG		
PPS with 10–90 wt% PEEK	Processability, strength, and impact resistance	Robeson 1982
PPS/PEEK/PMP, GF, organosilane	Mold release and reduced molding flash	Hindi et al. 1994
Low-temperature glasses (LTG) with 35 wt% PPS	Rigidity, dimensional stability, strength	Frayer 1993, 1994

[-ϕ-C$(CH_3)_2$-ϕ-O-ϕ-SO_2-ϕ-O-$]_n$ (T_g = 196 °C and CUT = 160 °C), *Astrel*™ [-ϕ-ϕ-SO_2-ϕ-O-ϕ-SO_2-$]_n$ (T_g = 288 °C), *Victrex*™ PES [-ϕ-SO_2-ϕ-O-$]_n$ (T_g = 228–232 °C), *Radel*™ *R* PPSF [-ϕ-ϕ-O-ϕ-O-ϕ-SO_2-ϕ-O-$]_n$ (T_g = 220 °C), *Ultrason*™ *E*, *Talpa*™ *1000*, *Sumilite*™, polyimidesulfone, PISO, *Amoron*™ polythioethersulfone, PTES, etc. Then there is the sinterable polyphenylenesulfone, *Ceramer*™ [-ϕ-SO_2-ϕ-$]_n$ (T_g = 360 °C, $T_{decomp.}$ > 450 °C), used as an "additive" to high-performance polymers used in harsh environment (Ceramer 1996).

PSFs are transparent; flame resistant; have high strength, modulus, and hardness; and HDT > 200 °C. They show excellent resistance to thermal and irradiation degradation, but are difficult to process (high melt viscosity) and have low ESCR and poor weatherability. The latter properties can be improved by blending and/or reinforcing. PSF blends comprise high-performance resins, viz., PPE, PPS, PTFE, etc., with such compatibilizers/impact modifiers as *phenoxy*, EVAc-GMA (Gaafar 1990), SMA copolymers (Golovoy and Cheung 1994), siloxane-polyarylene polyether copolymers, or high temperature MBS. *Mindel*™ *A* and *Arylon*™ are examples of the commercial ASA/PSF blends. They show good processability, toughness, plateability, and heat and water resistance.

Addition of a small amount of PSF to a variety of resins improves hardness, the notched Izod impact strength, plateability, hydrolytic stability, and shape retention at high temperatures. Many PSF blends of or with engineering resins have been developed, viz., with PA, PEST, PC, PPE, or POM. They have high HDT, heat resistance, strength, stiffness, mechanical properties, and ESCR. Polysulfone blends have been foamed using water and either N_2 or CO_2 (Bland and Conte 1991). The blend comprised at least two sulfone polymers, e.g., PES and PSF, and at least one non-sulfone polymer (e.g., PS, PPE, PEI, PC, PA, PEST, PP, or PE). The nucleating agent was either talc, mica, silica, Zn-stearate, Al-stearate, TiO_2, or ZnO. The foams were used as insulation for high temperature structural applications. Since in the preceding part PPS blends with PSF were described, in Table 1.71 examples of PSF blends with other specialty resins are listed.

1.7.5 Polyetheretherketone (PEEK)

Polyaryletherketones (PAEK) are aromatic polymers with ether and ketone linkages in the chain, viz., PEK, PEEK, PEEKK, etc. Polyetheretherketone (*Victrex*™ PEEK), [-ϕ-CO-ϕ-O-ϕ-O-$]_n$, was commercialized in 1980 (T_g = 143 °C, T_m = 334 °C). Commercial blends of PEEK include *Sumiploy*™ PEEK/PES/PTFE, PEEK/LCP, *Cortem*™ PEEK/LTG, etc. Evolution of PEEK blends' technology is outlined in Table 1.72.

1.7.6 Polyimides (PI, PEI, or PAI)

Polyimides (PI) have imide group, -R-N = $(CO)_2$ = R′-, in the main chain. Owing to a variety of possible R and R′ groups, their T_g = 180–420 °C. To improve

Table 1.71 PSF/PI blends

Composition	Comments	References
1. PSF/PI		
PAI with 0.1–50 wt% of either PSF, PA, or PARA	Improved melt flow and good mechanical properties	Toray Industries, Inc. 1979, 1980, 1981
PES/PPBA (T_g = 200–300 °C)	For lacquers and homogenous, clear films	Patton and LaMarre 1983
PEI with PSF, PP, PEC, or PAr; with PC and PEST, PAr or PA, etc.	For good processability, improved flexural and impact strength	Giles, 1983, 1984
PI with 0.01–10 phr PSF solution cast	For films with good blocking resistance	Mitsubishi Chem., 1984
PI with PEI, PES, PAr, PC, PEEK, or PPE, e.g., PI: PEEK: PEI = 1:1:1	T_g = 175 °C, used as crack-resistant coatings with good adhesion to metal	Camargo et al. 1986
PI with PSF, PPS, PPE, or PEI	Moldability, heat and chemical resistance	Ohta et al. 1988
PES with PEI	Improved HDT	Melquist 1993
PES/sulfonyl *bis*(phthalic anhydride)-co-*bis*(*p*-amino cumyl) benzene	Processability, solubility, mechanical, and thermal properties	El-Hibri and Melquist, 1993
LCP-type PI with PES, PI, PEI, PAI, PEK, or PEEK	Remarkably good processability and excellent thermal stability	Okawa et al. 1994
PES/PI (e.g., *XU*-218 or *PI*-2080) miscible blends (single T_g, UCST)	High moduli, tensile strengths, and impact strengths	Karasz and MacKnight 1994
2. PSF blends with fluoropolymers		
PSF/PPS/5–40 wt% PTFE fibrils	Processability, lubricity, anticorrosive	Bailleux et al. 1984
PES/0.3–50 wt% low MW PTFE	Self-lubricity	Asai et al. 1991
PSF/PC or PET, $ZnBO_3$, and PTFE	Flame-retardant, synergistic properties	Jack et al. 1993
Fluorine-containing polycyanurates with PSF, PP, or PEEK	Flame-retardant, low thermal expansion, T_g = 180–320 °C, stable to 430–500 °C	Ardakani et al. 1994
3. PSF blends with other specialty resins		
PES, with poly(*p*-phenylene ether-co-*p*-phenylenesulfonyl)	Miscible, transparent solvent-cast films, with good water and chemical resistance	Newton 1981
PSF with 70 wt% polyether-amide (PEA)	Moldability, high HDT and mechanical properties	Hitachi Chemical Co., Ltd., 1983
PSF/acrylic elastomer/ polyphosphates	Thermal stability, flame retardancy, toughness	Schmidt, 1983
PEEK/PAES with HDT = 157 °C	Low warpage and shrinkage, rigidity, stress-cracking, solvent, and impact resistance	Harris and Robeson 1986, 1987
PES, PEEK, and 20 wt% PEI	Mechanical properties and heat resistance	Rostami 1987
PES/95-75 wt% PEEK	Chemical and hot-water resistance	Tsumato et al. 1987

(*continued*)

Table 1.71 (continued)

Composition	Comments	References
PAEK, PAE, or PPE, blended with LCP, PI, PAES, or PEST	Processability (warp-free moldings), mechanical properties, and high HDT	Harris and Michno 1988
PES with phenoxy	Chemical resistance and tensile strength	Kraus et al. 1991
PSF with PVP or PEG, radiation cross-linked	For selectively permeable membranes or hollow fibers	Kobayashi and Tanaka 1992
Biodegradable PLA with either PSF, PC, PI, PPE, etc.	To improve the thermal properties	Nemphos and Kharas 1993
PES dissolved in oligooxybenzoyl acid and then polymerized to POBA	Molecular composites, polymerizing while shearing	Tochioka 1993

Table 1.72 PEEK blends with specialty resins

Composition	Comments	References
PEEK/PAI and optionally with PPS	Solvent resistance, hydrolytic stability	Harris and Gavula 1986
95–75 wt% PEEK with PES	Chemical and hot-water resistance	Tsumato et al. 1987
POM/10 phr of PEEK and/or PEI	Wear resistance without loss of slipperiness	Suzuki and Nagahama 1987
PEK/PAI and zinc sulfate hydrate	Good moldability and high impact strength	Smyser and Brooks 1990
LTG with either PEK, PEEK, PPS, PEI, LCP, PC, PET, PBT, or fluorinated polymers	Processability, mechanical properties, stiffness – *Cortem*™ *Alloys* with either LCP or with PEEK	Bahn et al. 1991
Crystalline and amorphous PEK with PAr	Good flowability and processability	Falk and Herrmann-Schoenherr 1992
POM-b-PC with PES, PEEK, PA, or PAN	Film-forming thermoplastic polymeric alloys	Dhein et al. 1993
ASA, PC, PEST, PEC, PPE, PPS, PEEK, PES, PSF, and/or PPE	Toughened by 30–80 wt% elastomer, e.g., SEBS and core-shell graft copolymers	Niessner et al. 1994
PPS blends with PEEK	Improved mold release and reduced flash	Hindi et al. 1994
PI, PAI, PSF, PEI, PES, PEEK, PPS, or PPE and a polyether-b-polyamide or polyether-b-polyester	Easy to mold blends, flexible and elastic, with excellent chemical and thermal resistance	Movak et al. 1994
PEKK/PEI = 70/30 w/w co-reacted through the terminal amine group of PEI and ketone one of PEKK	Resulted compound with strain hardening was water foamable at T = 335–350 °C, whereas neither PEKK nor PEI can be foamed	Brandom et al. 1997

Table 1.73 PI blends

Composition	Comments	References
PEI with PAr	Moldability and mechanical properties	Holub and Mellinger 1981
PEI/PAI = 1:1	Mechanical properties and ESCR	Maresca et al. 1981
Polyarylethers with PEI	Good ESCR	Robeson et al. 1981
PEI, poly(carbonate-b-siloxane), and EPDM, ABS, MBS or MMBA	Processability and impact strength	Giles and White 1983
PEI, PA-6, and PEI-b-PA	Moldability and impact strength	Robeson and Matzner 1984
PEI with polyestercarbonate (PEC)	High HDT and tensile strength	Quinn 1984
PEI/0.5–20 wt% of a fluoropolymer	Mold release, heat resistance, and shrinkage	Sumitomo Chem. 1985
PI with PAI in the full range of composition	Foamed during the final stage of the condensation reaction at T = 120–320 °C	Long and Gagliani 1986
PI, with PPS, PPE, PEI, and PSF	Moldability, heat stability, chemical resistance, and mechanical strength	Ohta et al. 1988
PEI with PPE-MA	Mechanical performance	White and van der Meer 1989
PEK with either PES, PEI, PEEK, PEST, PAr or PPS, and filler	Processability, mechanical strength, as well as heat and flame resistance	Murakami et al. 1991
PEI, PBT, and triallyl cyanurate and triallyl isocyanurate	High thermal deformation resistance and HDT	Hosoi 1991
Low-temperature glasses with PEI	High modulus, mechanical performance	Bahn et al. 1991
Polyether-b-polyimide-b-siloxane copolymer with low MW PEI	Impact-resistant materials with excellent processability and HDT	Durfee and Rock 1993
PPS/PEI with 30 wt% GF	High flow and no flash	*Supec™ CTX530*
Fluoro-elastomers dispersed in a resin, e.g., PI, PAI, PSF, PEI, PES, PEEK, PPS, PPE, etc.	Moldings: flexible, elastic, self-lubricating, having excellent chemical and thermal resistance	Movak et al. 1994
LCP-PI with either PI, PEI, PAI, PES, PEK or PEEK	Remarkably good processability and excellent thermal stability	Okawa et al. 1994
PBI with 0–95 wt% of PEI	Thermo-oxidative stability	Haider and Chenevey 1994
PI blended with PMS and then foamed by the thermal decomposition of PMS	Nano-foams showed increased craze zone size and higher crack stability than the not-foamed PI films	Plummer et al. 1995; Charlier et al. 1995

processability, flexible groups were incorporated into the main chain. Examples of blends of these resins are listed in Table 1.73.

Polyamideimides (PAI) were obtained by polycondensation of imides with aromatic diamines, [-N=(CO)$_2$=ϕ-CO-NH-R-NH-CO-ϕ=(CO)$_2$=N-]$_n$ (T_g = 275 °C, HDT = 265–280 °C). The resin has high tensile and impact strength from T = −190 to T = 260 °C, dimensional stability, good dielectric properties, solvent and chemical resistance, flame retardancy, good UV stability, and low outgassing in high vacuum. To improve processability, PAI was blended with PA, PSF, or PEST (Toray Industries, Inc. 1979).

Polyetherimide (PEI), $[\text{-N(CO)}_2\text{-}\phi\text{-O-}\phi\text{-C(CH}_3)_2\text{-}\phi\text{-O-}\phi\text{(CO)}_2\text{CN-}\phi-]_n$ (T_g = 215–220 °C, HDT = 217 °C, CUT = 170 °C, no weight loss at $T \leq 400$ °C), was commercialized as *Ultem*™. The resin has high tensile modulus (even at elevated temperatures), approaching that of many glass-reinforced resins. Commercial PEI blends include these with PC (*Ultem*™ *LTX* introduced in 1990), with PPS (*Supec*™ *CTX530*) (Utracki 1994), or with polyphenylsulfone (Sanner and Gallucci 2011).

Polyimidesulfone (PISO) was introduced in 1986 *Celazole*™ (T_g = 249–349 °C). This transparent resin with flexural modulus of 4.8 GPa and tensile strength of 63 MPa has shown excellent solvent and creep resistance.

1.7.7 Aromatic Amorphous Polyamides (PARA)

There is a great diversity of amorphous aromatic or semi-aromatic polyamides (PARA). The commercial resins include *Trogamid*™, *Quiana*™, *Amodel*™, etc. They have been blended to improve the mechanical properties and impact strength, as well as to enhance the barrier properties of the matrix resin to permeation by gases or liquids. Examples of blends with PARA are listed in Table 1.74. Blends of PARA were also discussed along other blends of polyamides.

Table 1.74 Blends with aromatic amorphous polyamides (PARA)

Composition	Composition	References
PARA with POM	Toughness and impact strength	Asahi Chem. Ind. 1969
PARA with semicrystalline PA	Improved oxygen barrier properties	Dynamit Nobel 1969
PAI with PA-66 or PARA	Processability and mechanical properties	Toray Ind. 1979, 1981
PARA with PC	Nacreous, resistant to oils and boiling water	Mitsubishi Chem. 1980
PARA with 5–95 wt% PPS	Improved moldability, HDT, and impact strength	Shue and Scoggins 1981
PARA with PA-6I6T	For strong fibers or films	Unitika Co., Ltd. 1982
PARA with PES	Increased HDT and mechanical performance	Hub et al. 1986
PPS with PPhA and GF	Stiff, high-performance reinforced alloys	Davies 1990
PARA with maleated PP or PE	Sliding electrical parts, resistance to thermal degradation in contact with Cu	Iwanami et al. 1990
PARA with rubber-modified PS	Transparent, having near-zero birefringence	Angeli and Maresca 1990
PARA with PAr are miscible	Processability, mechanical properties, solvent, weather, HDT, impact and stress-crack resistance	Bapat et al. 1992

Table 1.75 Blends with linear, aromatic polyesters (PAr)

Composition	Comments	References
PAr with PC and PET	Improved impact resistance	Koshimo 1973
PAr blends with PET	Transparent and impact resistant commercial blends	*U 8000* from Unitika or *Ardel*™ *D-240* from Amoco
PAr/PET = 1:1 with PA-6 or PPS	Enhanced mechanical properties	Asahara et al. 1977a, b
PAr with 1–99 wt% PPS	Processability, impact strength, fire and abrasion resistance	Matsunaga et al. 1978
PAr/PPS and dodecachloro-dodeca-hydro-dimethano-di-benzocyclooctene	Good hydrolytic stability, moldability, and flame retardancy	Salee 1980, 1981
PAr/PET/PPS with ABS or MBS	Improved hydrolytic stability	Salee 1982
PAr with PA-6, *U-polymer*™ X-9	Processability, mechanical properties	Unitika, Ltd. 1982, 1983
PAr with polybenzimidazole (PBI)	Miscible blends	Chen et al. 1990

1.7.8 Polyarylates (PAr)

These polyesters, $[\text{-O-}\phi\text{-C(CH}_3)_2\text{-}\phi\text{-CO}_2\text{-}\phi\text{-CO-}]_n$ ($T_g \approx 188$ °C and HDT = 120–175 °C), were introduced in 1974. The commercial resins include *U-polymer*™, *Ardel*™, *Durel*™, and *Arylon*™. Their advantages include transparency, good weatherability, and high HDT. PAr has been blended with nearly all resins, including ABS, EPDM, *ionomers*, LCP, PA, PB, PBI, PBT, PC, PEI, PEK, PET, *phenoxy*, PMB, PS, PPE, PPS, etc. Three types of PAr blends are of particular importance – those with polyesters, PEST, polyamides, PA, and polyphenylenesulfide, PPS. A summary of PAr blends is provided in Table 1.75.

1.7.9 Aliphatic Polyketone (COPO)

This copolymer of carbon monoxide with ethylene and propylene is semicrystalline, with $T_g = 15\text{–}20$ °C, $T_m = 110\text{–}242$ °C (Ballauf et al. 1941). *Carilon*™ resin (introduced in 1995) is a strictly alternating copolymer, $[\text{-CO-C}_2\text{H}_4\text{-}]_n$, obtained using metallocene catalyst. It has $T_m \approx 220$ °C, tensile strength $\sigma = 80$ MPa, and elongation at break $\varepsilon = 25\%$. The moldings have outstanding wear and friction resistance, high resilience over a wide temperature range, low sensitivity to water and organic solvents, and good barrier properties, but they are sensitive to UV. Several blends of COPO have been patented, e.g., with SAN (miscible blends), PA-6, and SEBS-MA (Machado 1992), with TPU (George 1992), and with POM and PVPh (Machado 1993).

1.7.10 Blends with Rigid-Rod Polymers

Three types of blends belong to this group: (1) molecular composites, i.e., the molecular LCP solutions, (2) immiscible blends of LCP, and (3) blends of electroconductive polymers.

1.7.10.1 Molecular Composites

In fiber-reinforced composites, the absolute size of the reinforcing fibers is not important, but good adhesion to matrix and the length-to-diameter ratio of the fiber, $L/D \geq 500$, are (Piggott 1986). Accordingly, reduction of the reinforcing particle size from, e.g., GF or CF, to rigid-rod molecules seems desirable. If the reinforcement is to be provided by individual macromolecules, the rigid-rod polymer must form molecular solution in selected thermoplastic resin. Such systems are known as *molecular composites*, MC, first generated in the late 1970s (see Table 1.76).

MC can be prepared by dissolution of either the rigid-rod polymer in a monomer that subsequently can be polymerized or by dissolving monomer of the rigid-rod polymer in a thermoplastic resin and then polymerizing it. The selections of the soluble monomer/polymer pair as well as control of the polymerization and phase

Table 1.76 Molecular composites

Composition	Comments	References
Poly(*p*-phenylenebenzobisthiazole) with poly(2,5,(6′)-benzimidazole)	MC of oriented macromolecules; films and fibers had high modulus and strength	Hwang et al. 1983
Poly(*p*-phenylene terephthalamide) (PPTA) with PA-6 or PA-66 in methanesulfonic acid	Coagulation resulted in MC that upon thermal treatment phase separated	Chuah et al. 1989a, b
Poly(2,5,(6′)-benzimidazole) with PAr	MC miscible system	Chen et al. 1990
Rigid-rod [-CO-$\phi(CF_3)$-$\phi(CF_3)$-CONH-$\phi(CF_3)$-$\phi(CF_3)$-NH-] in vinylpyridine or pyrrolidone	Polymerization of the monomeric solvent resulted in MC	Stein et al. 1992
Polybenzimidazoles, 5–95 wt% with PARA blended in DMF	Miscible by film transparency, single T_g, FTIR, and X-ray diffraction	Calundann et al. 1992; 1994
PES dissolved in polyoxybenzoyl or *p*-aceto-aminobenzoic acid, polymerizing the latter at the shear rate of 2.0–13 1/s	Solvent-free MC, high modulus and strength, for the manufacture of fibers or rod-shaped extrudates	Tochioka 1993
70–99 wt% PGI, and either PBI or LCP, with PET or PC	Good balance of toughness, tensile modulus, and HDT	Hallden-Abberton et al. 1994
Dissolution of PA or PO in lactams and then polymerizing it into a rigid-rod, e.g., poly(*p*-aminoethyl benzoate) (PAEB)	MC: N-(*p*-amino benzoyl) caprolactam in molten maleated PP, PA-6, PA-66, or PARA and then polymerized; PA modulus x2	Mülhaupt et al. 1994
Poly[2,2′-(*m*-phenylene)-5,5′-bis benzimidazole] (PBI) with 0–65 wt% PEEK	Mechanical, thermal, and chemical properties; for gaskets, seals, valve seats, and O-rings	Andres et al. 1995

separation rates are critical. The IPN approach may "lock" the dispersed structure into a metastable system with sufficient stability for processing (Utracki 1994).

1.7.10.2 Liquid-Crystal Polymers (LCP)

There are several commercial LCPs, viz., *Ekkcel*™ (degrades at $T_{process}$ 400 °C), *Xydar*™, *Vectra*™, *E-konol*™, *X-7G*, *Ultrax*™, *KU 1-90*, *Granlar*™, *Novoaccurate*™, *Rodron*™, *Victrex*™, etc. LCPs are mainly used for injection molding of parts that require exact dimensions and high performance.

Large quantity of LCP is used in blends. These are immiscible, highly oriented systems, where LCP domains provide reinforcement. Since LCPs are expensive, either the desired performance must be achieved using a small amount of melt processable LCP, or the other component of the blend is similarly priced. In blends LCP can (i) improve processability of engineering and specialty polymer (Froix et al. 1981; Cogswell et al. 1981, 1983, 1984), (ii) enhance crystallization of semicrystalline polymers (Hong et al. 1992), (iii) improve stiffness and other mechanical properties in applications where fatigue strength is important (Yamauchi et al. 1991), (iv) provide external protective layer for solvent and/or abrasion sensitive resins, etc. Excepting those with PP, the LCP blends with commodity resins are scarce (see Table 1.77).

1.7.10.3 Electro-Dissipative and Electroconductive Blends

Most organic polymers are insulators. However, there are applications requiring dissipation of the electrostatic charge (ESD) or even electrical conductivity (ECP) that would be comparable to that of metals. The ESD materials should have the surface resistivity $10^{12} \geq R \geq 10^5$ Ω cm. The resistivity of ECP should be $10^5 \geq R \geq 10^{-2}$ Ω cm.

The ESD behavior can be provided by blending in a flexible-chain polymer with an active -OH or -SH group, viz., polyvinyl alcohol (PVAl), ethylene-vinylacetate (EVAc), polyvinylphenol (PVPh), a copolymer of ethylene oxide and epichlorohydrin (EO-CHR), maleated copolymer, aliphatic polysulfides, etc. These low performance resins have been incorporated into a variety of alloys and blends (see Table 1.78).

By contrast, the ECP must have conjugated rigid-rod macromolecules. Several such polymers show high electrical conductivity (usually after doping), viz., polyacetylene (PAc), polyaniline (PANI), polypyrrole (PPy), polyparaphenylenes (PPP), or poly-3-octyl thiophene (POT). The resins are expensive, difficult to process, brittle, and affected by ambient moisture, thus blending is desirable. For uniaxially stretched fibers, the percolation threshold is 1.8 vol.%; hence, low concentration of ECP (usually 5–6 vol.%) provides sufficient phase co-continuity to ascertain conductivity similar to that of copper wires (see Table 1.78).

As a synthetic strategy, simple and versatile reactive blending will continue to play a pivotal role in the development of newer materials. For example, the blending technique is being used to produce bulk heterojunction polymer solar cells (polymer/fullerene) and to develop electrically conductive polymer blends using electrically conductive fillers and additives (Huang and Kipouras 2012).

Table 1.77 Liquid-crystal polymer blends

Composition	Comments	References
1. LCP blends with commodity resins		
PP/LCP with PP-MW as a compatibilizer	LCP macromolecules stretched by simultaneous flow and crystallization in a static mixer	Baird and Datta 1992
PP/LCP	LCP macromolecules stretched in a counterrotating pipe die	Haghighat et al. 1992
PP/LCP	LCP macromolecules stretched under high injection molding stresses	Heino et al. 1993
LCP/PE	Viscosity reduction	Alder et al. 1993
LCP/cycloolefins (COP)	Processability	Epple et al. 1992
LCP and radiation cross-linkable resins	For articles that strain recover upon heating	Toy et al. 1994
2. LCP blends with engineering resins		
Poly(1,4-benzamide) or terephthalamide dispersed in PA	Rigid microfibrils enhanced modulus and improved the thermal behavior	Takayanagi et al. 1980
PET with 2 phr of poly[bis (4-methoxy phenyl)terephthalate]	Processability and excellent mechanical properties	Toray Industries, Inc. 1980
30 wt% PET with LCP	Processability, mechanical properties, HDT = 167 °C	Celanese Corp. 1981, 1984
PC with a wholly aromatic polyester, LCP	Mechanical, tensile and flexural, properties	Froix et al. 1981
PPE or PAEK with LCP, PI, PAES, or PEST	Processability, mechanical properties, and HDT	Harris and Michno 1988
PS/PPE/2–98 wt% of a LCP, stretched into submicroscopic fibers	Tensile strength, high modulus, satisfactory elongation, good impact strength, and high HDT	Isayev 1991, 1993, 1994
PBT with *p*-hydroxybenzoic acid-ethyleneterephthalate ($T_m \leq 300$ °C)	Co-reaction to increase η, thus orientability and mechanical performance	Dekkers et al. 1992
PC with PAr and LCP	Low anisotropy, high HDT, heat, and impact resistance	Izumi et al. 1992
LCP with PP, PS, PC, PI, etc.	Multiaxial molecular orientation of LCP	Haghighat et al. 1992
LCP with PC and PET or PBT	Ductility, toughness, strength, HDT modulus	Cottis et al. 1993
PBT with segmented block copolymer, LCP-b-PBT	For fibers having high modulus and strength	Farris and Jo 1993
PEI-LCP with PC, PBT, or PA	Processability and mechanical behavior	Bonfanti et al. 1993
LCP block copolymer of the type $[\text{rod}]_x$-$[\text{coil}]_y$ with PET, PBT, PA	For spinning fibers with high mechanical properties and low shrinkage	Dashevsky et al. 1993, 1994
LCP dispersed in either PEST, PC, PA, or modified PPE	Replacements for fiber-reinforced plastics – recyclable blends	Tomita et al. 1993, 1994

(*continued*)

Table 1.77 (continued)

Composition	Comments	References
LCP with PA, ABS, PC, PBT, PPE, PP, PC, or their blends	Compatibilized blends, used as replacement for glass fiber composites	Tomita et al. 1993, 1994
LCP with 3–15 wt% PAr	Matrices for conventional composites	Roemer and Schleicher 1993, 1994
LCP with PEST, PC, PAs, PI, etc.	Polymerization of LCP in polymeric matrix	Gupta et al. 1994
Poly(*p*-phenylene terephthalamide)/PA or PARA, and PEKK or PAN	Biphasic solution in sulfuric acid, spun, coagulated, stretched into PPD-T fibrils	Coburn and Yang 1994
Hydroxyalkylated PPE, hydroxyl-containing PO, PA, and LCP	Moldability, solvent and heat resistance, mechanical strength	Arashiro et al. 1994
Compatibilized blends of PET with 10–15 wt% LCP	Processing, nontransparent material with good mechanical properties	Bonis and Adur 1995
3. LCP blends with specialty resins		
PES with a small amount of LCP	Improved flowability and processability	Cogswell et al. 1981
PPS, LC-polyesters and LC-poly (esteramides)	Processability and physical properties	Froix et al. 1981
PEI with 35–95 wt% LCP, self-reinforced polymer compositions	LCP fibers, tensile strength, modulus, elongation, impact strength, HDT	Isayev and Swaminathan 1989
LCP with PI, PAES, or PEST and either PAEK, PAE, or PPE	Processability, good mechanical properties, and high HDT	Harris et al. 1988
$\geq$ 0.01 wt% LCP with PET, PA, PC, PE, PP, PVC, PVDC, PPS, PVDF, PVF, or PMMA	Oriented films with small protrusions that resulted in low friction	Wong, C. P. 1990, 1994
LCP with either a *phenoxy* or an esteramide-based LC	Processability, thermal stability, and mechanical properties	Koning et al. 1990
LTG/LCP	*Cortem*™ *Alloys*: matrix LCP and $\leq$ 80 wt% of dispersed LTG; E = 14 GPa	Bahn et al. 1991
Amino-terminated PEI with polyester-type LCP	High tensile strength	Bookbinder and Sybert 1992
LCP with 2–98 wt% PEK	Toughness, excellent elasticity, and impact strength	Falk and Hermann-Schoenherr 1992
PPS with polyesteramide-type LCP	Accelerated crystallization rate of PPS	Minkova et al. 1992
LCP from *p*-hydroxybenzoic and 2,6-hydroxynaphthoic acids, with a non-thermotropic polymer, silane	Good phase morphology, interfacial adhesion, good thermal and mechanical behavior	Haider et al. 1993
PEI with 5–95 wt% LCP and *p*-amino benzoic acid or pyromellitic anhydride	Compatibilized moldable blends, useful as matrix for composites	Roemer and Schleicher 1993

(*continued*)

Table 1.77 (continued)

Composition	Comments	References
PI with polyimide-type LCP, $T_m \geq 300$ °C	Processability, chemical resistance, flame retardancy and mechanical strength	Asanuma et al. 1993
PI with PEK and/or LCP and other additives; *Aurum*™ PI/LCP	Processability, HDT ≥ 230 °C, strength, thermal, and chemical resistance	Tsutsumi et al. 1994
LC-type polyimide with either PI, PEI, PAI, PES, or PEK	Remarkably good processability and excellent thermal stability	Okawa et al. 1994
Polyglutarimide with PBI, or LCP, and PET or PC	Good balance of toughness, tensile modulus, and HDT	Hallden-Abberton et al. 1994
PAI, with 3–30 wt% LCP	Lower viscosity, unaffected mechanical properties	Lai et al. 1994
PPS with a polymer of 6-hydroxy-2-naphthoic acid and 4-hydroxybenzoic acid, or terephthalic acid and 4-amino phenol	Processability and properties, used to mold parts for the electronic industry, particularly connectors	Yung and Linstid 1995
LCP blended with another LCP	Processability, HDT ≥ 200 °C, impact strength	Charbonneau et al. 1995

Table 1.78 Electro-dissipative and electroconductive blends

Composition	Comments	References
1. Electro-dissipative blends: ESD systems		
Aliphatic polysulfides (TM) with polybutadienes (PB)	To mold static charge-free rolls and guides for textile industry	Patric 1942
PO with 2 wt% PVAl	Mechanical, hygroscopic, antistatic properties	Minekawa et al. 1969
PC, with PET and ≥ 1 wt% of an elastomer containing acidic groups	High tensile strength, good impact resistance, and electrical conductivity	Mitsubishi Chemical Industries Co. Ltd. 1983
ABS and ≤ 20 wt% EO-CHR	Antistatic thermoplastic compositions	Federl and Kipouras 1986
EO-CHR with ABS, HIPS, MBS, SMA or PS/PPE, and an acrylic (co)polymer	Rapid dissipation of static charge, reduced delamination, and improved ductility	Gaggar et al. 1988; 1989
PVC, CPVC, PC, PEST, EP, PF, or styrenics with EO-CHR	Antistatic properties	Barnhouse and Yu 1988; Yu 1988
PC/PAI and a $C_{2\text{-}10}$ diamine	Processability, impact strength, appearance, mechanical, and antistatic properties	Shimamura and Suzuki 1991
PS with EO-CHR and PCL	static dissipative and tensile elongation	Giles and Vilasagar 1994

(*continued*)

Table 1.78 (continued)

Composition	Comments	References
2. Electroconductive blends: ECP systems		
PAc was polymerized into PE	PE with catalyst exposed to acetylene	Galvin and Wnek 1982
Polypyrrole electrochemically polymerized within a matrix resin	Electrically conducting material with improved mechanical properties over those of PPy	Lindsey and Street 1985
PVC with “doped” PANI and an additive	Intrinsically electrically conductive films or fibers	Kulkarni and Wessling 1992, 1993, 1994
Amine-terminated PANI melt-blended with SMA	Materials were suitable for the use as electric conductors	Jongeling 1993
Polyaniline tosylate (PANI) and PETG	For films, inks, fibers, and coatings, in shielding, antistatic, and adhesives	Shacklette et al. 1993
Poly-3-octyl thiophene with PP, PVC, PS, PE, EVAc, PVC/ABS, etc., and dopant, e.g., I_2	Blends were formed into desired shapes and used either as EMI or ESD materials	Kokkonen et al. 1994
PANI with dodecylbenzene sulfonic acid heat treated and then mixed with either PS, PE, PS, ABS, or PP	Soluble thermoplastic ECPBs could be modified by mixing with protonic acid and metallic salts	Karna et al. 1994
Fluorine-containing polycyanurates and a thermoplastic polymer, e.g., PSF, PPE, PEEK	Heat or electrically conducting materials, for electronic packaging, adhesives, in the fabrication of electronic parts	Ardakani et al. 1994
PANI or PPy with polymeric dopant – sulfonated: -PE, -SEBS, -PS, etc.	Electrically conductive polymeric systems with good mechanical properties	Cross and Lines 1995
Matrix polymer and an electrically conducting thermotropic liquid-crystal polymer, LCP	Matrix: PO, EPR, CPE, CSR, PS; dispersed: PANI, PAc, PPy, poly (3-undecylthiophene), poly (3-dodecylthiophene), or polyparaphenylene	Ho and Levon 1995
SBR matrix and PANI filler	Conductivity, swelling, thermal and mechanical properties found to depend on PANI concentration and ratio between PANI-DBSA and PSS	Martins et al. 2006

The material developed by these authors consists of two polyolefin copolymers with different melt flow rates and filled with electrically conductive fillers and other additives. Two of the resins used are propylene/ethylene copolymers with different flow rates and flow ratios ranging from 2:3 to 1:90. The conductive filler particles include copper, silver, iron, or carbon black. These conductive resins can be molded or extruded, and applications range from circuit boards to shielding to implants.

Clearly, blending is an important technique to obtain conducting materials based on intrinsically conductive polymers and conventional as well as rubbery plastics. In a recent study, Martins et al. (2006) prepared an electrically conductive thermoplastic elastomer by blending butadiene-styrene copolymer (SBR) and polyaniline (PANI) doped with dodecylbenzene sulfonic acid (DBSA) and poly (styrene sulfonic acid) (PSS). PSS also acted as a compatibilizer between PANI and SBR. PANI was doped by reactive processing with DBSA and PSS to produce the conductive complex PANI-DBSA-PSS. This complex was mixed with 90, 70, and 50% (w/w) SBR in an internal mixer with counterrotating blades. A similar strategy can be utilized to formulate thermally conducting plastics (Agarwal et al. 2008).

1.8 Biobased and Biodegradable Blends

In the recent past, there have been intense efforts aimed at developing alternatives to oil-based chemicals and polymers to reduce reliance on petroleum and natural gas (Stewart 2007). Biomass is the feedstock of the biobased economy, and, in practice, this means the use of corn and soybeans (for polyurethanes), although the hope is to eventually utilize agricultural and forest residues. Enzymes or microbial action are employed to convert biomass into useful chemicals and plastics. All the major plastic companies have initiated research programs in this area (Reisch 2002).

Only a few biobased polymers are commercially available (Mohanty et al. 2005). Polymers known as polyhydroxyalcanoates (PHA) are polyesters that are synthesized using bacteria, starting from either sucrose or starch. Varying the nutrient composition changes the chemical makeup of the polymer obtained (Hodzic 2005). This polymer has been commercialized by the Metabolix company under the trade name Mirel, and there are other similar products as well. Alternatively, one may obtain monomers from biomass and then carry out the polymerization using standard techniques. The most important polymer produced in this manner is polylactic acid (PLA) which is a linear polyester; here lactic acid is obtained from the fermentation of corn stover. In the past, the major application of PLA was in resorbable surgical sutures and in implantable drug-delivery devices. Although implantable medical devices are still being made from PLA and its blends (Wang et al. 2012), the material is increasingly being used in packaging where mechanical and thermal properties are not especially important. PLA production has increased significantly in the last 20 years since Cargill Inc. was able to produce high molecular weight PLA using ring-opening polymerization of lactide (Auras et al. 2010). The biodegradability property of PLA is due to the fact that the ester linkages are susceptible to hydrolysis, especially at high temperatures and in the presence of water; once the molecular weight is reduced, bacteria can degrade the material easily.

Biodegradable polymers are attractive since they are less likely to end up in landfills or contribute to the buildup of plastic trash that persists in the environment for a very long time. Biodegradability has also been explored in agriculture to prevent excessive moisture loss and weeds growth and to alleviate the recyclability problems – an agricultural film should last as long as it is needed and then disintegrate under the influence of either microorganisms and/or UV irradiation.

A biodegradable polymer is one that can decompose to small molecules, such as carbon dioxide, under the action of microorganisms is a specified amount of time (Mohanty et al. 2005). Most biopolymers are biodegradable, e.g., a large family of polysaccharides. They have been used in biodegradable blends with synthetic polymers. Some synthetic polymers, viz., PET, are susceptible to biodegradation when copolymerized with polylactones. Polymers with controlled, reversed miscibility, viz., polyglycoles, are also biodegradable. Polymers with carbon backbones, viz., PE or PP, may be susceptible to biodegradation after incorporation of ketone side groups, -C(R)(COR′)- (Guillet 1973). Biodegradable polybutylene succinate or adipate, *Bionolle*™, has been commercially introduced in 1996 by Showa Denko. Similarly, Novamont introduced fully biodegradable *Mater-Bi*™. The latter materials are blends of starch and other polymers, viz., poly-ε-caprolactone, ethylene-vinyl alcohol, etc.

1.8.1 PLA Blends

Lactic acid produced from the fermentation route is 99.5 % L-lactic acid and condensation polymerization leads to low molecular weight PLLA or poly (L-lactide) (Nampoothiri et al. 2010; Rasal et al. 2010). High molecular weight polymer can be produced by ring-opening polymerization, and one can also adjust the ratio of L- to D-lactic acid units (Auras et al. 2010). Even so, it is not considered to be an engineering polymer since it has poor thermal and hydrolytic stability. Although it has stiffness and strength comparable to commercial polymers like polystyrene and PET (Imre and Pukanszky 2013), it suffers from low values of ductility, HDT, and toughness. Some of these properties can be improved by blending PLA with plasticizers or with other plastics.

The elongation to break of PLA is less than 10 %, but it can be significantly enhanced by the incorporation of low molecular weight plasticizers which are also biocompatible; these include oligomeric lactic acid and low molecular weight polyethylene glycol (PEG) (Martin and Averous 2001). As is normal with the use of plasticizers, however, there is a concomitant reduction in both the elastic modulus and the glass transition temperature. A variation of this procedure has been reported by Rasal and Hirt (2010) who blended PLA with polyacrylic acid followed by physical blending with PEG in solution. Films made from the mixture showed a tenfold increase in toughness compared to neat PLA with little or no decrease in tensile strength and modulus. Note that with time, low molecular weight additives can migrate to the surface of a part due to reasons such as physical aging and this phenomenon may be accompanied by an increase in polymer crystallinity (Auras et al. 2010*;* Rasal et al. 2010); an increase in crystallinity is usually accompanied by a reduction in ductility.

A lowering in PLA modulus and T_g can be avoided if PLA is blended with other polymers. However, it is not miscible with many plastics, and the use of block copolymers or the use of reactive blending is generally necessary. Candidate polymers may be biodegradable or nonbiodegradable. In the former category are starch, PGA, and PHA (Yu et al. 2006), while in the latter category are polyolefins, vinyl and vinylidene polymers, and elastomers and rubber (Detyothin et al. 2010). PLA has been blended extensively with starch due to its plentiful supply, low cost, and biodegradable nature (Yu et al. 2010). However, it is hydrophilic, and it tends to swell in the presence of water. To promote compatibility of starch with the hydrophobic PLA, one may use coupling agents such as methylene diphenyl diisocyanate (MDI) or functionalize the polyester by grafting highly reactive groups such as maleic anhydride with the expectation that covalent bonds will be formed by reaction with the hydroxyl groups on starch (Rzayev 2011). It is found that mechanical properties of PLA such as modulus, yield strength, and impact strength can all be improved by blending with starch in the presence of MDI. The use of other additives, such as resorcinol di(phenyl phosphate), can endow the blends with flame retardancy (Pack et al. 2012). Several PLA blends have now been commercialized, and these find application mainly in packaging and agriculture. The recent review by Imre and Pukanszky (2013) may be consulted for details.

Approaches that can be employed to toughen PLA with the use of different blend constituents and how the toughening protocols modify mechanical properties have been described by Anderson et al. (2008). The most significant improvement in toughness of PLA has been reported by McCarthy et al. (1999) who made blends of PLA with polybutylene-succinate adipate (PBSA). PBSA is a biodegradable polymer, but it is not biobased. A 70/30 (weight%) PLA/PBSA blend exhibited about a 5-fold increase in tensile elongation to break and about a 25-fold increase in tensile toughness. More recently, Krishnaswamy (2013) and Krishnaswamy et al. (2013) have described blends of PLA and PHA which have about 31–58 % increase in tensile elongation and 21–35 % greater tensile toughness than PLA alone.

As mentioned earlier, a major application of PLA is in food packaging. Cheung et al. (2012) have described blends of PLA with styrenic polymers compatilbilized with styrene-based copolymers like SEBS, SMA, and SMMA that can be extruded and thermoformed to produce very low-density food service foam articles with good mechanical properties. Li et al. (2012) have described the development of a biodegradable gloss film that contains 60–99 % PLA and the rest PP. In general, biodegradable polymer blends are prepared by blending a thermoplastic resin with a biodegradable one. Specific examples are given in Table 1.79. Blending must produce dispersion that after disintegration of the biodegradable part, the thermoplastic powder will not contaminate the environment.

1.9 Blending and Recycling

Recycling is becoming increasingly important. Its methods depend on the polymer type and source. Within the resin manufacturers' plant recycling is the easiest. This is known as postindustrial recycling. In processing plants, where commingled polymeric scrap is generated, it is more difficult, but it is still possible by separating the different components (Jody et al. 1997). The most difficult is recycling of

Table 1.79 Biodegradable polymer blends

Composition	Comments	References
PVAl/vinylacetate grafted starch	Biodegradable, better properties than PVAl	Yoshitake et al. 1978
PHBA, with 10–40 wt% CPE	Biodegradability, impact properties and HDT	Holmes et al. 1982
PLA/PEO, EVAc, EVAl, EPDM, SBR, etc.	Biodegradable, flexible alloys	Kharas and Nemphos 1992
EVAl/poly(hydroxybutyrate-valerate)	Biodegradability and good impact properties	Webb et al. 1992
PS, PO, NR, SBR, PI, PB, or CA, a polysaccharide and bioagent	Cellulose with 1 wt% of bacteria, fungi, and/or enzymes	Guttag 1992, 1994
LDPE, starch, and a copolyacrylate	Biodegradable blends	Willett 1992
Maleated starch, PE or PP, and 1–35 wt% acrylic copolymer	Biodegradable films with good mechanical properties	Tomka 1992; Tomka et al. 1993
Amylose/PA/PEST/POM/gelatins	For manufacturing transparent packaging films	Meier 1993
Starch, latex of either polymer or elastomer, and 0–20 phr fillers	The mixture could be molded or extruded to form parts useful for food packaging	Munk 1993
Starch/poly [unsaturated fatty acids + diamines + diol-based glycols]	The blends were used to manufacture packaging films or moldings	Ritter et al. 1993
PO/PHB/A-B block copolymers of poly(meth)acrylic esters	For disposable napkins, ostomy bags, and ordinary wrapping	Ballard and Buckmann 1993
Plasticized polylactic or a lactic acid-hydroxycarboxylic acid copolymer	Flexible and hydrolyzable materials, useful for absorbing oils and body fluids	Morita et al. 1993
PLA/PC or PSF, PI, PPE, siloxanes, silicones, PMMA, etc.	Improved HDT of biodegradable polymers	Nemphos and Kharas 1993, 1994
Hydroxypropyl-starch or urea-starch, and either PA or PEST	For the manufacture of printable moldings or films	Buehler et al. 1993, 1994
PS, PE, PP, TPU, PEST, PA, etc., with 5–99 wt% of either carbohydrates, proteins, or lipids	Reactively blended biodegradable interpolymers, with good mechanical properties, and limited water absorption	Vaidya and Bhattacharya 1994
A polar polymer, polysaccharide, and fatty acid (hydroxy) peroxide	Good performance until exposed to suitable environment for degradation	Chapman and Downie 1994
Synthetic polymer, peracid, and starch	Superior mechanical properties, biodegradability	Hsu et al. 1994
LLDPE with starch and ≥ 1 ionic compound	For high-frequency sealable multilayer packaging films, biodegradation	Dehennau et al. 1994
Nonconsumable agricultural products with an adhesive	Biodegradable tableware from impact-molded, coated particles	Liebermann 1994
PEG with PA, PE-co-acrylic or methacrylic acid, EVAc, EVAl	Degradable and/or recyclable plastic articles with inverse solubility characteristic	Petcavich 1994

(*continued*)

Table 1.79 (continued)

Composition	Comments	References
TPU and/or *phenoxy*, EVAl, COPO, cellulose, and/or polyalkylene oxide	Attractive physical, optical, and barrier properties and were melt processable without PVAl degradation	La Fleur et al. 1994
Starch with biologically degradable aliphatic polyesters, hydrophobic protein, PVAl, or cellulose esters and a hygroscopic material	Absorbed water was released during either extrusion or injection molding at T = 200 °C, causing the mixture to foam to density $\rho = 160\ kg/m^3$	Tomka 1998

postconsumer polymers which show up in municipal solid waste (MSW) and ultimately end up in landfills. Indeed, the magnitude of the problem has been increasing at a rapid rate. The plastic component of MSW in the USA has risen from 390,000 t in 1960 to 30.7 million tons in 2007 (Merrington 2011). Three basic methods of recycling have been used: (i) direct, where cleaned resins are incorporated into virgin material, (ii) reprocessing the commingled plastics either by blending or transforming into plastic wood or plastic concrete, and (iii) feedstock type that may involve depolymerization or pyrolysis. To the following text, only the method (ii) is important. It can be subdivided into (1) compatibilization and upgrading of resins in direct recycling, (2) compatibilization and upgrading of commingled plastics for reprocessing, and (3) recycling of polymer blends (Akovali et al. 1998).

The essential difficulty in recycling commingled plastic is the fact that mixed plastics have poor mechanical, thermal, and flow properties even when the individual components have very desirable ones. In particular, plastic mixtures have low ductility and poor impact strength (Liang and Gupta 2001). This limits their use to less demanding applications such as flower pots, park benches, and plastic lumber. To reuse postconsumer plastics in high-value applications, it is necessary to first separate plastic waste by chemical type. A variety of techniques, such as float-sink tanks and hydrocyclones, can be used to separate mixed plastics based on differences in density. For plastics with overlapping density, other methods, such as froth flotation, can be employed (Merrington 2011). A relevant question then is the purity level that must be attained in such a separation process. The higher the purity, the better is the performance, but the higher also is the cost of the separation process.

One way to address the issue of residual contaminants present in polymer recovered from postconsumer waste is to use regrind in an inner layer in a multilayer article. Shelby et al. (2012) have described several such transparent polymer compositions made from a variety of polymer pairs that exhibit excellent barrier properties while retaining processability and good mechanical property. Another approach is to blend the separated plastic with virgin plastic. This procedure also allows one to standardize the flow properties if the virgin polymer is available in different molecular weights (Liang and Gupta 2002). Even so, it is necessary to compatibilize the recycled material since it remains a multicomponent blend.

To do this, one may (i) add at least one ingredient with highly reactive groups that can interact with several polymeric components, e.g., ethylene-acrylate-maleic anhydride, glycidyl methacrylate-ethylene-vinylacetate, and ethylene-glycidyl methacrylate-methylmethacrylate (the copolymer may compatibilize and toughen); (ii) add a low molecular weight additive that at different stages of the reactive blending binds to different components, viz., ethylene-glycidyl methacrylate, triglycidylisocyanurate, etc.; and (iii) add a cosolvent, for example, *phenoxy*. A significant penetration of properly designed copolymer into the homopolymer phases has been reported (Brown 1989).

The morphology can be stabilized by (i) thick interphase, (ii) partial cross-linking, or (iii) addition of an immiscible polymer with a suitable spreading coefficient (Yeung et al. 1994). The adhesion between the phases in the solid state is improved by (i) addition of a copolymer that covalently bonds the phases, (ii) reduction of size of the crystalline domains, (iii) adequate adhesion, e.g., by the use of polyetherimine, PEIm (Bjoerkengren and Joensson 1980), and (iv) dispersing at high stresses, either in the melt (Patfoort 1976) or in solid state (Shaw 1993; Khait 1994, 1995).

Chemical re-stabilization of recycled material against the thermal- and light-induced degradation is essential. Addition of 0.1–0.5 wt% of a sterically hindered phenol and a phosphite at a ratio varying from 10:1 to 1:10 is recommended (Pauquet et al. 1994). For outdoor applications, hindered amine light stabilizers with UV absorbers of the benzotriazole type are to be used (Herbst et al. 1995, 1998). Examples of blends used for polymer recycling are listed in Table 1.80. For more details, see ▶ Chap. 20, “Recycling Polymer Blends” in this book.

1.10 Conclusions and Outlook

Blends like composites are integral parts of the plastic industry. Their sales are estimated at more than US$ 100 billion per annum. The blends provide widening selection of performance characteristics, tunable for specific applications at a reasonable cost. In effect, this technology is a shortcut to development of complex polymeric species.

Considering the range of possibilities and constraints, polymer blends provide a fertile field of polymer research. Polymer blending not only requires understanding of intrinsic properties of polymers but also a broad knowledge of numerous disciplines such as thermodynamic principles of miscibility and compatibilization, surface and interfacial properties, morphology, rheology, processing, and performance during the service life of the material. Decades of research have enriched our understanding about the science and technology of polymer blends. As a result, polymer blends and blending techniques are finding applications in multidisciplinary fields.

Performance during its service life is crucial to the widespread application of any material. It has been estimated, for example, that at least 15–25 % of all failures of plastic materials in commercial use are related to the problem of environmental

Table 1.80 Polymer blends for recycling

Composition	Comments	References
PS with 1–10 wt% PE and CSR	Improved impact, elongation, and strength (CPE or CSR is a compatibilizer for scrap)	Herbing and Salyer 1963
LLDPE/PS shear-compatibilized	Blends with good mechanical properties	Patfoort 1976
PS or HIPS, with PP and SEBS	SEBS is expensive but useful in recycling	Holden and Gouw 1979
PS with PO, S-b-B stabilizers	Recycling requires higher concentration of stabilizers than virgin resins	Sadrmohaghegh et al. 1985
sPS and sPS copolymer with MA or GMA and an elastomer reactive with it	Recyclable, impact resistant, good elongation, and retention of physical properties	Okada 1994
PO with 30–40 wt% PS recycled without compatibilization	High properties due to stable co-continuous morphology	Morrow et al. 1994
PA with PA/LDPE, EGMA	Recyclable blends, good performance	Timmermann et al. 1994
$\geq$ 2 PO, PS, polydienes – either virgin, recycled, or both	Blending at T in between the melting points of the components	Lai and Edmondson 1995
Rubber scrap with rosin and fatty acids, esters and unsaponifiables, and PE, PET, TPU, PU, PVC, etc.	Cryogenically comminuting rubber, drying it, blending with plasticizer/binding agent, heating, and blending with polymers	Segrest 1995
Automotive scrap plastic parts comprising PC, PEST, ABS, PA, etc., with 5–15 wt% MBS	Compounding in a TSE, devolatilization, filtering of paint flakes; closed-loop control system for properties	Lieberman 1995
Branched PET with recycled PET and a chain extender or a cross-linking agent	Foaming and extruding the mixture	Muschiatti and Smillie 1995
Recycling of manufactured polymer blends	Recent concepts in polymer blends recycling	Jose et al. 2011

stress cracking (ESCR) (Arnold 1996). The development of polymer blends technology has provided a strategic route to avoid ESCR of amorphous engineering polymers and allowed these engineering blends (Xenoy®, Noryl®, Gemax®, Triax, Elemid, Macroblend) to be used in various aggressive environments. For automotive applications, blends have been formulated with high T_g polymers (PC, PPO) with crystalline polymers (PBT, PA 66) (Robeson 2007). As applications of amorphous polymers expand in adverse environments, newer commercial blends will be developed, and the reader is referred to the recent review by Robeson (2013). This effort is likely to be aided by computational methods that have been developed in the science and technology of polymer blends. Molecular dynamics provide means of computation of the specific interactions and miscibility (Coleman et al. 1991) or the interfacial energy in a polymer blend (Yao and Kamei 1995).

Indeed, commercial computer programs are available for designing blends with specific sets of properties.

The phase behavior and morphology of phase-separated polymer blends play a vital role in the design of membrane transport properties (Robeson 2010). Numerous applications of polymeric membranes involving gas and liquids are known. Although different transport models have been utilized successfully to relate morphology with transport properties, there is enough room for improvements as membrane applications continue to grow in such areas as gas separation.

Formulation of biodegradable polymer blends is already on the rise, and these blends are being used successfully in applications ranging from agriculture to consumer goods, to packaging, and to automotives. Blends of biodegradable polymers, however, behave differently than those of commodity polymers. Miscibility-structure-property relationship of these blends will continue to emerge. Progress has been made in developing self-extinguishing biodegradable polymer blends (PLA/ECOFLEX). As the use of biodegradable polymer blends increases, demand for flame-retardant formulations will rise as well.

Another rapidly evolving field is biomedical engineering and particularly tissue engineering that seeks to regenerate or repair damaged or diseased tissues and organs. Scaffolds are being fabricated by combining the solid-state foaming and immiscible polymer blending methods. Biodegradable dipeptide-based polyphosphazene-PLAGA blends have been reported to be a promising material for mechanically competent scaffolds for bone tissue engineering (Deng et al. 2010). Undoubtedly, biodegradable and biocompatible polymer blends will play an increasing role in the fabrication of tissue engineering scaffolds in the future.

One usually wishes to know what would be the final properties of a polymer blend once it has been conceptually designed but before it is actually made. That is what molecular modeling does. However, there is always a compromise between simulation complexity, accuracy, and speed of prediction. Studies are being carried out which could open up the possibility of computer-aided design of polymer blends with desired physical and mechanical properties.

Although great strides have been made in the past, opportunities still exist to improve and solve numerous polymer blend problems. Research and technical innovation will continue to impact polymer blend development and production. We are confident that polymer blends will continue to contribute to the development of our modern society.

1.11 Cross-References

- ▶ Applications of Polymer Blends
- ▶ Commercial Polymer Blends
- ▶ Compounding Polymer Blends
- ▶ Interphase and Compatibilization by Addition of a Compatibilizer

▶ Miscible Polymer Blends
▶ Morphology of Polymer Blends
▶ Polyethylenes and their Blends
▶ Properties and Performance of Polymer Blends
▶ Reactive Compatibilization
▶ Recycling Polymer Blends
▶ Rheology of Polymer Alloys and Blends
▶ Thermodynamics of Polymer Blends

Abbreviations

aPP Amorphous polypropylene
AA Acrylic acid
AAS Copolymer from acrylonitrile, styrene and acrylates; ASA
ABS Acrylonitrile-butadiene-styrene
ABSM Acrylonitrile-butadiene-styrene-methylmethacrylate
ACM Copolymer of acrylic acid ester and 2-chloroethyl vinyl ether
AES Quarterpolymer from acrylonitrile, ethylene, propylene, and styrene
AF Aniline-formaldehyde
AN Acrylonitrile
ANM Acrylate rubber, based on ethyl acrylate with acrylonitrile
ASA Copolymer from acrylonitrile, styrene and acrylates
BMMM Butyl methacrylate-methylmethacrylate copolymer
bPC Branched polycarbonate
BR Butadiene rubber; polybutadiene
CA Cellulose acetate
CAS Chemical Abstracts Service
CB Carbon black
CBR Cis-polybutadiene rubber
CF Carbon fiber
CHR Epichlorohydrin
CMC Critical micelle concentration
COP Cycloolefin
COPO Copolymer of carbon monoxide with polyolefins (ethylene or propylene)
COPO-VAc Carbon monoxide-ethylene-vinylacetate copolymer
CPA Copolyamide
CPB Chlorinated polybutadiene
CPE Chlorinated polyethylene
CPVC Chlorinated polyvinylchloride
CR Elastomeric polychloroprene
CRU Constitutional repeating unit
CSM Chlorosulfonated polyethylene rubber
CSR Core-shell rubber

CTM Cavity transfer mixer
CUT Continuous use temperature
DBSA Dodecylbenzene sulfonic acid
DOP Dioctyl phthalate
EAA Ethylene-acrylic acid copolymer
EBA Ethylene butyl acrylate
ECP Electroconductive polymer
EEA Ethylene-ethylacrylate copolymer
EFK Aromatic polyester
EFM Extensional flow mixer
EGMA Poly(ethylene-glycidyl methacrylate)
EHEMA Ethylene-hydroxyethyl methacrylate
EMAA Ethylene-methacrylic acid copolymer
EMAC Ethylene-methacrylate copolymer
EMMA Ethylene-methylmethacrylate copolymer
EO Ethylene oxide
EoS Equation of state
EP Epoxy resin. Also engineering polymer
EPDM Ethylene-propylene-diene elastomer
EPDM-MA Maleated ethylene-propylene-diene elastomer
EPR Ethylene propylene rubber
ESCR Environmental stress-cracking resistance
ESD Electrostatic charge dissipation
ESI Ethylene-co-styrene interpolymer
ETFE Ethylene-tetrafluoroethylene
EVAc Ethylene-vinylacetate
EVAc-CO Ethylene-vinyl acetate-carbon monoxide copolymer
EVAl Ethylene vinyl alcohol
FEP Fluorinated ethylene-propylene
GF Glass fiber
GMA Glycidyl methacrylate
GP Gutta-percha
HDPE High-density polyethylene
HDT Heat deflection temperature, heat distortion temperature
HEMA Hydroxyethyl methacrylate
HIPS High impact polystyrene
IIR Isobutene-isoprene rubber (butyl rubber)
IPN Interpenetrating polymer network
iPS Isotactic polystyrene
IR Synthetic *cis*-1,4-polyisoprene
IUPAC International Union of Pure and Applied Chemistry
JSW Japan steel works
LCP Liquid-crystal polymer
LCST Lower critical solubility temperature

LDPE Low-density polyethylene
LLDPE Linear low-density polyethylene
LTG Low-temperature glass
MA Maleic anhydride
MABS Methylmethacrylate-acrylonitrile-butadiene-styrene
MBA Copolymer from methylmethacrylate, butadiene and acrylonitrile
MBS Copolymer from methylmethacrylate, butadiene and styrene
MC Molecular composite
MDI Methylene diphenyl diisocyanate
MDL MDL Information Systems, Inc.
MDPE Medium density polyethylene
MD/TD Machine direction/transverse direction
MeABS Graft copolymer of ABS and methylmethacrylate
MeSAN Graft copolymer of SAN and methylmethacrylate
MF Melamine formaldehyde
MI Melt index
MFR Melt flow rate
mLDPE Metallocene-catalyzed low-density polyethylene
mLLDPE Metallocene-catalyzed linear low-density polyethylene
MMA Methylmethacrylate
MMBA Poly(methylmethacrylate-co-butyl acrylate)
MMMA Methylmethacrylate-methylacrylate copolymer
MMVAc-AA Copolymer of methylmethacrylate, vinylacetate and acrylic acid
MPS Poly(α-methyl styrene)
MSW Municipal solid waste
MW Molecular weight
MWD Molecular weight distribution
NBR Elastomeric copolymer from butadiene and acrylonitrile; nitrile rubber
NC Nitrocellulose
NDB Negatively deviating blend
NPDB Negative and positive deviating blend
NR Natural rubber
P4MP Poly(4-methyl-1-pentene)
PA Polyamides, nylon
PAc Polyacetylene
PACE Polyacetylene
PAE Polyarylether
PAEB Poly(*p*-aminoethyl benzoate)
PAEK Polyaryletherketone
PAES Polyarylethersulfone
PAI Polyamide-imide
PAN Polyacrylonitrile
PANI Polyaniline
PAr Polyarylate

PARA Polyarylamide; aromatic amorphous polyamide
PArSi Poly(aryloxysiloxane)
PB Polymer blend; polybutadiene
PB-1 Poly-1-butene
PBA Polybutylacrylate
PBG Polybutyleneglycol
PBI Polybenzimidazole
PBMA Poly(butyl methacrylate)
PBSA Polybutylene-succinate adipate
PBT Polybutylene terephthalate
PC Polycarbonate
PCHA Polycyclohexyl acrylate
PCHE Polycyclohexylethylene
PCHMA Polycyclohexyl methacrylate
PCL Polycaprolactone
PCO Polycycloolefin
PCS Poly-2-chlorostyrene
PCTF Polychlorotrifluoroethylene
PCTFE Polychlorotrifluoroethylene
PCTG Copolymer of cyclohexanedimethanol, terephthalic acid and ethylene glycol
PDB Positively deviating blend
PDMDPhS Poly(dimethyl-diphenyl siloxane)
PDMS Polydimethylsiloxane, polysiloxane
PDPS Polydiphenylsiloxane
PE Polyethylene
PEA Polyethylacrylate; polyesteramide; polyether-amide
PEBA Polyether-block-amide
PEC Polyestercarbonate
PEEI Copolyesteretherimide
PEEK Polyether ether ketone; polyaryletherketone
PEG Polyethylene glycol
PEI Polyetherimide
PEIm Polyetherimine
PEK Polyetherketone
PEKK Polyetherketone
PEMA Polyethylmethylacrylate
PEN Poly(ethylene-2,6-naphthalene dicarboxylate)
PEO Polyethylene oxide
PEOX Poly(2-ethyl-2-oxazoline)
PES Polyethersulfone
PEST Thermoplastic polyester
PET Polyethylene terephthalate
PETG Polyethyleneterephthalateglycol

PF Phenol-formaldehyde
PGA Polyglycolic acid
PGI Polyglutarimide
PHA Polyhydroxyalcanoate
PHB Poly-3-hydroxybutyrate
PHBA Poly(β-hydroxybutyric acid)
PHT Polyhexamethyleneterephthalate
PHZ Polyphosphazene
PI Polyimide
PIB Polyisobutylene
PISO Polyimide-sulfone
PLA Polylactic acid
PMA Polymethacrylate
PMB Poly*p*-methylenebenzoate
PMI Polymethacrylimide
PMMA Poly(methylmethacrylate), acrylic
PMP Poly-4-methyl-1-pentene
PMPhS Polymethylphenylsiloxane
PMS Polymethylstyrene
PNDB Positive and negative deviating blend
PO Polyolefin
POBA Polyoxybenzoyl acid, rigid-rod polymer
POCA Polyoxycyanoarylene
POD Polyoctadecene
POM Polyoxymethylene
POT Poly-3-octyl thiophene
PP Polypropylene
PPA Polyphthalamide
PPBA Polyparabanic acid
PPCO Polypropylene carbonate
PPE Polyphenylene ether
PPG Propylene glycol
PPhA Polyphthalamide
PPMA Poly-*n*-propyl methacrylate
PpMS Poly-*p*-methylstyrene
PPP Polyparaphenylene
PPS Polyphenylenesulfide
PPSS Polyphenylenesulfidesulfone
PPT Polypropylene terephthalate
PPTA Poly(*p*-phenylene terephthalamide)
PPy Polypyrrole
PS Polystyrene, styrenic
PSF Polysulfide; polysulfone
PSIB Polyisobutylene-block-polystyrene

PSOX Polystyrene grafted with 2-oxazoline
PSS Poly(styrene sulfonic acid)
PSU Polyarylsulfone
PTES Polythioethersulfone
PTFE Polytetrafluoroethylene
PTO Polytransoctanamer
PVA Polyvinylacetate
PVAl Polyvinyl alcohol
PVB Polyvinyl bromide
PVC Polyvinyl chloride, vinyl
PVCAc Poly(vinylchloride-co-vinylacetate)
PVDC Polyvinylidenechloride
PVDC-MeA Vinylidenechloride-methylacrylate copolymer
PVDF Polyvinylidene fluoride
PVF Polyvinyl fluoride
PVFO Polyvinyl formal
PVME Poly vinyl methyl ether
PVP Polyvinylpyrrolidone
PVPh Polyvinylphenol
SAA Poly(styrene-acrylic acid)
SAN Styrene-acrylonitrile copolymer
SAN-MAc Copolymer of SAN and methacrylic acid
SB Styrene-butadiene block copolymer
SBR Styrene-butadiene rubber
SBS Styrene-butadiene-styrene block copolymer
SEB Styrene-ethylene/butylene
SEBS Styrene-ethylene-butylene-styrene block copolymer
SEP Styrene-ethylene-propylene block copolymer
SH Strain hardening
SI Styrene-isoprene block copolymer
SIS Styrene-isoprene-styrene block copolymer
SMA Poly(styrene-co-maleic anhydride)
SMI Copolymer from styrene and maleimide
SMM Styrene-methylmethacrylate copolymer
SMMA Styrene methylmethacrylate
sPhPS Syndiotactic poly(*p*-phenyl styrene)
sPP Syndiotactic polypropylene
sPS Syndiotactic polystyrene
SSE Single-screw extruder
TM Thio-rubber
TMPC Polycarbonate of tetramethyl bisphenol-A
TPE Thermoplastic elastomer
TPU Thermoplastic polyurethane
TPV Thermoplastic vulcanizate

TS Thermoset polyester
TSE Twin-screw extruder
UF Urea-formaldehyde
UHMWPE Ultra-high molecular weight polyethylene
UHMW-PMMA Ultra-high molecular weight poly(methylmethacrylate)
UHMW-PS Ultra-high molecular weight polystyrene
ULDPE Ultra low-density polyethylene
VCM Vinyl chloride monomer
VPh Vinylphenol
VLDPE Very low-density polyethylene
XLPE Cross-linked polyethylene

References

H. Abe, T. Fujii, M. Yamamoto, S. Date, U.S. Patent 5,278,233, 11 Jan 1994, to Sumitomo Chem
K. Abe, H. Sakano, A. Inoue, S. Tajima, Jap. Pat. 093,465, 05 Aug 1977, to Sumitomo Naugatuck
V. Abolins, D.L. Reinhardt, U.S. Patent 3,983,090, 28 Sept 1976; Can. Pat. 994,040, 27 July 1976, to General Electric Co.
V. Abolins, J.E. Betts, F.F. Holub, Europ. Pat. Appl. 129,825, 02 Jan 1985, to General Electric Co.
I.A. Abu-Isa, P.M. Graham, U.S. Patent 5,194,468, 16 Mar 1993, to General Motors Corp.
S. Agarwal, M.M.K. Khan, R.K. Gupta, Polym. Eng. Sci. **48**, 2474 (2008)
O.C. Ainsworth, U.S. Patent 4,978,703, 18 Dec 1990, to The Dow Chemical
O.C. Ainsworth, U.S. Patent 5,286,795, 15 Feb 1994, to The Dow Chemical
A. Ajji, L.A. Utracki, Polym. Eng. Sci. **36**, 1574 (1996)
M. Akega, Jap. Pat. 03 92,324, 17 Apr 1991, to Teijin Chem.
M.K. Akkapeddi, B. Van Buskirk, A.C. Brown, PCT Int. Appl. W088/08433, 03 Nov 1988, to AlliedSignal
M.K. Akkapeddi, B. Van Buskirk, T.J. Kraft, U.S. Patent 4,902,749, 20 Feb 1990, to AlliedSignal
M.K. Akkapeddi, B. Van Buskirk, A.C. Brown, U.S. Patent 5,162,440, 10 Nov 1992a, to AlliedSignal
M.K. Akkapeddi, B. Van Buskirk, T.J. Kraft, U.S. Patent 5,115,018, 19 May 1992b, to AlliedSignal
M.K. Akkapeddi, B. Van Buskirk, T.J. Kraft, U.S. Patent 5,210,134, 11 May 1993, to AlliedSignal
G. Akovali, C.A. Bernardo, J. Leidner, L.A. Utracki, M. Xanthos (eds.), *Frontiers in the Science and Technology of Polymer Recycling*. NATO ASI Series E, vol. 351 (Kluver, Dordrecht, 1998)
H.A.K. Al Ghatta, PCT Int. Appl. WO 94 09,069, 28 Apr 1994, to M. & G. Ricerche
P.T. Alder, J.G. Dolden, D.G. Othen, PCT Int. Appl. 008,231, 29 Apr 1993, to British Petroleum
T. Alfrey, J.J. Bohrer, H.F. Mark, *Copolymerization* (Interscience, New York, 1952)
A.H. Ali, J.T.T. Hsieh, K.J. Kauffman, Y.V. Kissin, S.C. Ong, G.N. Prasad, A.L. Pruden, S.D. Schregenberger, U.S. Patent 5,284,613, 08 Feb 1994, to Mobil Oil Corp.
R.B. Allen, R.W. Avakian, U.S. Patent 4,683,247, 28 July 1987, to General Electric Co.
R.B. Allen, B.M. Bacskai, D.L. Roberts, R.C. Bopp, U.S. Patent 4,857,390, 15 Aug 1989, to General Electric Co.
Allied Chemical Corp., Neth. Pat. Appl. 6,410,654, 12 Mar 1965
Allied Chemical Corp., Neth. Pat. Appl. 6,410,561; 6,515,314, 31 May 1966
J. Alper, G.L. Nelson, *Polymeric Materials: Chemistry for the Future* (ACS, Washington, DC, 1989)
F.D. Alsewailem, R.K. Gupta, J. Disp. Sci. Technol. **23**, 135 (2002)
R.T. Alvarez, U.S. Patent 4,017,555, 12 Apr 1977

S.H. Anastasiadis, Adv. Polym. Sci. **238**, 179 (2011)

K.S. Anderson, K.M. Schreck, M.A. Hillmyer, Polym. Rev. **48**, 85 (2008)

T. Andres, H. Alvarez, O. R. Hughes, W. Cooper, C. Wang, U.S. Patent 5,391,605, 21 Feb 1995, to Hoechst Celanese Corp.

S.R. Angeli, L.M. Maresca, Europ. Pat. Appl. 370,243, 30 May 1990, to General Electric Co.

S.R. Angeli, Can. Pat. 2,059,914, 28 Aug 1992, to General Electric Co.

A. Aoki, T. Shiraki, T. Ibaragi, U.S. Patent 4,304,881, 08.12.1981, to Asahi Kasei Kogyo

T. Aoyama, K. Hara, Y. Okimura, A. K. Shu, H. Kobayashi, M. Izumi, Europ. Pat. Appl. 575,809, 29 Dec 1993; Jap. Pat. 53 39,433; Jap. Pat. 53 39,434, 21 Dec 1993, to Kanegafuchi Kagaku Kogyo

T. Aoyama, K. Hara, Y. Okimura, A. K. Shu, H. Kobayashi, M. Izumi, Jap. Pat. 60 73,192, 15 Mar 1994, to Kanegafuchi Kagaku Kogyo

Y. Arashiro, M. Kihara, H. Ohmura, F. Yamada, U.S. Patent 5,360,866, 01 Nov 1994, to Mitsubishi Petrochemical

A.A. Ardakani, J.T. Gotro, J.C. Hedrick, K. Papathomas, N.M. Patel, J.M. Shaw, A. Viehbeck, Europ. Pat. Appl. 581,314, 02 Feb 1994; Jap. Pat. 61 07,958, 19 Apr 1994, to IBM Corp.

C.B. Arends (ed.), *Polymer Toughening* (Marcel Dekker, New York, 1996)

P. Arjunan, U.S. Patent 5,281,651, 25 Jan 1994

P. Arjunan, U.S. Patent 5,391,625, 21 Feb 1995; U.S. Patent 5,397,833, 14 Mar 1995, to Exxon

B.C. Arkles, Ger. Offen. 3,314,355, 27 Oct 1983, to Petrarch Systems

B.C. Arkles, U.S. Patent 4,500,688, Feb 19, 1985, to Petrarch Systems

R. Armat, A. Moet, Polymer **34**, 977 (1993)

J.C. Arnold, Trends Polym. Sci. **4**, 403 (1996)

J.-L. Arraou, Caoutch. Plast., Juin-Juil., 1986, p. 79

H. Asahara, Y. Asai, K. Yasue, Jap. Pat. 100,552, 23 Aug 1977a, to Unitika, Ltd.

H. Asahara, Y. Asai, K. Yasue, Y. Okabayashi, Jap. Pat. 100,553, 23 Aug 1977b, to Unitika, Ltd.

Asahi Chemical Industry Co., Brit. Pat. 1,154,447, 11 June 1969; Fr. Pat. 1,570,281, 06 June 1969

Asahi Chemical Industry Co., Jap. Pat. 118,456, 17 Sept 1981

Asahi Chemical Industry Co., Jap. Pat. 021,442; 021,443; 021,449, 04 Feb 1982; Jap. Pat. 030,747; 030,748, 19 Feb 1982; Jap. Pat. 085,847, 28 May 1982

Asahi Chemical Industry Co., Jap. Pat. 007,443, 17 Jan 1983

Asahi Chemical Industry Co., Jap. Pat. 020,354, 02 Feb 1984; U.S. Patent, 4,438,236, 31 Jan 1984

Asahi Chemical Industry Co., Jap. Pat. 044,540, 09 Mar 1985; Jap. Pat. 047,063, 14 Mar 1985; Jap. Pat. 060,158, 06 Apr 1985; Jap. Pat. 071,661, 23 Apr 1985

Asahi Chemical Industry Co., Europ. Pat. Appl. 219,973, 29 Apr 1987

Asahi Fiber Glass Co., Jap Pat. 030,451, 27 Mar 1981

Asahi-Dow Limited, Jap. Pat. 112,957, 05 Sept 1981

K. Asai, T. Kobayashi, M. Maeda, Europ. Pat. Appl. 444,589, 04 Sept 1991, to Sumitomo Chemical Co.

T. Asanuma, T. Sasaki, S. Nakanishi, T. Inoue, Europ. Pat. Appl. 499,216, 19 Aug 1992, to Mitsui Toatsu

T. Asanuma, N. Koga, H. Oikawa, Y. Okawa, A. Yamaguchi, Europ. Pat. Appl. 564,299, 06 Oct 1993, to Mitsui Toatsu

R. Auras, L.-T. Lim, S.E.M. Selke, H. Tsuji (eds.), *Poly (Lactic Acid)* (Wiley, Hoboken, 2010)

R.W. Avakian, R.E. Jodice, U.S. Patent 4,587,272, 06 May 1986, to General Electric Co.

R.W. Avakian, C.M.E. Bailly, W.J.L. Hamersma, W.J.L.A. Hamersma, Europ. Pat. Appl. 274,140, 13 July 1988, to General Electric Co.

T. Aya, Y. Kubo, T. Sasagawa, Jap. Pat. 097,655, 01 Aug 1979, to Toray Industries

D.F. Aycock, S.P. Ting, U.S. Patent 4,600,741, 15 July 1986, to General Electric Co.

D.F. Aycock, S.P. Ting, U.S. Patent 4,642,358, 1987 to General Electric Co.

D.F. Aycock, S.P. Ting, U.S. Patent 5,331,060, 19 July 1994, to General Electric Co.

R. Babrowicz, B.C. Childress, K.R. Ahlgren, G.P. Shah, Europ. Pat. Appl. 597,502, 18 May 1994, to W. R. Grace & Co.

E. Badum, U.S. Patent 2,297,194, 29 Sept 1942, to Bergisch-Gladbach

M. Baer, E.H. Hankey, U.S. Patent 3,085,082, 09 Apr 1963, to Monsanto Chem.

M. Baer, E.H. Hankey, U.S. Patent 3,312,756, 04 Apr 1967; U.S. Patent 3,316,327, 25 Apr 1967, to Monsanto Chem.

S. Bagrodia, D.R. Fagerburg, J.J. Watkins, P.B. Lawrence, PCT Int. Appl. WO 01,240, 21 Jan 1993; PCT Int. Appl. WO 05,115 A1, 18 Mar 1993, to Eastman Kodak

S. Bagrodia, D.R. Fagerburg, P.B. Lawrence, J.J. Watkins, U.S. Patent 5,276,111, 04 Jan 1994a, to Eastman Kodak

S. Bagrodia, D.R. Fagerburg, J.J. Watkins, P.B. Lawrence, PCT Int. Appl. WO 94 09,071, 28 Apr 1994b, to Eastman Kodak

S.K. Bahl, P.J. Canterino, R. Shaw, Brit Pat. 2,152,515, 07 Aug 1985, to Mobil Oil

W.A. Bahn, G.H. Beall, J. Ference, C.J. Monahan, C.J. Quinn, P.S. Roussel, U.S. Patent 5,043,369, 27 Aug 1991, to Corning Inc.

F.W. Bailey, U.S. Patent 4,021,596, 03 May 1977, to Phillips Petroleum

C. Bailleux, M. Bernard, B. Dupont, G. Lozach, J.P. Mata, Fr. Pat. 2,535,332, 04 May 1984, to Electricité de France

D.G. Baird, A. Datta, PCT Int. Appl. 218,568, 29 Oct 1992, to Virginia Polytechnic Inst.

D.G.H. Ballard, A.J.P. Buckmann, PCT Int. Appl. 93 17,064, 02 Sept 1993, to Zeneca Ltd.

F. Ballauf, O. Bayer, L. Leichmann, Ger. Pat. 863,711, 27 Aug 1941, to Bayer

P.M. Bapat, J.E. Harris, Y.T. Chen, Europ. Pat. Appl. 477,757, 01 Apr 1992, to Amoco Corp.

J.P. Barnhouse, S.H. Yu, U.S. Patent 4,719,263, 12 Jan 1988, to B. F. Goodrich

J. Barraud, B. Boutevin, S. Gervat, Y. Parasie, J. Parisi, Europ. Pat. Appl. 565,424, 13 Oct 1993, to Alcatel Alsthom

C.A. Bartelo, M.Mori, *Adv. Additives & Modifiers for Polymer & Blends*, 3rd International Conference, Clearwater Beach, 23–25 Feb 1994

B.P. Barth, U.S. Patent 3,510,415, 05 May 1970, to Union Carbide Corp.

H.-J. Barth, H. Reinecke, G. Hottenbach, E. Kurtz, U.S. Patent 3,944,508, 16 Mar 1976, to Wacker Chem.

K.W. Bartz, L.P. Land, A.K. Mehta, A.A. Montagna, PCT Int. Appl. WO 06,169 A1, 01 Apr 1993a, to Exxon

K.W. Bartz, J.C. Floyd, P. Meka, F.C. Stehling, PCT Int. Appl. WO 006,168, 01 Apr 1993b, to Exxon

A.J. Batschinski, Z. Physik. Chem. **84**, 643 (1913)

L.A. Beer, Belg. Pat. 633,818, 19 Dec 1963, to Monsanto

E. Bencini, D. Ghidoni, Europ. Pat. 560,447, 15 Sept 1993, to Enichem Polimeri SARL

E.A. Benham, M.P. McDaniel, U.S. Patent 5,344,884, 06 Sept 1994, to Phillips

E.A. Benham, F.W. Bailey, J.D. Wehmeyer, M.P. McDaniel, U.S. Patent 5,378,764, 03 Jan 1995, to Phillips

H.R. Bhattacharjee, Y.P. Khanna, R. Kumar, J.J. Belles, PCT Int. Appl. 012,836, 1 Nov 1990, to AlliedSignal

P. Bier, C. Indner, Europ. Pat. Appl. 063,263, 27 Oct 1982, to Bayer

G. Biglione, G.C. Fasulo, Ger. Offen. 3,310,757, 29 Sept 1983, to Montedison

R. Binsack, E. Reese, J. Wank, Ger. Pat. 2,735,092, 15 Feb 1979; Ger. Pat. 2,755,025; 2,755,026, 13 June 1979, to Bayer

R. Binsack, D. Rempel, P. Bier, C. Lindner, Europ. Pat. Appl. 056,243, 21 July 1982, to Bayer

C.A.B.. Bjoerkengren, E.S. Joensson, Swed. Pat. 413,031, 31 Mar 1980, to Aktiebolag Akerlund och Rausing

D.G. Bland, J.J. Conte, U.S. Patent 5,017,622, 21 May 1991, to Dow Chemical

D.G. Bland, J.J. Conte, U.S. Patent 5,179,130, 12 June 1993; U.S. Patent 5,218,007, 08 June 1993, to Dow Chemical

W.G. Blasius Jr., Intl. Pat. Appl. PCT WO 92 013,917, 20 Aug 1992, to Novacor Chem.

W.G. Blasius Jr., U.S. Patent 5,290,862, 01 Mar 1994, to Novacor Chem.

R.B. Blodgett, Rubber Chem. Technol. **52**, 410 (1979)

U. Blumenstein, P. Klaerner, H. Schuch, H.-M. Walter, U.S. Patent 5,334,658, 02 Aug 1994, to BASF

L. Boehm, H.F. Enderle, H. Jastrow, Europ. Pat. Appl. 517,222, 09 Dec 1992, to Hoechst

V.C. Boger, A.G. Thomas, U.S. Patent 2,854,425, 30 Sept 1958, to B. F. Goodrich

E. M. Boldebuck, U.S. Patent 3,063,872, 13 Nov 1962, to General Electric Co.

C. Bonfanti, A. Lezzi, U. Pedretti, A. Roggero, F.P. La Mantia, Europ. Pat. Appl. 565,195, 13 Oct 1993, to Eniricerche

L.J. Bonis, A.M. Adur, SPE Techn. Pap. **41**, 3156 (1995)

D.C. Bookbinder, P.D. Sybert, U.S. Patent 5,135,990, 04 Aug 1992, to General Electric Co.

R.C. Bopp, K.G. Balfour, Europ. Pat. Appl. 550,204, 07 July 1993, to General Electric Co.

R.J.M. Borggreve, R.J. Gaymans, Polym. Commun. **30**, 71 (1989)

L.G. Bourland, U.S. Patent 4,388,443, 14 June 1983, to Atlantic Richfield

M. Bousmina, J.F. Palierne, L.A. Utracki, Polym. Eng. Sci. **39**, 1049 (1999)

O.M. Boutni, P.Y. Liu, Europ. Pat. Appl. 110,222, 13 June 1983, to General Electric Co.

D.K. Brandom, J.P. Desouza, D.G. Baird, G.L. Wilkes, J. Appl. Polym. Sci. **66**, 1543 (1997)

F. Brandstetter, A. Echte, H. Gausepohl, H. Naarmann, Europ. Pat. Appl. 048,400, 31 Mar 1982a, to BASF

F. Brandstetter, A. Echte, J. Hambrecht, H. Naarmann, Ger. Offen. 3,115,368, 18 Nov 1982b; Europ. Pat. Appl. 048,399, 31 Mar 1982, to BASF

F. Brandstetter, J. Hambrecht, B. Scharf, Europ. Pat. Appl. 062,838, 20 Oct 1982c, to BASF

F. Brandstetter, J. Hambrecht, H. Muenstedt, Ger. Offen. 3,149,812, 21 July 1983a, to BASF

F. Brandstetter, J. Hambrecht, B. Scharf, Ger. Offen. 3,203,488, 11 Aug 1983b, to BASF

F. Brandstetter, J. Hambrecht, G. Blinne, K.H. Illers, Ger. Offen. 3,202,370, 04 Aug 1983c, to BASF

R.L. Briggs, R.L. Price, U.S. Patent 3,096,300, 02 July 1963, to Dow Chemical

J.R. Briggs, R.G. Newburg, R.E. Clayton, U.S. Patent 2,854,435, 30 Sept 1958, to Esso

T.A. Bright, A. Deckers, M. Knoll, Ger. Offen., 4,138,574, 27 May 1993, to BASF

T.O. Broadhed, Europ. Pat. Appl. 209,294, 21 Jan 1987, to Du Pont Canada

K. Bronstert, R. Jung, J. Schwaab, D. Stein, Ger. Offen. 2,024,940, 02 Dec 1971, to BASF

G.T. Brooks, B.L. Joss, C.L. Myers, Europ. Pat. Appl. 572,267, 01 Dec 1993, to Amoco Corp.

G.T. Brooks, B.L. Joss, C.L. Myers, U.S. Patent 5,283,284, 01 Feb 1994, to Amoco Corp.

S.B. Brown, U.S. Patent 4,831,087, 16 May 1989, to General Electric Co.

S.B. Brown, in *Reactive Extrusion: Principles and Practice*, ed. by M. Xanthos (Hanser, Munich, 1992)

S.B. Brown, E.J. Fewkes Jr., Europ. Pat. Appl. 493,675, 08 July 1992, to General Electric Co.

S.B. Brown, E.J. Fewkes Jr., U.S. Patent 5,189,114, U.S. Patent 5,290,863, 01 Mar 1994, to General Electric Co.

S.B. Brown, D.J. McFay, J.B. Yates III, G.F. Lee PCT Int. Pat. Appl. WO 87 00,850, 12 Feb 1987, to General Electric Co.

T.F. Brownscombe, R.M. Bass, P.K. Wong, G.C. Blytas, W.P. Gergen, M. Mores, U.S. Patent 5,646,193, 08 July 1997, to Shell Oil

C.B. Bucknall, *Toughened Plastics* (Applied Science, London, 1977)

C.B. Bucknall, I.K. Partridge, M.V. Ward, J. Mater. Sci. **19**, 2064 (1984)

C.B. Bucknall, D.R. Paul, *Polymer Blends: Formulations and Performance*, vol. 1 and 2 (Wiley, New York, 2000)

C.B. Bucknall, D.R. Paul, Polymer **50**, 5539 (2009)

C.B. Bucknall, D.R. Paul, Polymer **54**, 320 (2013)

F. Bueche, J. Chem. Phys. **20**, 1959 (1952)

F. Bueche, J. Chem. Phys. **25**, 599 (1956)

F. Bueche, *Physical Properties of Polymers* (Interscience, New York, 1962)

F. Buehler, E. Schmid, H.J. Schultze, Europ. Pat. Appl. 536,679, 14 Apr 1993, to Ems-Inventa

F. Buehler, E. Schmid, H.J. Schultze, U.S. Patent 5,346,936, 13 Sept 1994, to Ems-Inventa

A.L. Bull, G. Holden, J. Elastom. Plast. **9**, 281 (1977)

K. Burg, E. Wolters, H. Cherdron, Ger. Offen. 2,037,823, 03 Feb 1972, to Hoechst

W.E. Burgert, Europ. Pat. Appl. 215,150, 25 Mar 1987, to Dow Chemical

A.M. Burnell, U.S. Patent 5,272,182, 21 Dec 1993, to General Electric Co.

P.M. Buschbaum, Polym. J. **45**, 34 (2013)

W.F. Busse, J. Phys. Chem. **36**, 2862 (1932)

J.D. Bussink, J.W.J. De Munck, P.C.A.M. van Abeelen, U.S. Patent 4,122,131, 24 Oct 1978, to General Electric Co.

S. Bywater, Adv. Polym. Sci. **4**, 66 (1965)

D.W. Caird, U.S. Patent 3,087,908, 30 Apr 1961, to Osaka Kinzoku Kogyo

M. Cakmak, A. Dutta, U.S. Patent 5,114,987, 19 May 1992, to Edison Polymer Innovation Corp.

G.W. Calundann, F. Herold, E.C. Chenevey, T.S. Chung, Europ. Pat. Appl. 510,818, 28 Oct 1992, to Hoechst Celanese Corp.

G.W. Calundann, F. Herold, E.C. Chenevey, T.S. Chung, U.S. Patent 5,290,884, 01 Mar 1994, to Hoechst Celanese Corp.

R. Camargo, F. Mercer, T.-C. Cheng, PCT. Intl. Appl. WO 86 04,079, 17 July 1986, to Raychem Corp.

G.A. Campbell, D.H. Rasmussen, U.S. Patent 5,358,675, 25 Oct 1994; U.S. Patent 5,369,135, 29 Nov 1994, to Mobil Oil Corp.

J.R. Campbell, J.R. Presley, U.S. Patent 5,380,796, 10 Jan 1995, to General Electric Co.

P.J. Canterino, J.P. Freudemann, Europ. Pat. Appl. 148,567, 17 July 1985, to Mobil Oil

P.J. Canterino, D.V. Dobreski, R.G. Shaw, U.S. Patent 4,579,912, 01 Apr 1986, to Mobil Oil

W.H. Carothers, Chem. Rev. **8**, 353 (1931)

W.H. Carothers, U.S. Patent 2,071,250; 2,071,251; 2,071,252; 2,071,253, 16 Feb 1937, to E. I. du Pont

W.H. Carothers, I. Williams, A.M. Collins, J.E. Kirby, J. Am. Chem. Soc. **53**, 4203 (1931)

J. Castelein, Europ. Pat. Appl. 060,525, 22 Sept 1982, to Montefina

J.Y. Cavaille, J. Perez, C. Jourdan, G.P. Johari, J. Polym. Sci. B Polym. Phys. **25**, 1847 (1987)

G. Cecchin, F. Guglielmi, Europ. Pat. Appl. 373,660, 20 June 1990, to Himont

Celanese Corporation, Fr. Demand, 2,484,430, 18 Dec 1981

Celanese Corporation, U.S. Patent 4,489,190, 30 June 1984

Ceramer™ Hoechst-Ticona, Techn. Inf. (1996)

R.J. Ceresa, N.E. Davenport, T.L. Trudgian, Brit. Pat. 1,112,024, 01 May 1968, to W. R. Grace & Co.

J. Cerny, R. Troncy, Fr. Pat. 2,473,534, 17 July 1981, to Rhône-Poulenc

G.R. Chambers, G.F. Smith, J.B. Yates III, U.S. Patent 5,384,359, 24 Jan 1995, to General Electric Co.

M.F. Champagne, M.M. Dumoulin, L.A. Utracki, J.P. Szabo, Polym. Eng. Sci. **36**, 1636 (1996)

G.M. Chapman, R.H. Downie, U.S. Patent 5,352,716, 04 Oct 1994, to Ecostar International

L.F. Charbonneau, B. Gupta, H.C. Linstid, L.C. Sawyer, J.P. Shepherd, U.S. Patent 5,393,848, 28 Feb 1995, to Hoechst Celanese Corp.

J.J. Charles, E.A. Coleman, Europ. Pat. Appl. 033,393, 12 Aug 1981, to GAF Corp.

J.J. Charles, R.C. Gasman, Ger. Offen. 2,825, 236, 25 Jan 1979, to GAF Corp.

Y. Charlier, J.L. Hedrick, T.P. Russell, Polymer **36**, 4529 (1995)

D. Chattopadhyaya, *History of Science and Technology in Ancient India* (Firma KLM PVT, Calcutta, 1986)

Y.T. Chen, D.P. Sinclair, Europ. Pat. Appl. 361,636, 04 Apr 1990, to Amoco Co.

P.N. Chen, T.S. Chung, P.J. Harget, U.S. Patent 4,963,628, 16 Oct 1990, to Hoechst Celanese Corp.

P.N. Chen, A. Forschirm, M. Glick, M. Jaffe, U.S. Patent 5,070,144, 03 Dec 1991, to Hoechst Celanese Corp.

Y.W. Cheung, D.V. Dobreski, R. Turner, M. Wheeler, Y.P. Handa, U.S. Patent 8,304,499, 6 Nov 2012, to Pactiv Corp.

K. Chiba, K. Yamada, T. Muraki, Jap. Pat. 079,942, 14 July 1978, to Toray Ind.

C.L. Child, R.B.F.F. Clarke, B.J. Habgood, Brit. Pat. 544,359, 09 Apr 1942, to ICI

J. Cho, Macromol. Res. **21**, 1360 (2013)

Y. Choi, J.B.P. Soares, Can. J. Chem. Eng. **90**, 646 (2012)

H.H. Chuah, T. Kyu, T.E. Helminiak, Polymer **30**, 1591 (1989a)

H.H. Chuah, L.-S. Tan, F.E. Arnold, Polym. Eng. Sci. **29**, 107 (1989b)

H.-K. Chuang, C.D. Han, Adv. Chem. Ser. **204**, 171 (1984)

D. Chundury, PCT Int. Appl. WO 013,170, 08 July 1993, to Ferro Corp.

D. Chundury, U.S. Patent 5,278,231, 11 Jan 1994, to Ferro Corp.

D. Chundury, A.S. Scheibelhoffer, U.S. Patent 5,321,081, 14 June 1994, to Ferro Corp.

J.C. Chung, M.K. Akkapeddi, Polymer Prepr. **34**(1), 614 (1993)

G.C. Chung, J.A., Kornfield, S.D. Smith, Macromolecules **27**, 964, 5729 (1994)

L. Clementini, A.F. Galambos, G. Lesca, K. Ogale, L. Spagnoli, M.E. Starsinic, L. Giuseppe, Europ. Pat. Appl. 552,810, 28 July 1993, to Himont Inc.

R.R. Clikeman, D.S. Cinoman, E.D. Weiler, E.D., U.S. Patent 4,650,824, 17 Mar 1987, to Rohm & Haas Co.

J.C. Coburn, H.H. Yang, U.S. Patent 5,366,781, 22 Nov 1994, to E. I. du Pont

F.N. Cogswell, B.P. Griffin, J.B. Rose, Europ. Pat. Appl. 030,417, 17 June 1981, to ICI

F.N. Cogswell, B.P. Griffin, J.B. Rose, U.S. Patent 4,386,174, 1983, to ICI

F.N. Cogswell, B.P. Griffin, J.B. Rose, U.S. Patent 4,433,083, 1984, to ICI

S.C. Cohen, WO Pat. 00,972, 1980, to General Electric Co.

S.C. Cohen, Can. Pat. 1,123,534, 11 May 1982, to General Electric Co.

R.H. Colby, C.J.T. Landry, M.R. Landry, T.E. Long, D.J. Massa, D.M. Teegarden, Europ. Pat. Appl. 530,648, 10 Mar 1993, to Eastman Kodak

R.H. Colby, C.J.T. Landry, M.R. Landry, T.E. Long, D.J. Massa, D.M. Teegarden, U.S. Patent 5,276,089, 04 Jan 1994, to Eastman Kodak

Q.P. Cole, U.S. Patent 2,912,410, 10 Nov 1959, to General Electric Co.

M.M. Coleman, J.F. Graf, P.C. Painter, *Specific Interactions and the Miscibility of Polymer Blends* (Technomics Publishing, Lancaster, 1991)

D.I. Collias, D.G. Baird, Polym. Eng. Sci. **35**, 1178 (1995)

R. Colombo, Ital. Pat. Appl. 370,578, 1939, to Lavorazione Materie Plastiche

W.R. Conrad, R.J. Reid, U.S. Patent 3,098,839, 23 July 1963, to Firestone Tire & Rub

H.W. Coover Jr., W.C. Wooten Jr., U.S. Patent 3,0058,949, 16 Oct 1962, to Eastman Kodak

O.J. Cope, U.S. Patent 3,435,093, 25 Mar 1969, to E. I. du Pont

A.Y. Coran, R. Patel, Ger. Offen. 2,757,430, 06 July 1978; U.S. Patent 4,130,534, 19 Dec 1978, to Monsanto

L. Corbellini, Ger. Offen. 1,137,859, 11 Oct 1962, to Montecatini

S. Cottis, H. Chin, W.H. Shiau, D. Shopland, U.S. Patent 5,262,473, 16 Nov 1993, to Enichem America

P.R. Couchman, J. Appl. Polym. Sci. **60**, 1057 (1996)

W.R. Coutant, Europ. Pat. Appl. 588,147, 23 Mar 1994, to Phillips

M.A. Cowan, Europ. Pat., Appl. 095,299, 30 Nov 1983, to Intercont. Plast.

J.M.G. Cowie, R. Ferguson, Macromolecules **22**, 2307 (1989)

J.M.G. Cowie, V. Arrighi, in *Polymer Physics: From Suspensions to Nanocomposites and Beyond*, ed. by L.A. Utracki, A.M. Jamieson (Wiley, Hoboken, 2010)

M.J. Cran, S.W. Bigger, Polym. Plast. Technol. Eng. **48**, 272 (2009)

H. Craubner, G. Illing, A. Hrugesch, Ger. Offen. 1,138,922, 31 Oct 1962, to BASF

J.W. Crawford, W.G. Oakes, Brit. Pat. 941,083, 06 Nov 1963, to ICI

J.W. Crawford, W.G. Oakes, Ger. Offen. 1,217,608, 16 May 1966, to ICI

R.W. Crawford, W.K. Witsiepe, Ger. Offen. 2,224,678, 30 Nov 1972, to E. I. du Pont

S.H. Cree, C.A. Wilson, S. A. de Vries, U.S. Patent 5,795,941, 18 Aug 1998, to Dow Chemical

M.G. Cross, R. Lines, U.S. Patent 5,378,402, 0 3 Jan 1995, to Raychem Limited

Daicel Chemical Industries, Jap. Pat. 049,656, 23 Mar 1982; Jap. Pat. 117,563, 22 July 1982

Daicel Chemical Industries, U.S. Patent 4,393,169, 12 July 1983

Daicel Chemical Industries, Jap. Pat. 06,253, 13 Jan 1984

Dainichiseika Color & Chem. Co., Jap. Pat. 053,552, 30 Mar 1982

Dainichiseika Color & Chem. Co., Jap. Pat. 83,039, 18 May 1983
Dainippon Ink & Chem., Jap. Pat. 025,355, 10 Feb 1982
Dainippon Ink & Chem., Jap. Pat. 008,760, 18 Jan 1983
P.O. Damm, P. Matthies, in *Handbook of Plastics Materials and Technology*, ed. by I.I. Rubin (Wiley, New York, 1990)
S. Dashevsky, K.S. Kim, S.W. Palmaka, PCT Int. Appl. 013,172, 08 July 1993, to Akzo
S. Dashevsky, K.-S. Kim, S.W. Palmaka, R.L. Johnston, L.A.G. Busscher, J.A. Juijn, U.S. Patent 5,346,970, 13 Sept 1994, to Akzo Nobel
S. Datta, D.J. Lohse, *Polymeric Compatibilizers: Uses and Benefits in Polymer Blends* (Hanser, Munich, 1996)
G.J. Davies, U. K. Patent Appl. 2,220,416, 10 Jan 1990, to T&N Technology
M. Davies, P.M. Hatton, Europ. Pat. Appl. 611,384, 24 Aug 1994, to ICI
J.H. Davis, Brit. Pat. 1,403,797, 20 Aug 1975, to ICI
J.A. Davis, J.K. Valaitis, Europ. Pat. Appl. 564,961, 13 Oct 1993, to Bridgestone/Firestone
J.A. Davis, J.K. Valaitis, U.S. Patent 5,286,798, 15 Feb 1994, to Bridgestone/Firestone
S. Davison, W.P. Gergen, U.S. Patent 4,041,103, 09 Aug 1977, to Shell Oil
S. Davison, W.P. Gergen, U.S. Patent 4,242,470, 30 Dec 1980, to Shell Oil
F. Dawans, D. Binet, U.S. Patent 4,255,524, 10 Mar 1981, to Institut Francais du Petrole
R.L. Dawson, U.S. Patent 5,206,294, 27 Apr 1993, to E. I. du Pont
J. De Boer, J.M.H. Heuschen, U.S. Patent 4,788,252, 29 Nov 1988, to General Electric Co.
C. De Rosa, F. Auriemma, Prog. Polym. Sci. **31**, 145 (2006)
B.D. Dean, U.S. Patent 4,937,297, 26 June 1990, to Amoco
B.D. Dean, U.S. Patent 5,115,046, 19 May 1992, to Amoco
P. Debye, J. Appl. Phys. **15**, 338 (1944)
P. Debye, J. Appl. Phys. **17**, 319 (1946)
P.G. de Gennes, *Scaling concepts in polymer physics* (Cornell University Press, Ithaca, 1979)
C. Dehennau, T. Depireux, I. Claeys, Europ. Pat. Appl. 587,216, 16 Mar 1994, to Solvay
M.E.J. Dekkers, U.S. Patent 5,290,881, 01 Mar 1994, to General Electric Co.
M.E.J. Dekkers, D.K. Yoshimura, M.P. Laughner, U.S. Patent 5,171,778, 15 Dec 1992, to General Electric Co.
J.W. DeMunck, J.H.G. Lohmeijer, Europ. Pat. Appl. 177,989, 16 Apr 1986, to General Electric Co.
M. Deng, L.S. Nair, S.P. Nukavarapu, T. Jiang, W.A. Kanner, X. Li, S.G. Kumbar, A.L. Weikel, N.R. Krogman, H.R. Allcock, C.T. Laurencin, Biomaterials **31**, 4898 (2010)
A.J. DeNicola Jr., M.R. Conboy, U.S. Patent 5,286,791, 15 Feb 1994, to Himont
A.J. DeNicola, T.A. Giroux, U.S. Patent 5,370,813, 06 Dec 1994, 26 Mar 1990, to Himont
A.J. DeNicola Jr., J.A. Smith, M. Felloni, U.S. Patent 5,414,027, 09 May 1995, to Montell North America
A.J. DeNicola Jr., J.A. Smith, M. Felloni, U.S. Patent 5,605,936, 25 Feb 1997, to Montell North America
J.L. Derudder, U.S. Patent 4,960,836, 02 Oct 1990, to General Electric Co.
J.L. Derudder, I.-C.W. Wang, Europ. Pat. Appl. 537,014, 14 Apr 1993, to General Electric Co.
S. Detyothin, A. Kathuria, W. Jaruwattanayon, S.E.M. Selke, R. Auras, in *Poly (Lactic Acid)*, ed. by R. Auras, L.-T. Lim, S.E.M. Selke, H. Tsuji (Wiley, Hoboken, 2010)
R. Dhein, W. Ebert, H. Hugl, H. Ohst, Ger. Pat. 4,142,765, 24 June 1993, to Bayer
R.L. Dieck, S.C. Cohen, PCT Int. Appl. 000,972, 15 May 1980, to General Electric Co.
R.L. Dieck, R.J. Kostelnik, Europ. Pat. Appl. 071,773, 16 Feb 1983, to General Electric Co.
R.L. Dieck, E. J. Quinn, U.S. Patent 4,026,839, 31 May 1977; U.S. Patent 4,055,520, 25 Oct 1977; U.S. Patent 4,061,606, 06 Dec 1977, to Armstrong Cork
R.L. Dieck, A.D. Wambach, PCT Int. Appl. 001,167, 12 June 1980, to General Electric Co.
L.K. Djiauw, U.S. Patent 5,320,899, 14 June 1994, to Shell Oil
A.J. Dijkstra, M.E.G. Jones, Ger. Offen. 1,814,073, 24 July 1969, to ICI
D.D. Dixon, M.E. Ford U.S. Patent 4,137,280, 30 Jan 1979, to Air Products & Chemicals

F.Z. Dobkowski, Polymer **25**(3), 110 (1980)

D.V. Dobreski, J.J. Donaldson, U.S. Patent 5,290,866, 01 Mar 1994, to Mobil Oil Corp.

H. Doerffurt, F. Waeteraere, Ger. Offen. 2,555,691, 16 June 1977, to Dynamit Nobel

M. Doi, *Introduction to polymer physics* (Clarendon, Oxford, 1995)

M. Doi, S.F. Edwards, *The Theory of Polymer Dynamics* (Oxford University Press, New York, 1986)

M. Doi, A. Onuki, J. Phys. (Paris) **2**, 1631 (1992)

A.K. Doolittle, J. Appl. Phys. **22**, 1031 (1951)

L. D'orazio, R. Greco, C. Mancarella, E. Martucelli, G. Ragosta, C. Silvester, Polym. Eng. Sci. **22**, 536 (1982)

S. Dorudiani, C.B. Park, M.T. Kortschot, Polym. Eng. Sci. **38**, 1205 (1998)

Dow Chemical Co., Brit. Pat. 942,363, 20 Nov 1963

Dow Chemical Co., Neth. Pat. Appl. 6,507,478, 20 Dec 1965

M. Droescher, M. Bartmann, K. Burzin, R. Feinauer, C. Gerth, W. Neugebauer, H. Jadamus, W. Ribbing, J. Lohmar, Europ. Pat. Appl. 205,816, 30 Dec 1986 to Hüls

R.S. Drzal, B.S. Ehrlich, L.H. La Nieve III, Europ. Pat. Appl. 116,450, 02 Jan 1986, to Upjohn Co.

M.A. Drzewinski, U.S. Patent 5,248,732, 28 Sept 1993, to Enichem

M.A. Drzewinski, U.S. Patent 5,286,794, 15 Feb 1994; U.S. Patent 5,292,809, 08 Mar 1994, to Enichem

M. Dubois, B. Guyot, R. Thommeret, Europ. Pat. Appl. 554,932, 11 Aug 1993, to Solvay

D.L. Dufour, U.S. Patent 4,329,272, 11 May 1982, to Monsanto

D.L. Dufour, Europ. Pat. Appl. 272,239, 22 June 1988, to Monsanto

M.M. Dumoulin, Ph.D. thesis, Ecole Polytechnique, Montreal, 1988

D.P. Durbin, R.L. Danforth, R.G. Lutz, U.S. Patent 4,377,647, 22 Mar 1983, to Shell Oil

N.E. Durfee Jr., J.A. Rock, Can. Pat. Appl. 2,050,182, 01 Mar 1993, to General Electric Co.

R.R. Durst, Ger. Offen. 2,009,407, 12 Nov 1970, to General Tire & Rubber

R.R. Durst, U.S. Patent 3,907,929, 23 Sept 1975, to General Tire & Rubber

A. Dutta, M. Cakmak, Rubber. Chem. Techn. **65**, 932 (1992)

Dynamit Nobel, Fr. Pat. 2,004,607, 28 Nov 1969

E. I. du Pont de Nemours & Company, Brit. Pat. 550,931, 01 Feb 1942

T. Eckel, G. Fennhoff, W. Jakob, K. Oott, J. Schoeps, D. Wittmann, Europ. Pat. Appl. 570,797, 24 Nov 1993, to Bayer

O.M. Ekiner, J.W. Simmons, U.S. Patent 5,248,319, 28 Sept 1993, to E. I. du Pont

M.J. El-Hibiri, G.S. Jack, W.E. Kelly, S.R. Patel, U.S. Patent 5,151,462, 29 Sept 1992, to Amoco Corp.

M.J. El-Hibri, J.L. Melquist, U.S. Patent 5,206,311, 27 Apr 1993, to Amoco Corp.

S. Ellebrach, S. Chum, SPE Techn. Pap. **44**, 1795 (1998)

M.D. Ellul, U.S. Patent 5,290,886, 01 Mar 1994, to Advanced Elastomer System

D.D. Emrick, U.S. Patent 3,268,627, 23 Aug 1966, to Standard Oil Co.

S.J. Enderle, U.S. Patent 4,480,054, 30 Oct 1984, to E. I. Du Pont

H. Endo, T. Ishii, Europ. Pat. Appl. 122,601, 24 Oct 1984, to Idemitsu Petrochem.

T. Endo, O. Kanoto, N. Matsunaga, Europ. Pat. Appl. 354,802, 14 Feb 1990, to Polyplastics

U. Epple, M.-J. Brekner, U.S. Patent 5,359,001, 25 Oct 1994, to Hoechst

U. Epple, M.-J. Brekner, H. Cherdron, PCT Int. Appl. 016,585, 01 Oct 1992, to Hoechst

Esso, Brit. Pat. 851,028, 12 Oct 1960

Esso, Brit. Pat. 893,540, 11 Apr 1962

J.C. Falk, U.S. Patent 4,302,555, 24 Nov 1981, to Borg-Warner Chem.

U. Falk, O. Hermann-Schoenherr, Europ. Pat. Appl. 513,655, 19 Nov 1992, to Hoechst

Farbwerke Hoechst, Fr. Pat. 1,588,354, 10 Apr 1970

R.J. Farris, B.W. Jo. PCT Int. Appl. WO 93 01,238, 21 Jan 1993, to University of Massachusetts

K.-P. Farwerck, H. Lauke, G.E. McKee, F. Seitz, N. Guentherberg, H. Ohlig, S. Besecke, H. Kroeger, W. Loth, N. Niessner, L. Schlemmer, D. Wagner, Europ. Pat. Appl. 534,235, 31 Mar 1993, to BASF

R.A. Fava, U.S. Patent 4,160,792, 10 July 1979, to ARCO
R.A. Fava, U.S. Patent 4,284,735, 18 Aug 1981, to ARCO
R.A. Fava, K.W. Doak, U.S. Patent 4,221,880, 09 Sept 1980, to ARCO
R. Fayt, R. Jerôme, Ph. Teyssié, J. Polym. Sci., Polym. Lett. Ed. **24**, 25 (1986a); Makromol. Chem. **187**, 837 (1986)
R. Fayt, Ph. Teyssié, D. Hanton, Fr. Pat. 2,582,659, 05 Dec 1986b, to Isover Saint Gobain
A.R. Federl, G. Kipouras, U.S. Patent 4,588,773, 13 May 1986, to Borg-Warner Chem.
F. Fenouillot, P. Cassagnau, J.-C. Majeste, Polymer **50**, 1333 (2009)
J.D. Ferry, R.F. Landel, M.L. Williams, J. Appl. Phys. **26**, 359 (1955)
M. Fikentscher, C. Heuce, Ger. Offen. 654,989, 1930, to I. G. Farbenindustrie
M. Fikentscher, W. Wolff, Ger. Offen. 660,793, 1931, to I. G. Farbenindustrie
W.K. Fischer, So. Afric. Pat. 72 00,388, 23 Aug 1972, to Uniroyal
J.-D. Fischer, W. Siol, U.S. Patent 5,218,050, June 1993, to Röhm
J.-D. Fischer, W. Siol, U.S. Patent 5,380,801, 10 Jan 1995, to Röhm
E.D. Flexman Jr., U.S. Patent 5,318,813, 07 June 1992, to E. I. du Pont
D.W. Fox, S.J. Shafer, L.M. Maresca, D.C. Clagett, Europ. Pat. Appl. 322,558, 05 July 1989, to General Electric Co.
P.D. Frayer, *NRCC/IMI symposium Polyblends-'93*, Boucherville, 26–27 Oct 1993
P.D. Frayer, *PPS Regional Meeting*, Akron, 4–7 Apr 1994
J. M. J. Fréchet, I. Gitsov, C. J. Hawker, L. Lochman, K. Wooley, *4th SPSJ International Polymer Conference*, Yokohama, 29 Nov–3Dec 1992
W.T. Freed, U.S. Patent 3,920,602, 18 Nov 1975, to Celanese Corp.
S. Freinkel, *Plastic: A Toxic Love Story* (Houghton Mifflin Harcourt, Boston, 2011)
D. Freitag, G. Fengler, L. Morbitzer, Angew. Chem. Int. Ed. **30**, 1598 (1991)
H.H. Frey, Ger. Offen. 1,045,089, 20 Nov 1958; Ger. Offen. 1,111,383, 13 Oct 1958, to Hoechst
P. Freyburger, U.S. Patent 180,568, 1876
K. Friedrich, in *Crazing in Polymers*, ed. by H. H. Kausch. Adv. Polym. Sci. **52/53** (Springer, Berlin, 1983)
Chr. Friedrich, W. Gleinser, E. Korat, D. Maier, J. Wesse, J. Rheol. **39**, 1411 (1995)
H.G. Fritz, R. Anderlik, Kautschuk Gummi Kunstst. **46**, 374 (1993)
M.F. Froix, N.S. Trouw, R.R. Schwarz, Fr. Demand 2,483,442, 04 Dec 1981, to Celanese Corp.
H.C. Fromuth, L.A. Cohen, W.T. Freed, D.S. Cinoman, Europ. Pat. Appl. 494,542, 15 July 1992, to Röhm & Haas
K.D. Fudge, U.S. Patent 4,666,946, 19 May 1987, to Atlantic Richfield
K. Fuhr, F. Mueller, K.H. Ott, J. Schoeps, H. Peters, W. Ballas, Europ. Pat. Appl. 463,495, 02 Jan 1992, to Bayer
S. Fuji, S.P. Ting, Europ. Pat. Appl. 226,851, 01 July 1987, to General Electric Co.
H. Fujie, Europ. Pat. 558,256, 01 Sept 1993, to Teijin
M. Fujii, Y. Ohtsuka, Chem. High Polym. **13**, 54 (1954)
S. Fujii, H. Ishida, M. Morioka, A. Saito, R. van der Meer, PCT Intl. Appl. 005,304, 11 Sept 1987, to General Electric Co.
Y. Fujita, T. Kawamura, K. Yokoyama, K. Yokomizo, S. Toki, U.S. Patent 5,298,557, 29 Mar 1994, to Tonen Corp.
G. Fujiwara, Jap. Pat. 041,456, 07 Dec 1971, to Toray Industries
K. Fukuda, H. Kasahara, Europ. Pat. Appl. 044,703, 27 Jan 1982; Jap. Pat. 105,452, 30 June 1982, to Asahi-Dow
O. Fukui, Y. Inuizawa, S. Hinenoya, Y. Takasaki, Fr. Pat. 2,522,331, 02 Sept 1983, to Ube Industries
M. Fukushima, H. Mitarai, Jap. Pat. 022,852, 30 June 1971, to Japan Synthetic Chem.
N. Fukushima, I. Namazue, T. Saito, K. Hieda, Jap. Pat. 116,053, 10 Sept 1979, to Sumitomo Chem.
M. Furuta, T. Maruyama, Europ. Pat. Appl. 356,194, 28 Feb 1990, to Sumitomo Chem.

G.M. Gaafar, Europ. Pat. Appl. 383,977, 29 Aug 1990, to General Electric Co.

S.K. Gaggar, J.M. Dumler, T.B. Cleveland, Europ. Pat. Appl. 294,722, 14 Dec 1988, to Borg-Warner Chem.

S.K. Gaggar, J.M. Dumler, T.B. Cleveland, U.S. Patent 4,857,590, 15 Aug 1989, to Borg-Warner Chem.

D.M. Gale, U.S. Patent 4,117,033, 26 Sept 1978, to E. I. du Pont

G.M. Gale, U. K. Pat. Appl. 80 30,586, 1980, to RAPRA

P. Galli, M. Spataro, Europ. Pat. Appl. 077,532, 27 Apr 1983, to Montedison

R.R. Gallucci, PCT Intl. Appl. 006,168; 006,169, 25 Aug 1988, to General Electric Co.

R.R. Gallucci, D.C. Bookbinder, U.S. Patent 4,806,597, 21 Feb 1989, to General Electric Co.

R.R. Gallucci, R. van der Meer, R.W. Avakian, PCT Intl. Appl. 005,372, 05 Dec 1985, to General Electric Co.

M.E. Galvin, G.E. Wnek, Polym. Commun. **23**, 795 (1982)

R.J. Gambale, D.C. Clagett, L.M. Maresca, S.J. Shafer, U.S. Patent 5,280,088, 18 Jan 1994, to General Electric Co.

R.J. Gambale, L.M. Maresca, D.C. Clagett, S.J. Shafer, Europ. Pat. Appl. 285,692; 285,693, 12 Oct 1988, to General Electric Co.

F.W. Gander, E.F. Hoegger, W.P. Kane, U.S. Patent 4,020,126, 26 Apr 1977, to E. I. du Pont

R.A. Garcia, R.J. Martinovich, U.S. Patent 4,451,607, 29 May 1984, to Phillips

K.N. Gary, Can. Pat. Appl. 2,063,492, 20 Sept 1993

H. Gausepohl, G. Heinz, B. Schmitt, Europ. Pat. Appl. 048,388, 31 Mar 1982, to BASF

R. Gelles, W.P. Gergen, R.G. Lutz, Europ. Pat. Appl. 211,467, 25 Feb 1987, to Shell

R. Gelles, R.G. Lutz, W.P. Gergen, Europ. Pat. Appl. 261,748, 30 Mar 1988, to Shell

R. Gelles, W.P. Gergen, R.G. Lutz, M.J. Modic, U.S. Patent 5,371,141, 06 Dec 1994, to Shell

General Electric Company, Neth. Pat. Appl. 6,517,152, 06 July 1966

General Electric Company, Jap. Pat. 100,159, 09 June 1984

E.R. George, U.S. Patent 5,166,252, 24 Nov 1992, to Shell Oil

W.P. Gergen, S. Davison, U.S. Patent 4,090,996, 05 May 1977, to Shell Oil

W.P. Gergen, S. Davison, U.S. Patent 4,088,711, 09 May 1978, to Shell Oil

W.P. Gergen, R. G. Lutz, U.S. Patent 4,818,786, 04 Apr 1989, to Shell Oil

A.M. Gessler, W.H. Haslett Jr., U.S. Patent 3,037,954, 05 June 1962, to Esso

J.K. Gianchandai, A. Hasson, R.J. Wroczynski, J B. Yates III, Europ. Pat. Appl. 550,206, 07 July 1993, to General Electric Co.

H. Gilch, D. Michael, Ger. Offen. 1,901,552, 13 Aug 1970, to Bayer

H.F. Giles Jr., U.S. Patent 4,390,665, 28 June 1983, to General Electric Co.

H.F. Giles Jr., U.S. Patent 4,455,410, 19 June 1984, to General Electric Co.

H.F. Giles Jr., U.S. Patent 4,657,987, 14 Apr 1987, to General Electric Co.

H.F. Giles Jr., R.P. Hirt Jr., U.S. Patent 4,579,910, 01 Apr 1986, to General Electric Co.

H.F. Giles Jr., J.N. Sasserath, U.S. Patent 4,579,909, 01 Apr 1986, to General Electric Co.

B.S. Giles, S. Vilasagar, Europ. Pat. Appl. 596,704, 11 May 1994, to General Electric Co.

H.F. Giles Jr., D.M. White, U.S. Patent 4,387,193, 28 June 1983, to General Electric Co.

Glanzstoff, Brit. Pat. 1,091,256, 15 Nov 1967

M. Glotin, R. Parsy, P. Abadie, Ger. Offen. 3,909,273, 05 Oct 1989, to Atochem.

K.J. Godbey, P.G. Martin, U.S. Patent 5,264,219, 23 Nov 1993, to Minnesota Mining & Manufacturing

K.J. Godbey, P.G. Martin, PCT Int. Appl. WO 94 03,539, 17 Feb 1994, to Minnesota Mining & Manufacturing

D.A. Godfrey, U.S. Patent 5,382,615, 17 Jan 1995, to Eastman Chemical

E.J. Goedde, F.F. Holub, P.S. Wilson, Ger. Offen. 2,917,941, 13 Nov 1980, to General Electric Co.

W. Goetz, M. Laun, W. Betz, W. Heckmann, Ger. Offen. 4,127,720, 25 Feb 1993, to BASF

K.B. Goldblum, Ger. Offen. 1,266,974, 10 July 1963, to General Electric Co.

K.B. Goldblum, Belg. Pat. 634,842, 13 Jan 1964, to General Electric Co.

A. Goldel, P. Potschke, in *Polymer Carbon Nanotube Composites*, ed. by T. McNally, P. Potschke (Woodhead Publishing, Cambridge, 2011)

A. Goldel, G. Kasaliwal, P. Potschke, G. Heinrich, Polymer **53**, 411 (2012)

R.C. Golike, Belg. Pat. 619,351, 27 Dec 1962, to E. I. du Pont

A. Golovoy, M. Cheung, U.S. Patent 5,281,664, 25 Jan 1994, to Ford Motor Co.

P.M. Gomez, Europ. Pat. Appl. 515,344, 25 Nov 1992, to Monsanto

Goodrich (B. F.) Co., Brit. Pat. 539,834, 25 Sept 1941

Goodrich (B. F.) Co., Brit. Pat. 830,226, 09 Mar 1960

W.F. Gorham, A.G. Farnham, U.S. Patent 3,117,945, 14 Jan 1964, to Union Carbide Corp.

J.C. Goswami, U.S. Patent 4,031,045, 21.06.1977, to Stauffer Chem.

S. Gotoh, K. Nagaoka, Europ. Pat. 570,972, 24 Nov 1993, to Sumitomo Chem.

A.C. Gowan, U.S. Patent 3,361,851, 02 Jan 1968, to General Electric Co.

A.C. Gowan, U.S. Patent 3,472,810, 14 Oct 1969, to General Electric Co.

T.S. Grabowski, U.S. Patent 3,130,177, 21 Apr. 1964a, to Borg-Warner Corp.

T.S. Grabowski, U.S. Patent 3,134,746, 26 May 1964b, to Borg-Warner Corp.

T.S. Grabowski, U.S. Patent 3,267,175, 16 Aug 1966, to Borg-Warner Corp.

T.S. Grabowski, So. Afric. Pat. 07,675, 25 Apr 1970, to Borg-Warner Corp.

T.S. Grabowski, Brit. Pat. 1,253,226, 10 Nov 1971; Ger. Offen. 2,051,890, 06 May 1971, to Borg-Warner Corp.

T.S. Grabowski, Fr. Pat. 1,604,656, 11 Feb 1972; U.S. Patent 3,649,712, 14 Mar 1972, to Borg-Warner Corp.

H.P. Grace, Chem. Eng. Commun. **14**, 225 (1982)

W.W. Graessley, Adv. Polym. Sci. **16**, 1 (1974)

M.R. Grancio, D.F. Steward, J.F. Cass, Europ. Pat. Appl. 042,153, 23 Dec 1981, to Sweetheart Plastics

M.R. Grancio, D.F. Steward, J.F. Cass, U.S. Patent 4,386,187, 31 May 1983, to Sweetheart Plastics

J.E. Granda, J.J. Quinlan, J.J. Garland, U.S. Patent 4,013,597, 22.03.1977, to ARCO

J.A. Grande (ed.), Modern Plast. **74**, 37 (Sept 1997)

T.S. Grant, R.L. Jalbert, Europ. Pat. Appl. 226,910, 01 July 1987; U.S. Patent 4,654,405, 31 Mar 1987, to Borg-Warner Chemicals, Inc.

T.S. Grant, R.L. Jalbert, Europ. Pat. Appl. 305,878, 08 Mar 1989, to Borg-Warner Chemicals, Inc.

M. Gray, Brit. Pat. 5,056, 1879

S.J. Greaves, D.A. Harrison, K.M. Jones, PCT Int. Appl. WO 93 23,449, 25 Nov 1993, to ICI

W.S. Greenlee, J.C. Vyvoda, R.W. Wypart, U.S. Patent 5,157,076, 20 Oct 1992, to B. F. Goodrich Co.

U.R. Grigo, N.R. Lazear, M.W. Witmann, Ger. Offen. 3,325,702, 26 Jan 1984, to Mobay Chem.

G. Groeninckx, D. Dompas, T. Hasegawa, M. Isogawa, M. Kadokura, *NRCC/IMI symposium Polyblends-'95*, Boucherville, 9–20 Oct 1995

M.J. Guest, P.F.M. Van der Berghen, L.M. Aerts, A. Gkogkidis, A. De Bert, Europ. Pat. Appl. 440,441, 07 Aug 1991, to Dow Chemical

J.E. Guillet, in *Polymer Science and Technology*, vol. 3, ed. by J. E. Guillet (1973), Plennm, New York, p. 1

R.K. Gupta, *Polymer and Composite Rheology*, 2nd edn. (Marcel Dekker, New York, 2000)

B. Gupta, J.P. Shepherd, L.F. Charbonneau, PCT Int. Appl. WO 94 04,612, 03 Mar 1994, to Hoechst Celanese Corp.

E. Guth, H.F. Mark, Monatsh **65**, 93 (1934)

A. Guttag, U.S. Patent 5,120,089, 1992

A. Guttag, U.S. Patent 5,346,929, 13 Sept 1994

W.R. Haaf, U.S. Patent 4,167,507, 11 Sept 1979, to General Electric Co.

W.R. Haaf, PCT Int. Appl. 001,254, 14 Apr 1983, to General Electric Co.

W.R. Haaf, Europ. Pat. Appl. 491,191, 24 June 1992, to General Electric Co.

W.R. Haaf, G.F. Lee Jr., Ger. Offen. 2,750,515, 29 June 1978, to General Electric Co.

A. Haas, F. Raviola, Europ. Pat. Appl. 042,743, 13 Jan 1982, Soc. Chim. Charbonnages

M.T. Haggard, 4,710,522, 01 Dec 1987, to Mobil Oil Corp.

R.R. Haghighat, R.W. Lusignea, L. Elandjian, PCT Int. Appl. WO 92 17,545, 15 Oct 1992, to Foster-Miller

K. Hahn, U. Guhr, H. Hintz, R. Gellert, U.S. Patent 5,093,375, 03 Mar 1992, to BASF

M.I. Haider, E.C. Chenevey, U.S. Patent 5,277,981, 11 Jan 1994, to Hoechst Celanese Corp.

I.M. Haider, S. Kenig, V.J. Sullivan, Europ. Pat. 568,945, 10 Nov 1993, to Hoechst Celanese Corp.

M.P. Hallden-Abberton, N.M. Bortnick, W.J. Work, Eur. Pat. Appl. 594,433, 27 Apr 1994, to Rohm & Haas

R.H. Halliwell, Fr. Pat. 1,411,274, 17 Sept 1965, to E. I. du Pont

R.H. Halliwell, Brit. Pat. 1,047,069, 02 Nov 1966, to E. I. du Pont

T. Hamada, S. Yakabe, A. Ito, U.S. Patent 5,283,282, 01 Feb 1994, to Asahi Kasei Kogyo

J. Hambrecht, K. Gerberding, W.F. Mueller, B. Schmitt, Ger. Offen. 3,434,977, 03 Apr 1986, to BASF

C.F. Hammer, Macromolecules **4**, 69 (1971)

C.F. Hammer, U.S. Patent 3,780,140, 18 Dec 1973, to E. I. du Pont

C.Y. Han, U.S. Patent 5,324,796, 28 June 1994, to General Electric Co.

T. Hancock, Brit. Pat. 004,768, 1823

H. Hanezawa, Y. Ono, Jap. Pat. 03 292,314, 24 Dec 1991, to Asahi Chem.

E.H. Hankey, A. Kianpour, U.S. Patent 3,145,187, 18 Aug 1964, to Monsanto

D. Hardt, V. Serini, H. Vernaleken, H.E. Braese, Ger. Offen. 2,402,176, 1975, to Bayer

J.E. Harris, J.P. Gavula, Europ. Pat. Appl. 116,450, 02 Jan 1986, to Upjohn

J.E. Harris, M.J. Michno Jr., U.S. Patent 4,755,556, 05 July 1988, to Amoco Corp.

J.E. Harris, L.M. Robeson, Europ. Pat. Appl. 176,989, 09 Apr 1986, to Union Carbide Corp.

J.E. Harris, L.M. Robeson, Europ. Pat. Appl. 215,580, 25 Mar 1987, to Union Carbide Corp.

J.E. Harris, L.M. Robeson, B.H. Eckstein, M.D. Clifton, Europ. Pat. Appl. 257,150, 02 Mar 1988, to Amoco Corp.

C.R. Hart, Ger. Pat. 2,122,734, 02 Dec 1971, to ICI

R. Hasegawa, T. Kawamura, Y. Nakamura, H. Kubota, Jap. Pat. 041,444, 18 Apr 1974, to Teijin Chem.

M. Hashimoto, Jap. Pat. 246,755, 04 Nov 1986, to Dainippon Ink & Chemicals

T. Hashimoto, T. Ohashi, U.S. Patent 4,546,127, 08.10.1985, to Bridgestone Tire

M. Hashimoto, Y. Akana, H. Hori, Europ. Pat. Appl. 368,281, 16 May 1990, to Mitsui Petrochem

A. Hasson, J.B. Yates, Europ. Pat. 557,654, 01 Sept 1993, to General Electric Co.

M. Hasuo, T. Okano, M. Ito, Jap. Pat. 262,853, 26 Dec 1985, to Mitsubishi Chem.

S.J. Hathaway, R. A. Pyles, U.S. Patent 4,732,934, 1988, to General Electric Co.

S.J. Hathaway, R. A. Pyles, U.S. Patent 4,800,218, 1989, to General Electric Co.

S.G. Hatzikiriakos, K.B. Migler (eds.), *Polymer Processing Instabilities* (Marcel Dekker, New York, 2005)

D.I. Hauser, M.B. Colella, W.G. Blasius Jr., J.M. Haines, Europ. Pat. Appl. 532,171, 17 Mar 1993, to Novacor Chem.

A.S. Hay, J. Am. Chem. Soc. **81**, 6335 (1959)

A.S. Hay, Belg. Pat. 635,349, 24 Jan 1964, to General Electric Co.

A.S. Hay, U.S. Patent 3,306,874; 3,306,875, 28 Feb 1967, to General Electric Co.

A.S. Hay, U.S. Patent 3,402,144, 17 Sept 1968, to General Electric Co.

R.A. Hayes, U.S. Patent 2,755,270, 17 July 1956, to Firestone Tire & Rubber

R.A. Hayes, Ger. Offen. 1,232,741, 19 Jan 1967, to Firestone Tire & Rubber

J.G. Hedberg, L.M. Magner, U.S. Patent 3,209,055, 28 Sept 1965, to E. I. du Pont

G. Heger, M. Oeller, Eur. Pat. Appl. 583,706, 23 Feb 1994, to Bayer

G. Heger, E. Piejko, J. Buekers, L. Morbitzer, A. Karbach, Ger. Offen. 4,110,484, 01 Oct 1992, to Bayer

M. Heino, J. Seppaelae, M. Westman, PCT Int. Appl. WO 93 24,574, 09 Dec 1993, to Neste Oy

E. Helfand, Y. Tagami, J. Polym. Sci. Polym. Lett. **9**, 741 (1971)

E. Helfand, Y. Tagami, J. Chem. Phys. **56**, 3593 (1972)

R. Henn, K. Hahn, W. Loth, W. Heckmann, U. Blumenstein, H.-D. Schwaben, K.-H., Wassmer, H. Tatzel, U.S. Patent 5,525,636, 11 Jun 1996, to BASF
D.E. Henton, U.S. Patent 4,218,544, 19 Aug 1980, to Dow Chemical
D.E. Henton, Europ. Pat. Appl. 056,246; 056,247, 21 July 1982, to Dow Chemical
D.E. Henton, U.S. Patent 4,439,582, 27 Mar 1984, to Dow Chemical
D.E. Henton, A. Chen, P.J. Moses, B.S. Ehrlich, D.E. Beyer, PCT Int. Appl. WO 92 20,744, 26 Nov 1992, to Dow Chemical
D.E. Henton, D.M. Naeger, F.M. Plaver, U.S. Patent 5,219,933, 15 June 1993, to Dow Chemical
L.R. Hepp, Europ. Pat. Appl. 113,096, 11 July 1984, to General Electric Co.
S.J. Hepworth, J.D. Seddon, J.E. Priddle, Ger. Offen. 2,011,608, 01 Oct 1970, to ICI
J.A. Herbing, I.O. Salyer, U.S. Patent 3,092,607, 4 June 1963, to Monsanto Chemical Co.
H. Herbst, K. Hoffmann, R. Pfaendner, F. Sitek, *Proceed. of National Seminar on Emerging Trends in Plastic Recycling Technologies and Waste Management*, Goa, 27–28 May 1995
H. Herbst, K. Hoffmann, R. Pfaendner, H. Zweifel, in *Frontiers in the Science and Technology of Polymer Recycling*, ed. by G. Akovali, C.A. Bernardo, J. Leidner, L.A. Utracki, M. Xanthos. NATO ASI Series, vol. 351 (Kluver, Dordrecht, 1998)
O. Herrmann-Schoenherr, H.T. Land, Eur. Pat. Appl. 568,917, 10 Nov 1993, to Hoechst
O. Herrmann-Schoenherr, H.T. Land, Jap. Pat. 60 57,160, 01 Mar 1994, to Hoechst
A. Heslinga, P.J. Greidanus, U.S. Patent 4,332,917, 01 June 1982; U.S. Patent 4,338,417, 06 June 1982, to Nederlandse Centrale Organisatie voor Toegepast-Natuurwetenschappelijk Onderzoek
H. Heywang, Ger. Offen. 1,221,323, 21 July 1966, to Siemens and Halske
T. Hikasa, H. Mendori, T. Hamanaka, T. Igarashi, Y. Shida, U.S. Patent 5,308,700, 03 May 1994, to Sumitomo Chem.
R.W. Hill, R.P. Anderson, S.V. Scroggins, U.S. Patent 3,539,662, 10 Nov 1970, to Gulf R&D Co.
S. Himei, M. Takine, K. Akita, Jap. Pat. 000,949, 18 Jan 1967, to Kanegafuchi Chem.
M.H. Hindi, M.W. Woods, N. Harry, T. Wakida, U.S. Patent 5,300,552, 05 Apr 1994, to Phillips
K. Hinselmann, V. Ladenberger, K. Bronstert, G. Fahrbach, Ger. Offen. 2,137,274, 08 Feb 1973, to BASF
M. Hirai, T. Tatsuda, T. Yoshida, Europ. Pat. Appl. 284,086, 28 Sept 1988, to Sumitomo Naugatuck
M. Hirai, T. Tatsuda, T. Yoshida, U.S. Patent 4,855,355, 08 Aug 1989, to Sumitomo Naugatuck
M. Hirai, T. Tatsuda, T. Yoshida, Can. Pat. 1,307,863, 22 Sept 1992, to Sumitomo Naugatuck
T. Hirai, N. Amano, SPE Techn. Pap. **39**, 1256 (1993)
T. Hiri, H. Kotama, Jap. Pat. 005,224, 09 Feb 1971, to Toray Industries
Hitachi Chemical Company, Ltd., Jap. Pat. 052,348, 28 Mar 1983
N. Hizasumi, T. Uehara, H. Ohba, K. Hirose, Europ. Pat. Appl. 336,680, 11 Oct 1989, to Kureha Chem.
K.-S. Ho, K. Levon, U.S. Patent 5,391,622, 21 Feb 1995, to Neste Oy
S.Y. Hobbs, R.C. Bopp, V.H. Watkins, Polym. Eng. Sci. **23**, 380 (1983)
A. Hodzic, in *Natural Fibers, Biopolymers and Biocomposites*, ed. by A.K. Mohanty, M. Misra, L.T. Drzal (Taylor and Francis, Boca Raton, 2005)
S.M. Hoenig, D.P. Flores, S.P. Ginter, U.S. Patent 4,474,928, 02 Oct 1984, to Dow Chemical
H. Hoenl, A. Jung, P. Klaerner, B. Ostermayer, S. Seelert, Europ. Pat. Appl. 545,181, 09 June 1993, to BASF
G.H. Hofmann, U.S. Patent 5,352,735, 04 Oct 1994, to E. I. du Pont
G.H. Hofmann, Plast. Technol. **55** (1998)
J.P. Hogan, R.L. Banks, U. S. Pat. Appl. 333,576, 27 Jan 1953, to Phillips
J.P. Hogan, R.L. Banks, Belg. Pat. 530,617, 24 Jan 1955, to Phillips
T. Hoki, N. Miura, U.S. Patent 4,652,590, 24 Mar 1987, to Dow Chemical Co.
G. Holden, L.H. Gouw, Europ. Pat. Appl. 004,685, 17 Oct 1979, to Shell.
G. Holden, D.R. Hansen, Europ. Pat. Appl. 308,001, 22 Mar 1989, to Shell

W.D. Holland, J.M. Schmitt, R.M. Griffith, Ger. Offen. 2,018,606, 29 Oct 1970, to American Cyanamid

P.A. Holmes, A.B.. Newton, F.M. Willmouth, Europ. Pat. Appl. 052,460, 26 May 1982, to ICI

F.F. Holub, U.S. Patent 4,908,418; 13 Mar 1990, to General Electric Co.

F.F. Holub, G.A. Mellinger, U.S. Patent 4,258,155, 24 Mar 1981, to General Electric Co.

F.F. Holub, J.A. Rock, Europ. Pat. Appl. 325,718; 325,719, 02 Aug 1989, to General Electric Co.

R. Holzer, K. Mehnert, Ger. Offen. 1,145,792, 21 Mar 1963, to Hoechst

R. Holzer, K. Mehnert, U.S. Patent 3,262,292, 1966, to Hoechst

S.M. Hong, B.C. Kim, K.U. Kim, I.J. Chung, Polym. J. **24**, 727 (1992)

M. Hongo, H. Shigemitsu, N. Yamamoto, A. Yanagase, Europ. Pat. Appl. 249,964, 23 Dec 1987, to Mitsubishi Rayon

A. Honkanen, M. Arina, R. Holstii, Finn. Pat. 064,805, 30 Sept 1983, to Neste Oy

J.F. Hoover, Europ. Pat. Appl. 524,731, 27 Jan 1993, to General Electric Co.

K. Horiuchi, T. Kamiya, Jap. Pat. 001,639, 16 Jan 1974, to Teijin Chem.

Y. Hoshi, A. Kaneko, Jap. Pat. 014,220, 17 Sept 1962, to Kureha Chemical Works

Y. Hoshi, A. Kaneko, Brit. Pat. 928,799, 12 June 1963, to Kureha Chemical Works

Y. Hoshi, A. Kaneko, Belg. Pat. 635,851, 01 Feb 1965, to Kureha Chemical Works

N. Hosoi, Jap. Pat. 03 167,258, 19 July 1991, to Sumitomo Electric Industries

R.J. Hoxmeier, U.S. Patent 5,276,095, 04 Jan 1994, to Shell Oil

H.-W. Hsu, S.-C. Liuo, S.-F. Jiang, J.-H. Chen, H.-M. Lin, H.-D. Hwu, M.-L. Chen, M.-S. Lee, T. Hu, U.S. Patent 5,308,897, 14 Jan 1994, to Industrial Technology Research Institute, Taiwan

G.-H. Hu, H. Cartier, Intl. Polym. Process. **13**, 111 (1998)

J. Huang, GP. Kipouras, U.S. Patent 8,273,268, 25 Sept 2012, to PolyOne Corp.

H.H. Hub, G. Blinne, H. Reimann, P. Neumann, G. Schaefer, Ger. Offen. 3,444,339, 05 June 1986, to BASF

Huels., Brit Pat., 1,247,068, 22 Sept 1971

T. Huff, U.S. Patent 4,087,485, 02 May 1978, to Exxon

T. Huff, Europ. Pat. Appl. 015,066, 03 Sept 1980, to Exxon

M.L. Huggins, G. Natta, V. Desreux, H. Mark, J. Polym. Sci. **56**, 153 (1962)

M.L. Huggins, G. Natta, V. Desreux, H. Mark, Pure Appl. Chem. **12**, 645 (1966)

M.A. Huneault, Z.H. Shi, L.A. Utracki, “Polyblends-‘93,” *NRCC/IMI Symposium*, Boucherville, 26–27 Oct 1993

M.A. Huneault, M.F. Champagne, A. Luciani, J.-F. Hetu, L.A. Utracki, *Polymer Processing Society European Meeting*, Stuttgart, 25–28 Oct 1995a

M.A. Huneault, Z.H. Shi, L.A. Utracki, Polym. Eng. Sci. **35**, 115 (1995b)

M.J. Hurwitz, W.G. DeWitt III, Ger. Offen. 2,017,398, 22 Oct 1970, to Rohm & Haas

W.-F. Hwang, D.R. Wiff, C. Verschoore, G.E. Price, Polym. Eng. Sci. **23**, 784 (1983)

C.C. Hwo, U.S. Patent 5,369,181, 29 Nov 1994, to Shell Oil

C.C. Hwo, U.S. Patent 5,585,411, 17 Dec 1996, to Shell Oil

I.G. Farbenindustrie, Brit. Pat. 505,651, 08 May 1939

S. Ichinoe, Jap. Pat. 002,149, 31 Jan 1967, to Kureha Chem.

F. Ide, K. Deguchi, Jap. Pat. 035,175, 11 Nov 1971, to Mitsubishi Rayon

F. Ide, K. Okano, K. Deguchi, Jap. Pat. 023,645, 01 July 1972, to Mitsubishi Rayon

Idemitsu Kosan Co., Jap. Pat. 057,456, 05 Apr 1983

Idemitsu Petrochemical Company, Limited, Jap. Pat. 096,640, 08 June 1983

Idemitsu Petrochemical Company, Limited, Jap. Pat. 027,947, 14 Feb 1984

H. Ikeda, S. Aotani, K. Takahashi, K. Arai, Jap Pat. 001,561, 08 Jan 1976, to Japan Synthetic Rubber

M. Ikeguchi, Y. Nagata, Jap. Pat. 083,741, 12 Aug 1974, to Nippon Steel Chem.

K. Ikura, H. Shigemori, N. Nawa, Y. Sugimura, Jap. Pat. 041,444, 18 Apr 1974, to Teijin Chem.

C.S. Ilendra, N. Bortnick, R.K. Graham, W.J. Work, U.S. Patent 5,128,410, 07 July 1992, to Rohm & Haas

C.S. Ilendra, N. Bortnick, W.J. Work, U.S. Patent 5,229,456, 20 July 1993, to Rohm and Haas

G. Illing, U.S. Patent 3,536,680, 1970; Ger. Offen. 1,900,179, 30 July 1970, to Werner & Pfleiderer

G. Illing, Ger. Offen. 2,140,041, 22 Feb 1973, to Werner & Pfleiderer

H. Imabayashi, K. Ishikawa, Y. Ishida, U.S. Patent 5,306,790, 26 Apr 1994, to Idemitsu Petrochem.

M. Imaizumi, R. Fujihira, J. Suzuki, K. Yoshikawa, R. Ishioka, *14th International Polymer Processing Society Meeting, PPS-14*, Yokohama, 08–12 June 1998

B. Imre, B. Pukanszky, Europ. Polym. J. (2013, in press), **49**, 1215

Industrial Technology Institute, Japan, *Japan New Materials Report*, 9/10, 2 (1996)

A.F. Ingulli, H.L. Alter, So. Afric. Pat. 6,806,262, 06 Mar 1969, 10 Dec 1970, to Uniroyal

A.F. Ingulli, H.L. Alter, Ger. Offen. 2,025,467, 10 Dec 1970, to Uniroyal

H.H. Irving, U.S. Patent 3,010,936, 1961, to Borg Warner Chemicals

A.I. Isayev, U.S. Patent 5,021,475, 1991, to University of Akron

A.I. Isayev, U.S. Patent 5,260,380, 1993, to University of Akron

A.I. Isayev, U.S. Patent 5,283,114, 01 Feb 1994, to University of Akron

A.I. Isayev, S. Swaminathan, U.S. Patent 4,835,047, 30 May 1989, to University of Akron

H. Ishida, H. Kabaya, U.S. Patent 5,292,789, 08 Mar 1994, to GE Plastics Japan

S. Ishida, J. Masamoto, Jap. Pat. 018,144, 18 Feb 1974; Jap. Pat. 040,346, 15 Apr 1974, to Asahi Chem.

S. Ishida, K. Sato, Jap. Pat. 035,188, 11 Nov 1970, to Asahi Chem.

T. Ishihara, U.S. Patent 4,814,393, 21 Mar 1989, to General Electric Co.

N. Ishihara, T. Seimiya, M. Kuramoto, M. Uoi, Macromolecules **19**, 2464 (1986)

A. Ishio, K. Kobayashi, Europ. Pat. Appl. 463,738, 02 Jan 1992, to Toray

K. Ishioka, Jap. Pat. 03 217,448, 25 Sept 1991, to NOK Corp.

H. Ito, Y. Kawachi, M. Morimoto, Europ. Pat. Appl. 379 154, 25 July 1990, to Mitsubishi Rayon

IUPAC (International Union of Pure and Applied Chemistry), Pure Appl. Chem. **40**, 479 (1974)

IUPAC, Pure Appl. Chem. **48**, 373 (1976)

IUPAC, Pure Appl. Chem. **53**, 733 (1981)

IUPAC, J. Polym. Sci. Polym. Lett. Ed. **22**, 57 (1984)

IUPAC, Pure Appl. Chem. **57**, 149 (1985a)

IUPAC, Pure Appl. Chem. **57**, 1427 (1985b)

IUPAC, Pure Appl. Chem. **59**, 691 (1987)

IUPAC, Pure Appl. Chem. **61**, 1769 (1989a)

IUPAC, Pure Appl. Chem. **61**, 769 (1989b)

IUPAC, Pure Appl. Chem. **61**, 234 (1989c)

IUPAC, Pure Appl. Chem. **68**, 2287 (1996)

IUPAC, Pure Appl. Chem. **73**, 845 (2001)

IUPAC, Pure Appl. Chem. **74**, 1921 (2002)

IUPAC, Pure Appl. Chem. **84**, 2167 (2012)

K. Iwanaga, Y. Tanaka, K. Takemoto, Jap. Pat. 2,077,429, 16 March 1990, to Tosoh Corp.

K. Iwanami, K. Kitano, K. Narukawa, K. Aoki, Y. Yagi, M. Sakuma, T. Mikami, M. Esaki, F. Kato, Europ. Pat. Appl. 333 518, 20 Sept 1989, to Nippondenso

K. Iwanami, K. Kitano, Y. Yagi, T. Mikami, Europ. Pat. Appl. 382,559, 16 Aug 1990, to Tonen Sekiyu Kagaku

H. Iwata, T. Otani, S. Arakawa, S. Deguchi, Jap. Pat. 157,153, 11 Dec 1979, to Mitsubishi Rayon

S.I. Izawa, A. Nakanishi, Jap. Pat. 22,590, 22 Mar 1973, to Asahi-Dow

S.I. Izawa, K. Sotoyama, Y. Sugawara, Jap. Pat. 39,015; 39,017; 39,018, 21 Nov 1973a, to Asahi-Dow

S.I. Izawa, J. Sugiyama, N. Kosaka, Can. Pat. 1,144,680, 12 Apr 1983, to Asahi-Dow

S.I. Izawa, K. Toyama, K. Harada, Y. Sugawara, U.S. Patent 3,781,382, 25 Dec 1973b, to Asahi-Dow

M. Izumi, M. Kajioka, T. Yamagishi, K. Yoshino, T. Wakui, Europ. Pat. Appl. 470,557, 12 Feb 1992, to Kawasaki Steel Corp.

G.S. Jack, M.J. El-Hibri, W.E. Kelly, S.R. Patel, Europ. Pat. Appl. 535,785, 07 Apr 1993, to Amoco Corp.
H. Jadamus, W. Ribbing, R. Feinauer, W. Schaefer, Ger. Offen. 3,442,273, 22 May 1986 to Hüls
H. Jadamus, W. Ribbing, R. Feinauer, W. Schaefer, U.S. Patent 4,656,220, 07 Apr 1987 to Hüls
H. Jager, E.J. Vorenkamp, G. Challa, Polym. Commun. **24**, 290 (1983)
A.L. Jankens, Belg. Pat. 625,004, 20 May 1963, to Dow Chemical
Japan Synthetic Chem. Ind., Fr. Pat. 2,000,728, 04 Mar 1971
Japan Synthetic Rubber Co., Jap. Pat. 053,553, 27 Mar 1985; Jap. Pat. 079,060, 04 May 1985; Jap. Pat. 086,151, 15 May 1985; Jap. Pat. 108,454, 13 June 1985
K.B. Jarrett, A.A. Williams, Brit. Pat. 850,947, 12 Oct 1960, to ICI
M. Jayabalan, J. Appl. Polym. Sci. **27**, 43 (1982)
M. Jayabalan, T. Balakrishnan, J. Cellular. Plast. **21**(6), 399 (1985)
D. Jean, G. Devauchelle, Fr. Pat. 2,682,960, 30 Apr 1993, to Labinal
A.D. Jenkins, J. Kahovec, P. Kratochvil, I. Mita, I.M. Papisov, L.H. Sperling, R.F.T. Stepto, *Source-Based Nomenclature for Non-Linear Macromolecules and Macromolecular Assemblies*, draft report for the IUPAC Commission on Macromolecular Nomenclature, May 1993
B.J. Jody, B. Arman, D.E. Karvelas, J.A. Pomykala, E.J. Daniels, U.S. Patent 5,653,867, 1997
R.G. Jones (ed.) *The Purple Book*, 2nd edn. (RSC Publishers, 2009), Cambridge, UK
W.J. Jones, R.A. Mendelson, Europ. Pat. Appl. 135,492, 27 Mar 1985, to Monsanto
M.E.B. Jones, E. Nield, C.R. Hart, U.S. Patent 3,562,200, 09 Feb 1971, to ICI
T.J.M. Jongeling, Eur. Pat. Appl. 538,939, 28 Apr 1993, to DSM
T.C. Jordan, J.L. Webb, Europ. Pat. Appl. 497,004, 05 Aug 1992, to General Electric Co.
T.C. Jordan, J.L. Webb, U.S. Patent 5,334,672, 02 Aug 1994, to General Electric Co.
J. Jose, P. Jyotishkumar, S.M. George, S. Thomas, in *Recent Developments in Polymer Recycling*, ed. by A. Fainleib, O. Grigoryeva (Transworld Research Network, Trivandrum, 2011)
K. Kabuki, K. Matsuno, O. Tanaka, Jap. Pat. 73 055,948, 06 Aug 1973, to Tokyo Shibaura Electric.
G. Kakefuda, T. Ito, Jap. Pat. 034,904, 13 Oct 1971, to Hitachi Chemical
T. Kakizaki, S. Horie, T. Mizutani, Jap Pat. 117,555, 12 Sept 1979a
T. Kakizaki, S. Horie, H. Sano, Jap Pat. 146,887, 16 Nov 1979b, to Mitsubishi Petrochem.
M.R. Kamal, G. Lohfink, L. Arghyris, S. Hozhabr-Ghelichi, PCT Int. Appl. 006,837, 30 Apr 1992, to McGill University
K. Kamata, R. Handa, M. Hongo, Jap. Pat. 121,855, 21 Nov 1974, to Mitsubishi Rayon
K. Kamata, Y. Kinoshita, M. Hongo, H. Nakanishi, Jap. Pat. 129,246, 11 Nov 1978a, to Mitsubishi Rayon
K. Kamata, I. Sasaki, M. Hongo, Jap. Pat. 137,251, 30 Nov 1978b, to Mitsubishi Rayon
K. Kamata, Y. Kinoshita, H. Nakanishi, Jap. Pat. 000,055, 05 Jan 1979, to Mitsubishi Rayon
K. Kamata, I. Sasaki, H. Mori, Jap. Pat. 003,471, 11 Jan 1980, to Mitsubishi Rayon
R.P. Kambour, U.S. Patent 3,639,508, 1970, to General Electric Co.
R.P. Kambour, Europ. Pat. Appl. 263,378, 13 Apr 1988, to General Electric Co.
W. Kaminsky, Pure Appl. Chem. **70**, 1229 (1998)
W. Kaminsky, K. Kulper, H.H. Brintzinger, F.R.W.P. Wild, Angew. Chem. Int. Ed. Engl. **24**, 507 (1985)
W. Kaminsky, R. Engehausen, K. Zoumis, W. Spaleck, J. Rohrmann, Makromol. Chem. **193**, 1643 (1992)
M. Kamosaki, S. Tokuhara, M. Kita, N. Nakashima, Jap. Pat. 146,748; 146,753, 20 Dec 1978, to Daicel
R. Kamps, G. Lange, G. Leimann, F. Paul, W. Pfandl, P. Friedemann, Europ. Pat. Appl. 598,213, 25 May 1994, to Siemens
A. Kanai, S. Hata, M. Miura, Jap. Pat. 031,796, 25 Mar 1978, to Mitsubishi Petrochem.
Kanegafuchi Chem. Co., Fr. Pat. 1,499,542, 27 Oct 1967
Kanegafuchi Chem. Co., Jap Pat. 004,642, 11 Jan 1984

F.E. Karasz, W.J. MacKnight, U.S. Patent 5,286,812, 15 Feb 1994, to University of Massachusetts

H.G. Karian (ed.), *Handbook of Polypropylene and Polypropylene Composites* (Marcel Dekker, New York, 2003)

T.P. Karjala, Y.W. Cheung, M.J. Guest, in *Metallocene-Catalyzed Polymers*, ed. by G.M. Benedict, B.L. Goodall (SPE Plastics Design Library, Norwich, 1998)

T. Karna, J. Laakso, T. Niemi, H. Ruohonen, E. Savolainen, H. Lindstrom, E. Virtanen, O. Ikkala, A. Andreatta, U.S. Patent 5,340,499, 23 Aug 1994, to Neste Oy

H. Kasahara, K. Fukuda, H. Suzuki, Europ. Pat. Appl. 046,040, 17 Feb 1982, to Asahi-Dow

T. Kasuya, T. O. Omichi, H. Maehara, Jap. Pat. 011,546, 27 May 1969, to Asahi Chem.

R. Kato, I. Soematsu, T. Mori, Jap. Pat. 003,108, 09 Feb 1967, to Toa Gosei Chem.

T. Katsumata, Jap. Pat. 03 119,048, 21 May 1991, to Polyplastics

T. Katsumata, N. Matsunaga, Europ. Pat. Appl. 519,749, 23 Dec 1992, to Polyplastics

T. Katsumata, N. Matsunaga, Europ. Pat. Appl. 549,338, 30 June 1993, to Polyplastics

T. Katsumata, N. Matsunaga, U.S. Patent 5,378,748, 03 Jan 1995, to Polyplastics

S. Katsura, Jap. Pat. 028,539, 08 Feb 1986, to Mitsubishi Petrochem.

H.S. Kaufman, U.S. Patent 3,105,827, 01 Oct 1963, to Minnesota Mining and Manufacturing

M. Kawai, M. Miyauchi, Jap. Pat. 124,150, 27 Nov 1974, to Teijin Chem.

H. Kawai, T. Munemaru, T. Inoue, R. Kimura, Jap. Pat. 043,539, 21 Nov 1978, to Institute for Production and Development Science

T. Kawaki, A. Amagai, M. Ishikawa, T. Yamada, Y. Hirai, H. Ban, Eur. Pat. Appl. 492,947, 01 July 1992, to Mitsubishi Gas Chem.

T. Kawaki, A. Amagai, M. Ishikawa, T. Yamada, Y. Hirai, H. Ban, U.S. Patent 5,321,097, 14 June 1994, to Mitsubishi Gas Chem.

T. Kawaki, A. Amagai, T. Yamada, H. Harada, H. Ban, U.S. Patent 5,387,652, 07 Feb 1995, to Mitsubishi Gas Chem.

T. Kawauzra, S. Aibe, M. Kawazoe, U.S. Patent 5,679,744, 21 Oct 1997, to The Yokohama Rubber Co., Ltd.

C. Kennedy, *ICI, The Company That Changed Our Lives* (Hutchinson Limited, London, 1986)

A. Képes, Fr. Pat. 1,175,241, 23 Mar 1959, to Soc. anon. des manufacturers des glaces et produits chimiques de Saint-Gobain, Chauny & Cirey

R.J. Kern, U.S. Patent 2,806,015, 10 Sept 1957, to Monsanto Chem.

H. Keskkula, D.A. Maass, K.M. McCreedy, U.S. Patent 4,460,744, 17 July 1984, to Dow Chemical

K. Khait, SPE Techn. Pap. **40**, 3006 (1994)

K. Khait, SPE Techn. Pap. **41**, 2066 (1995)

M.M.K. Khan, R.F. Liang, R.K. Gupta, S. Agarwal, Korea Australia Rheol. J. **17**, 1 (2005)

G.B. Kharas, S.P. Nemphos, Europ. Pat. Appl. 515,203, 25 Nov 1992, to Novacor Chem.

W.N. Kim, C.M. Burns, Polym. Eng. Sci. **28**, 1115 (1988)

W.N. Kim, C.M. Burns, J. Polym. Sci. Polym. Phys. **28**, 1409 (1990)

S.-K. Kim, J.-W. Choi, U.S. Patent 5,747,587, 05 May 1998, to Cheil Industries

B.K. Kim, M.S. Kim, H.M. Jeong, K.J. Kim, J.K. Jang, Angew. Makromol. Chem. **194**, 91 (1992)

H.S. Kim, B.S. Jin, Y.C. Kwon, K. Seong, in *Encyclopaedic Dictionary of Commercial Polymer Blends*, ed. by L.A. Utracki (ChemTec, Toronto, 1994)

K. Kishida, J. Kobayashi, N. Ohsaka, Jap. Pat. 077,858, 26 Nov 1977, to Mitsubishi Rayon

K. Kishida, H. Mori, M. Kaneta, Jap. Pat. 001,246, 09 Jan 1978a, to Mitsubishi Rayon

K. Kishida, H. Mori, H. Fukunaga, H. Nakanishi, Jap. Pat. 018,661, 21 Feb 1978b, to Mitsubishi Rayon

H. Kishikawa, K. Yasuno, S. Kitamura, Ger. Offen. 2,119,376, 11 Nov 1971, to Sumitomo Chem.

T. Kishimoto, Jap. Pat. 059,952, 25 May 1976, to Mitsui Petrochem.

M. Kita, K. Hashimoto, Jap. Pat. 131,043, 13 June 1987, to Daicel Huels

K. Kitamura, Jap. Pat. 002,748, 08 Jan 1986, to Teijin Chem.

N. Kitayama, H. Keskkula, D.R. Paul, Polymer **41**, 8041 (2000a)

N. Kitayama, H. Keskkula, D.R. Paul, Polymer **41**, 8053 (2000b)

N. Kitayama, H. Keskkula, D.R. Paul, Polymer **42**, 3751 (2001)

T. Kobayashi, K. Shinohara, PCT Int. Appl. WO 93 05,107, 18 Mar 1993, to E. I. du Pont

T. Kobayashi, K. Tanaka, Can. Pat. 2,064,301, 29 Sept 1992, to Toray

T. Kobayashi, K. Miyazaki, M. Nakamura, U.S. Patent 5,594,038, 14 Jan 1997; U.S. Patent 5,646,194, 08 July 1997, to Sekisui Chemical

Y. Kobayashi, W. Zheng, E.F. Meyer, J.D. McGervey, A.M. Jamieson, R. Simha, Macromolecules **22**, 2302 (1989)

F.F. Koblitz, R.G. Petrella, A.A. Dukert, A. Christofas, U.S. Patent 3,253,060, 28 Nov 1966, to Pennwalt Chemical

J.E. Kochanowski, U.S. Patent 4,334,030, 08 Jun 1982, to General Electric Co.

T. Kodaira, H. Ishida, H. Kabaya, U.S. Patent 5,310,821, 10 May 1994, to GE Plastics Japan

H. Koenig, G. Wick, F. Thomczik, A. Thielemann, Ger. Offen. 1,165,255, 12 May 1964, to Hüls

P. Koetzing, K. Diebold, Kunststoffe **85**, 2046 (1995)

M.I. Kohan, U.S. Patent 4,351,916, 28 Sept 1982; Europ. Pat. Appl. 047,529, 17 Mar 1982, to E. I. du Pont

B. Köhler, W. Rüsseler, B. Sarabi, K. Reinking, F. Jonas, Europ. Pat. Appl. 510,475, 28 Oct 1992, to Bayer

H. Kojima, A. Taoka, K. Takiguchi, Jap. Pat. 027,905, 11 Sept 1970, to Mitsubishi Monsanto Chem.

M. Kojima, M. Tanahashi, Jap. Pat. 014,710, 02 May 1972, to Chisso

T. Kokkonen, T. Karna, J. Laakso, P. Nuholm, J.-E. Sterholm, H. Stubb, U.S. Patent 5,279,769, 18 Jan 1994, to Neste Oy

H. Komoto, Jap. Pat. 020,243, 28 Sept 1972, to Asahi Chem.

M. Kondo, K. Tominari, Jap. Pat. 079,260, 11 Apr 1987, to Mitsui Petrochem.

C.E. Koning, J.A.J. Kingma, L. Prinsen, Europ. Pat. Appl. 365,101, 25 Apr 1990, to Stamicarbon

C.E. Koning, H.J. Vroomans, Europ. Pat. Appl. 463,238, 02 Jan 1992, to Stamicarbon

E. Konrad, E. Tschunkur, U.S. Patent 1,973,000, 1934, to I. G. Farbenindustrie

R.M. Kopchik, U.S. Patent 4,255,322, 10 Mar 1981, to Rohm & Haas

A. Koshimo, Jap. Pat. 025,053, 02 Apr 1973, to Unitika

A. Koshimo, H. Sakata, T. Okamoto, H. Hasegawa, Jap. Pat. 051,945, 051,946, 051,947, 051,948, 21 July 1973, to Unitika

A. Koshirai, A. Nakata, N. Yamamoto, Europ. Pat. Appl. 468,772, 11 Mar 1992, to Mitsubishi Rayon

A. Koshirai, A. Nakata, N. Yamamoto, U.S. Patent 5,288,798, 22 Feb 1994, to Mitsubishi Rayon

T. Kotaka, *International Symposium on Elongational Flow of Polymeric Systems*, Yamagata U., Yonezawa, 13–15 June 1998

K. Kotama, Jap. Pat. 009,740, 23 Mar 1972, to Mitsubishi Rayon

A.M. Kotliar, J. Polym. Sci. Macromol. Rev. **16**, 367 (1981)

K. Koyama, T. Takahashi, Y. Naka, J. Takimoto, *13th International Annual Meeting* (Polymer Processing Society, New York, 1997)

S. Kozakura, S. Kuze, K. Tanaka, Europ. Pat. Appl. 496,257; 496,258, 29 July 1992, to Idemitsu Petrochem.

S. Kozakura, S. Kuze, K. Tanaka, U.S. Patent 5,314,949, 24 May 1994, to Idemitsu Petrochem.

M. Kozlowski, Polym. Networks Blends **4**, 39 (1994)

M. Kozlowski, Polym. Networks Blends **5**, 163 (1995)

E.O. Kraemer, W.D. Lansing, J. Am. Chem. Soc. **55**, 4319 (1933)

N.P. Krasnikova, E.V. Kotova, E.P. Plotnikova, M.P. Zabugina, G.V. Vinogradov, V.E. Dreval, Z. Pelzbauer, Kompoz. Polim. Mater. **21**, 37 (1984)

M. Kraus, I. Katsnelson, M. Heisler, PCT Int. Appl. 018,664, 12 Dec 1991, to Gelman Sci.

H.J. Kress, C. Lindner, L. Morbitzer, H. Peters, K.H. Ott, J. Schoeps, Ger. Offen. 3,514,185, 23 Oct 1986, to Bayer

J. Kressler, N. Higashida, T. Inoue, W. Heckmann, F. Seitz, Macromolecules **26**, 2090 (1993)

R.K. Krishnaswamy, U.S. Patent Appl. 2013006546, Mar 2013

R.K. Krishnaswamy, J. van Walsem, O.P. Peoples, Y. Shabtai, A.R. Padwa, U.S. Patent Appl., June 2013

W. Kuhn, Kolloid Z. **68**, 2 (1930)

W. Kuhnel, P. Spielau, U.S. Patent 4,255,372, 10 Mar 1981, to Dynamit Nobel

V.G. Kulkarni, B. Wessling, Europ. Pat. Appl. 497,514, 05 Aug 1992, to Americhem.

V.G. Kulkarni, B. Wessling, Europ. Pat. Appl. 536,915, 14 Apr 1993, to Americhem.

V.G. Kulkarni, B. Wessling, U.S. Patent 5,290,483, 01 Mar 1994, to Americhem.

H. Kumabe, A. Morimoto, Y. Kitagawa, N. Shiraishi, Fr. Pat. 2,151,639, 25 May 1973, to Japan Synthetic Rubber

A. Kumar, R.K. Gupta, *Fundamentals of Polymer Engineering*, 2nd edn. (Marcel Dekker, New York, 2003)

V. Kumar, N.P. Suh, Polym. Eng. Sci. **30**, 1323 (1990)

V. Kumar, J.E. Weller, R. Murray, SPE Techn. Pap. **41**, 2202 (1995)

J.A. Kuphal, L.M. Robeson, J.G. Santangelo, U.S. Patent 4,940,733, 10 July 1990, to Air Products & Chem.

K. Kyo, Y. Asai, Jap Pat. 129,248, 11 Nov 1978, to Unitika

T. Kyu, Europ. Pat. Appl. 392,763, 17 Oct 1990, to Edison Polym. Innov. Corp.

E.E. La Fleur, R.M. Amici, W.T. Freed, W.J. Work, W.G. Carson, U.S. Patent 5,147,930, 1992, to Rohm & Haas

E.E. La Fleur, R.M. Amici, W.J. Work, U.S. Patent 5,189,097, U.S. Patent 5,322,892, 21 June 1994a, to Rohm & Haas

E.E. La Fleur, R.M. Amici, W.T. Freed, W.J. Work, W.G. Carson, U.S. Patent 5,296,537, 22 Mar 1994b, to Rohm & Haas

E.E. La Fleur, W.J. Work, R.M. Amici, N.M. Bortnick, N.L. Holy, Eur. Pat. Appl. 583,109, 16 Feb 1994c, to Rohm & Haas

F.P. La Mantia (ed.), *Thermotropic Liquid Crystal Polymer Blends* (Technomics, Lancaster, 1993)

S.-Y. Lai, M.S. Edmondson, U.S. Patent 5,408,004, 18 Apr 1995, to Dow Chemical

X.-Y. Lai, D.-F. Zhao, F. Lai, U.S. Patent 5,344,895, 06 Sept 1994, to University of Massachusetts Lowell

R. Langworth, U.S. Patent 3,299,176, 17 Jan 1967, to E. I. du Pont

H.H. Lank, E.L. Williams, *The Du Pont Canada History* (Du Pont Canada, Montréal, 1982)

O.E. Larsen, Can. Pat. 1,120,630, 23 Mar 1982, to Phillips

R.L. Lauchlan, Ger. Offen. 2,035,147, 28 Jan 1971, to Uniroyal

R.L. Lauchlan, G.A. Shaw, Fr. Pat. 2,011,783, 06 Mar 1970, to Uniroyal

R.L. Lauchlan, H.E. Snodgrass, Ger. Pat. 2,312,971, 27 Sept 1973, to Uniroyal

M.K. Laughner, PCT Int. Appl. WO 93 19,128, 30 Sept 1993; U.S. Patent 5,262,476, 16 Nov 1993, to Dow Chemical

M.K. Laughner, U.S. Patent 5,286,790, 15 Feb 1994, to Dow Chemical

M.K. Laughner, C.P. Bosnyak, B.N. Herron, PCT Int. Appl. 003,504, 05 Mar 1992, to Dow Chemical

D. Lausberg, C. Taubitz, M. Knoll, Ger. Offen. 3,617,070, 26 Nov 1987, to BASF

R.E. Lavengood, A.F. Harris, A.R. Padwa, Europ. Pat. Appl. 202,214, 20 Nov 1986, to Monsanto

R.E. Lavengood, R. Patel, A.R. Padwa, U.S. Patent 4,777,211, 11 Oct 1988, to Monsanto

A. Lazzeri, C.B. Bucknall, J. Mater. Sci. **28**, 6788 (1993)

G.F. Lee Jr., U.S. Patent 4,123,410, 31 Oct 1978; U.S. Patent 4,128,602; 4,128,603; 4,128,604; 05 Dec 1978, to General Electric Co.

G.F. Lee Jr., U.S. Patent 4,143,095, 06 Mar 1979, to General Electric Co.

G.F. Lee Jr., U.S. Patent 4,242,263, 39 Dec 1980, to General Electric Co.

G.F. Lee Jr., U.S. Patent 4,311,633, 19 Jan 1982, to General Electric Co.

G.F. Lee Jr., U.S. Patent 4,383,082, 10 May 1983, to General Electric Co.

G.F. Lee Jr., Europ. Pat. Appl. 133,487, 27 Feb 1985, to General Electric Co.

G.F. Lee Jr., U.S. Patent 4,972,021, Nov 20, 1990, to General Electric Co.

G.F. Lee Jr., U.S. Patent 5,324,782, 28 June 1994, to General Electric Co.

S.-T. Lee, SPE Techn. Pap. **42**, 1948 (1996)

S.-T. Lee, U.S. Patent 5,428,093, 27 June 1995, to Sealed Air Corp.

Y.S. Lee, K.H. Char, Macromolecules **27**, 2603 (1994)

Y.C. Lee, Q.A. Trementozzi, Europ. Pat. Appl. 002,961, 11 July 1979, to Monsanto

Y.C. Lee, Q.A. Trementozzi, Europ. Pat. Appl. 007,931, 20 Feb 1980; U.S. Patent 4,223,096, 16 Sept 1980, to Monsanto

Y.C. Lee, Q.A. Trementozzi, U.S. Patent 4,305,869, 1981, to Monsanto

Y.C. Lee, Q.A. Trementozzi, U.S. Patent 4,341,695, 27 July 1982, to Monsanto

R.W. Lee, M.S. Ott, C.O. Castro, U.S. Patent 5,281,670, 25 Jan 1994, to Shell Oil

M.-H. Lee, C. Tzoganakis, C.B. Park, Polym. Eng. Sci. **38**, 1112 (1998)

J.P. Lehane Jr., U.S. Patent 3,137,672, 16 June 1964, to Hercules Powder

R. Leibler, W. Ringenberg, Ger. Offen. 3,518,538, 27 Nov 1986, to Roehm

E. Leitz, D. Wittmann, K.-H. Ott, A. Karbach, Ger. Offen. 4,114,589, 05 Nov 1992, to Bayer

H.J. Leugering, H. Schaum, So. Afric. Pat. 004,328, 08 Jan 1970, to Hoechst

H. Li, Y. Yang, R. Fujitsuka, T. Ougizawa, T. Inoue, Polymer **40**, 927 (1999a)

H.-L. Li, Y. Ujihira, A. Nanasawa, Y.C. Jean, Polymer **40**, 349 (1999b)

F. Li, T.J. Coffy, Daumerie, U.S. Patent 8,268,913, 18 Sept 2012 to Fina Technology

Y.F. Liang, U.S. Patent 4,708,983, 24 Nov 1987, to Phillips

Y.F. Liang, U.S. Patent 4,889,898, 26 Dec 1989, to Plastics Engineering

R. Liang, R.K. Gupta, SPE ANTEC **3**, 2753 (2001)

R. Liang, R.K. Gupta, SPE ANTEC **3**, 2948 (2002)

Z. Liang, H.L. Williams, J. Appl. Polym. Sci. **43**, 379–392 (1991)

H. Liang, B.D. Favis, Y.S. Yu, A. Eisenberg, Macromolecules **32**, 1637 (1999)

M. Lieberman, U.S. Patent 5,424,013, 13 June 1995

B.E. Liebermann, U.S. Patent 5,354,621, 11 Oct 1994, to Beltec International

S.-C. Lin, S. Burks, *Optimization of PVDF Performance via Polymer Blends*, SPI Fluoropolymer Conference, Oct 1993

C. Lindner, V. Damrath, K.E. Piejko, K.H. Ott, Ger. Pat. Appl. 3,822,667, 11 Jan 1990; Europ. Pat. Appl. 349,845, 10 Jan 1990, to Bayer

S.E. Lindsey, G.B. Street, Synth. Met. **10**, 67 (1985)

C.R. Lindsey, D.R. Paul, J.W. Barlow, J. Appl. Polym. Sci. **26**, 1 (1981)

D.W. Liou, Y.C. Sun, Ger. Offen. 4,311,436, 21 Oct 1993, to Dow Chem.

P.Y. Liu, PCT Int. Appl. 003,222, 30 Sept 1982, to General Electric Co.

P.Y. Liu, Ger. Offen. 3,300,855; 3,300,857, 11 Aug 1983, to General Electric Co.

P.Y. Liu, U.S. Patent 4,424,303, 03 Jan 1984; PCT Intl. Appl. 001,164, 29 Mar 1984; Europ. Pat. Appl. 119,533, 26 Sept 1984, to General Electric Co.

P.Y. Liu, H.F. Giles Jr., U.S. Patent 4,629,760, 16 Dec 1986, to General Electric Co.

J.H.G.M. Lohmeijer, J. Bussink, J.W.M. Noordermeer, U.S. Patent 4,618,637, 21 Oct 1986, to General Electric Co.

J.V. Long, J. Gagliani, U.S. Patent 4,621,015, 04 Nov 1986

Lonza Elektrizitätswerke & Chem. Fabriken, Swiss Pat. 253,413; 253,414, 01 Nov 1948

Lonza Limited, Brit. Pat. 964,578, 02 July 1964

G.L. Loomis, R.J. Statz, Europ. Pat. Appl. 101,833, 07 Mar 1984, to E. I. du Pont

G.L. Loomis, R.J. Statz, U.S. Patent 4,613,533, 1986, to E. I. du Pont

A.-V. Lourenço, Compt. Rend. **49**, 813 (1859)

A. Luciani, L.A. Utracki, Intl. Polym. Process. **6**, 299–309 (1996)

A. Luciani, M.F. Champagne, L.A. Utracki, Polym. Network Blends **6**(41), 51 (1996)

A. Luciani, M.F. Champagne, L.A. Utracki, J. Polym. Sci. B Polym. Phys. Ed. **35**, 1393 (1997)

A. Lund, L. Agren, PCT Int. Appl. 000,548, 07 Jan 1993, to Uponor Innovation

A. Lustiger, Can. Pat. Appl. 2,083,664, 21 June 1993, to Exxon

A. Lustiger, C.N. Marzinsky, R.R. Mueller, SPE Techn. Pap. **44**, 1506 (1998)

J. Lyngaae-Jørgensen, L.A. Utracki, Makromol. Chem. Macromol. Symp. **48/49**, 189 (1991)

J. Lyngaae-Jørgensen, K. Lunde Rasmussen, E.A. Chtcherbakova, L.A. Utracki, Polym. Eng. Sci. **39**, 1060 (1999)

J.M. Machado, U.S. Patent 5,175,210, 29 Dec 1992; U.S. Patent 5,369,180, 29 Nov 1992, to Shell Oil

J.M. Machado, U.S. Patent 5,210,137, 11 May 1993, to Shell Oil

P. Maj, P. Blondel, Europ. Pat. Appl. 550,308, 07 July 1993, to Elf Atochem.

Y. Makabe, T. Hatsu, Y. Yamamoto, Jap. Pat. 03 126,752, 29 May 1991, to Toray

K. Makino, I. Umeda, K. Sugiura, Jap. Pat. 016,943, 24 Jan 1986, to Japan Synthetic Rubber

L.M. Maresca, S.J. Shafer, U.S. Patent 4,788,249, 29 Nov 1988, to General Electric Co.

L.M. Maresca, M. Matzner, L.M. Robeson, U.S. Patent 4,250,279, 10 Feb 1981, to Union Carbide Corp.

H. Mark, in *ACS Book Series: Profiles, Pathways, and Dreams*, ed. by J.I. Seeman (ACS, Washington, DC, 1993)

G. Marrucci, G. Ianniruberto, Phil. Trans. R. Soc. Lond. A **361**, 677 (2003)

O. Martin, L. Averous, Polymer **42**, 6209 (2001)

R.J. Martinovitch, R.P. March, U.S. Patent 3,074,616, 22 Jan 1963, to Phillips

C.S. Martins, R. Faez, M.C. Rezende, M.A. De Paoli, J. Appl. Polym. Sci. **101**, 681 (2006)

E. Martuscelli, C. Marchetta, L. Nicolais, *Future Trends in Polymer Science and Technology — Polymers: Commodities or Specialties?* (Technomics, Lancaster, 1987)

T. Maruyama, Y. Mizuno, Europ. Pat. Appl. 388,308, 16 May 1990, to Sumitomo Chem.

H. Maruyama, Y. Shinagawa, K. Nishida, O. Kakishita, Jap. Pat. 093,459, 05 Aug 1977, to Mitsubishi Plastics

W.C. Mast, C.E. Rehberg, T.J. Dietz, C.H. Fisher, Ind. Eng. Chem. **36**, 1022 (1944)

M. Mathos, Master thesis, Ecole Polytechnique de Montréal, 1993

M. Matner, E. Schwinum, L. Mott, U.S. Patent 4,001,163, 04 June 1977, to Monsanto

Y. Matsuda, Jap. Pat. 007,579, 1960, to Dainippon Celluloid

Y. Matsuda, T. Kinoshita, H. Marusawa, M. Saito, Jap. Pat. 05,384, 1960a, to Dainippon Celluloid

Y. Matsuda, T. Kinoshita, H. Marusawa, S. Yabumoto, T. Fujii, Jap. Pat. 06,135, 1960b, to Dainippon Celluloid

A. Matsuda, S. Shimizu, S. Abe, U.S. Patent 4,247,652, 27 Jan 1981, to Mitsui Petrochemical Ind.

A. Matsuda, S. Shimizu, S. Abe, U.S. Patent 4,212,787, 15 July 1988, to Mitsui Petrochemical Ind.

M. Matsukane, C. Azo, Jap. Pat. 054,160, 30 July 1973, to Teijin Chemicals

H. Matsunaga, S. Nakashio, K. Yonetani, T. Takemura, Jap. Pat. 74 38,954, 11 Apr 1974, to Sumitomo Chem.

H. Matsunaga, Y. Uemura, T. Saito, H. Ishida, Jap. Pat. 057,255, 24 May 1978, to Sumitomo Chem.

T. Matsuura, Y. Katayama, J. Shimada, Jap. Pat. 060,947, 31 May 1978, to Nippon Telegraph & Telephone Public Corp.

K. Matsuzaki, Jap. Pat. 03 0,756, 07 Jan 1991, to Asahi Chem. Co.

F.E. Matthews, Brit. Pat. 016,278, 14 July 1911

F.E. Matthews, Fr. Pat. 459,134, 27 Aug 1913

F.H.J. Maurer, J.H.M. Palmen, H.C. Booij, Rheol. Acta **24**, 243 (1985)

M. Mawatari, T. Tetsuo, S. Tsuchikawa, S. Kimura, Europ. Pat. Appl. 244,090, 04 Nov 1987, to Japan Synthetic Rubber

J. Mayumi, H., Omori, Europ. Pat. Appl. 268,981, 01 June 1988, to Mitsubishi Petrochem.

F.B. McAndrew, Ger. Pat. 2,051,028, 29 Apr 1971, to Celanese Corp.

S.P. McCarthy, R.A. Gross, W. Ma, U.S. Patent 5,883,199, 1999

W.J. McCracken, J. Cellular. Plast. **20**(2), 150 (1984)

J.E. McCready, U.S. Patent 3,947,403, 30 Mar 1976, to Goodyear Tire and Rubber

T.W. McCullough, B.D. Stevens, U.S. Patent 4,515,907, 07 May 1985, to Dow Chemical

J.E. McGrath, M. Matzner, U.S. Patent 3,655,822, 11 Apr 1972, to Union Carbide Corp.

G.H. McKee, F. Haaf, J. Hambrecht, K. Benker, R. Stephan, H. Breurer, Ger. Offen. 3,113,627, 21 Oct 1982, to BASF

A.K. Mehta, M.C. Chen, U.S. Patent 5,358,792, 25 Oct 1994, to Exxon

P. Meier, Ger. Pat. 4,139,468, 03 June 1993, to Ems-Inventa

J.L. Melquist, U.S. Patent 5,189,115, 23 Feb 1993, to Amoco Corp.

N.A. Memon, C.S. Myers, U.S. Patent 4,391,938, 05 July 1983, to Rohm & Haas

A. Merrington, in *Applied Plastics Engineering Handbook*, ed. by M. Kutz (Elsevier, Amsterdam, 2011)

R.B. Mesrobian, C.J. Ammondson, Brit. Pat. 889,354, 14 Feb 1962, to Continental Can Company

V. Metanomski (ed.), *Compendium of Macromolecular Nomenclature*, IUPAC Macromol. Div. (Blackwell, Oxford, 1991)

R.V. Meyer, P. Tacke, Ger. Offen. 2,654,168, 01 June 1978, to Bayer

J.M. Michel, Fr. Pat. 1,566,235, 09 May 1969, to Pechiney-Saint Gobain

E.A. Militskova, E.A. Pavlova, I.O. Stalnova, V.B. Cherkashin, USSR. Pat. 1,788,958, 15 Jan 1993, to USSR

A. Miller, N.G. Reddeman, Belg. Pat. 620,703, 14 Nov 1962, to Miliprint

G.W. Miller, U.S. Patent 3,646,159, 29 Feb 1972, to Baychem Corp.

A. Minegishi, Y. Naka, T. Takahashi, Y. Masubuchi, J. Takimoto, K. Koyama, Nihon Reor. Gakk. **25**, 215 (1997)

A. Minegishi, A. Nishioka, T. Takahashi, Y. Masubuchi, J. Takimoto, K. Koyama, *International Symposium on Elongational Flow of Polymeric Systems*, Yamagata U., Yonezawa, 13–15 June 1998

S. Minekawa, K. Yamaguchi, K. Toyomoto, E. Fujimoto, Y. Takeuchi, Jap. Pat. 008,585, 12 Sept 1969, to Asahi Chem.

S. Minekawa, K. Yamaguchi, K. Toyomoto, E. Fujimoto, Y. Takeuchi, Jap. Pat. 016,429, 06 May 1971, to Asahi Chem.

L.I. Minkova, M. Paci, M. Pracella, P. Magagnini, Polym. Eng. Sci. **32**, 57 (1992)

Mitsubishi Chem. Ind. Co., Jap. Pat. 157,648, 08 Dec 1980

Mitsubishi Chem. Ind. Co., Jap. Pat. 137,347, 24 Aug 1982

Mitsubishi Chem. Ind. Co., Jap. Pat. 076,448, 09 May 1983

Mitsubishi Chem. Ind. Co., Jap. Pat. 020,351, 02 Feb 1984

Mitsubishi Gas Chem. Co., Jap. Pat. 174,344, 27 Oct 1982

Mitsubishi Gas Chem. Co., Jap. Pat. 020,953, 02 Feb 1985

Mitsubishi Petrochem. Co., Jap. Pat. 195,147, 30 Nov 1982

Mitsubishi Petrochem. Co., Jap. Jap. Pat. 007,448, 17 Jan 1983; Jap. Pat. 162,653, 27 Sept 1983

Mitsubishi Petrochem. Co., Jap. Pat. 022,956, 06 Feb 1984

Mitsubishi Petrochem. Co., Jap. Pat. 086,161; 086,164, 15 May 1985

Mitsui Petrochem. Ind., Jap. Pat. 168,646, 05 Oct 1983; Jap. Pat. 213,039, 10 Dec 1983

K. Miyanishi, Y. Manabe, Jap Pat., 047,043, 22 Apr 1976, to Teijin Chemicals

Y. Mizuno, T. Maruyama, Europ. Pat. Appl. 349,339, 03 Jan 1990, to Sumitomo Chem.

M. J. Modic, R. Gelles, Europ. Pat. Appl. 255,184, 03 Feb 1988, to Shell

A.K. Mohanty, M. Misra, L.T. Drzal (eds.), *Natural Fibers, Biopolymers and Biocomposites* (Taylor and Francis, Boca Raton, 2005)

R.N. Mohn, D.R. Paul, J.W. Barlow, C.A. Cruz, J. Appl. Polym. Sci. **23**, 575 (1979)

A.N. Mollison, U.S. Patent 4,461,808, 24 July 1984, to DuPont Canada

H. Moncure Jr., U.S. Patent 3,480,694, 25 Nov 1969, to E. I. du Pont

C.W. Montgomery, Fr. Pat. 1,445,876, 15 July 1966, to Ethyl Corp.

D.Y. Moon, O.O. Park, Adv. Polym. Technol. **17**, 203 (1998)

D. Moorwessel, R. Glasser, G. Pfirrmann, Ger. Offen. 2,306,893, 22 Aug 1974, to BASF

A.W. Morgan, R.G., Ribaudo, U.S. Patent 4,228,245, 14 Oct 1980, to Bayer

Y. Morita, N. Kashiwa, Europ. Pat. Appl. 022,376, 14 Jan 1981, to Mitsui Petrochem.

K. Morita, K. Uchiki, H. Shinoda, U.S. Patent 5,223,546, 29 June 1993a; U.S. Patent 5,238,968, 24 Aug 1993b, to Mitsui Toatsu Chemicals

P.J.T. Morris, *The American Synthetic Rubber Research Program* (University of Pennsylvania Press, Philadelphia, 1989)

D.R. Morrow, T.J. Nosker, K.E. VanNess, R.W. Renfree, U.S. Patent 5,298,214, 29 Mar 1994, to Rutgers State University

M. Morton, in *History of Polymer Science and Technology*, ed. by R.B. Seymour (Marcel Dekker, New York, 1982)

G.S. Motz, U.S. Patent 4,226,961, 07 Oct 1980, to General Electric Co.

C.T. Movak, P.N. Nelson, S. Nam, W. DeMoully, K.D. Goebel, U.S. Patent 5,371,143, 06 Dec 1994, to Minnesota Mining & Manufacturing

P. Mukhopadhyay, C.K. Das, Polym. Plast. Technol. Eng. **28**, 537 (1989)

P. Mukhopadhyay, C.K. Das, J. Appl. Polym. Sci. **39**, 49 (1990)

P. Mukhopadhyay, C.K. Das, Int. J. Polym. Mater. **15**, 57 (1991)

P. Mukhopadhyay, H.P. Schreiber, Colloids Surf. A Physicochem. Eng. Asp. **100**, 47 (1995)

P. Mukhopadhyay, G. Chowdhury, C.K. Das, Kautschuk Gummi Kunststoffe **42**, 308 (1989)

P. Mukhopadhyay, G. Chowdhury, C.K. Das, J. Appl. Polym. Sci. **40**, 1833 (1990)

A. Mukohyama, Int. Pat. Appl. 08,233, 29 Apr 1993, to E. I. du Pont

R. Mülhaupt, J. Rosch, S. Hopperdietzel, E. Weinberg, H. Klein, U.S. Patent 5,312,875, 17 May 1994, to Rehau

D.H. Mullins, Brit. Pat. 958,399, 21 May 1964, to Union Carbide Corp.

W.G. Munk, Ger. Offen. 4,204,083 A1, 04 Mar 1993, to Nordmann Rassmann GmbH & Co.

H. Münstedt, S. Kurzbeck, *International Symposium on Elongational Flow of Polymeric Systems*, Yamagata U., Yonezawa, 13–15 June 1998

S. Murakami, H. Higuchi, S. Matsuo, Jap. Pat. 03 190,961, 20 Aug 1991, to Idemitsu Kosan

J.D. Murdock, N. Nelan, G.H. Segall, Ger. Offen. 1,217,606, 26 May 1960, to Canadian Industries

J.D. Murdock, N. Nelan, G.H. Segall, Brit. Pat. 901,386, 18 July 1962, to Canadian Industries

J.G. Murray, U.S. Patent 4,352,908, 05 Oct 1982, to Mobil Oil Corp.

L.C. Muschiatti, B.A. Smillie, U.S. Patent 5,391,582, 21 Feb 1995, to E. I. Du Pont

V.M. Nadkarni, J.P. Jog, in *Two – Phase Polymer Systems*, ed. by L.A. Utracki (Hanser, Munich, 1991)

S. Nagai, M. Hasegawa, H. Mimura, M. Kobayashi, Eur. Pat. Appl. 565,304, 13 Oct 1993, to Mitsubishi Gas Chem.

S. Nagai, M. Hasegawa, H. Mimura, M. Kobayashi, U.S. Patent 5,326,846, 05 July 1994, to Mitsubishi Gas Chem.

K. Nagasaki, T. Hata, K. Matsuzaki, Jap. Pat. 03 263,454, 22 Nov 1991, to Asahi Chem.

Y. Nagase, M. Kobayashi, T. Kato, S. Imuta, U.S. Patent 5,338,792, 16 Aug 1994, to Mitsui Petrochem.

S.V. Nair, A. Subramaniam, L.A. Goettler, J. Material Sci. **32**, 5347 (1997)

S.V. Nair, A. Subramaniam, L.A. Goettler, J. Material Sci. **33**, 3455 (1998)

K. Nakamura, K. Neki, Europ. Pat. Appl. 039,155, 04 Nov 1981, to Asahi Chem.

K. Nakamura, K. Toyomoto, Jap. Pat. 075,662, 22 July 1974, to Asahi Chem.

K. Nakamura, T. Kimura, H. Tsunoda, Jap. Pat. 083,174, 06 Nov 1973, to Sanyo Pulp.

H. Nakano, T. Inoue, S. Gotoh, M. Kihira, Europ. Pat. Appl. 484,941, 13 May 1992, to Mitsubishi Petrochem.

K.M. Nampoothiri, N.R. Nair, R.P. John, Bioresource Technol. **101**, 8493 (2010)

K.M. Natarajan, R. Mininni, Europ. Pat. Appl. 428,178, 22 May 1991, to Enichem.

K.M. Natarajan, P. Arjunan, D. Elwood, Europ. Pat. Appl. 540,120, 05 May 1993, to Enichem.

K.M. Natarajan, P. Arjunan, D. Elwood, U.S. Patent 5,296,550, 22 Mar 1994, to Enichem.

G. Natta, F. Danusso (eds.), *Stereoregular Polymers and Stereospecific Polymerization* (Pergamon Press, New York, 1967)

S.P. Nemphos, G.B. Kharas, Eur. Pat. Appl. 540,182, 05 May 1993, to Novacor Chem.

S.P. Nemphos, G.B. Kharas, U.S. Patent 5,300,576, 05 Apr 1994, to Novacor Chem.

D. Neuray, W. Nouverte, R. Binsack, D. Rempel, P.R. Mueller, Europ. Pat. Appl. 064,648, 17 Nov 1982, to Bayer

R. Newe, E. Lange, H. Hoffmann, K. Wetzel, East Ger. Offen. 207,381, 29 Feb 1984, to VEB Chemiekombinat Bitterfeld

S. Newman, D.R. Paul, *Polymer Blends*, vol. I and II (Academic, New York, 1978)

A.B.. Newton, Europ. Pat. Appl. 037,181, 07 Oct 1981, to ICI

K.L. Ngai, D.J. Plazek, Macromolecules **23**, 4282 (1990)

X.Q. Nguyen, L.A. Utracki, U.S. Patent 5,451,106, 19 Sept 1995, to National Research Council Canada

E. Nield, Ger. Offen. 2,122,735, 25 Nov 1971, to ICI

N. Niessner, G.E. Mac Kee, K. Ruppmich, Ger. Pat. 4,200,247, 15 July 1993, to BASF

N. Niessner, F. Seitz, W. Fischer, N. Guentherberg, K. Ruppmich, R. Moors, R. Weiss, Europ. Pat. Appl. 576,960, 05 Jan 1994, to BASF

Nippon Zeon Co., Jap. Pat. 129,245, 25 July 1984

T. Nishio, T. Sanada, T. Okada, Europ. Pat. Appl. 270,247, 08 June 1988, to Sumitomo Chem.

T. Nishio, Y. Suzuki, K. Kojima, M. Kakugo, Kobunshi Robunshu **47**, 331 (1990)

T. Nishio, T. Nomura, N. Kawamura, H. Sato, A. Uchikawa, I. Tsutsumi, Y. Goto, Europ. Pat. Appl. 519,725, 23 Dec 1992, to Mitsubishi Petrochem.

T. Nishio, T. Sanada, S. Hosoda, K. Nagaoka, T. Okada, U.S. Patent 5,288,786, 22 Feb 1994, to Sumitomo Chem.

A. Nishioka, S. Kato, Y. Kiyomatsu, M. Ichikawa, Y. Kitagawa, Jap. Pat. 074,552, 08 Oct 1973, to Japan Synthetic Rubber

A. Nishiyama, T. Nakakita, Jap. Pat. 03 252,455, 11 Nov 1991, to Ube Industries

M. Nishiyama, K. Ohtsuki, Y. Nakakita, H. Ozawa, Europ. Pat. Appl. 360,544, 28 Mar 1990, to Ube

M. Nishiyama, T. Nakakita, K. Ohtsuka, Jap. Pat. 03 100,055, 25 Apr 1991a, to Ube

M. Nishiyama, K. Ohtsuka, T. Nakakita, Jap. Pat. 03 91,562, 17 Apr 1991b, to Ube

G.E. Nizik, U.S. Patent 4,097,425, 27 Jan 1978, to General Electric Co.

G.E. Nizik, U.S. Patent 4,174,432, 13 Nov 1979, to General Electric Co.

K. Nyori, A. Kinoshita, I. Hatano, Jap. Pat. 010,928; 012,919, 04 Sept 1962, to Kanegafuchi Chem.

W.J.J. O'Connell, Fr. Dem. 2,213,959, 09 Aug 1974, to General Electric Co.

W.J.J. O'Connell, Jap. Pat. 076,450, 09 May 1983, to General Electric Co.

A.O. Ogah, J.L. Afikuwa, Int. J. Eng. Management Sci. **3**, 85 (2012)

T. Ogawa, N. Ito, K. Ohishi, R. Samejima, Jap. Pat. 031,241, 24 Apr 1973, to Sumitomo Chem.

T. Ohmae, Y. Toyoshima, K. Mashita, N. Yamaguchi, J. Nambu, U.S. Patent 5,010,136, 23 Apr 1991, to Sumitomo Chem.

T. Ohmae, Y. Toyoshima, K. Mashita, N. Yamaguchi, J. Nambu, Europ. Pat. Appl. 480,770, 15 Apr 1992, to Sumitomo Chem.

M. Ohta, K. Iiyama, S. Kawashima, S. Tamai, H. Oikawa, A. Yamaguchi, Europ. Patent Appl. 294,144, 07 Dec 1988, to Mitsui Toatsu Chem.

T. Ohta, O. Urakawa, Q. Tran-Cong, Macromolecules **31**, 6845 (1998)

T. Oita, T. Hara, R. Samejima, K. Tanabe, Jap Pat. 108,146, 20 Sept 1978, to Sumitomo Chem.

A. Okada, U.S. Patent 5,352,727, 04 Oct 1994, to Idemitsu Kosan

A. Okada, A. Masuyama, U.S. Patent 5,326,813, 05 July 1994, to Idemitsu Kosan

K. Okada, M. Karaiwa, A. Uchiyama, U.S. Patent 5,728,744, 17 Apr 1998a, to Mitsui Petrochem.

K. Okada, M. Karaiwa, A. Uchiyama, U.S. Patent 5,786,403, 28 July 1998b, to Mitsui Petrochem

O. Okada, H. Keskkula, D.R. Paul, J. Polym. Sci. Part B Polym. Phys. **42**, 1739 (2004)

K.T. Okamoto, K.D. Eastenson, S.C. Guyaniyogi, Europ. Pat. Appl. 566,106, 20 Oct 1993, to Himont

K.T. Okamoto, K.D. Eastenson, S.C. Guyaniyogi, U.S. Patent 5,290,856, 01 Mar 1994, to Himont

M. Okamoto, A. Kojima, T. Kotaka, Polymer **39**, 2149 (1998a)

M. Okamoto, H. Kubo, T. Kotaka, *14th International Polymer Processing Society Meeting*, *PPS-14*, Yokohama, 08–12 June 1998b

Y. Okawa, N. Koga, H. Oikawa, T. Asanuma, A. Yamaguchi, U.S. Patent 5,321,096, 14 June 1994, to Mitsui Toatsu Chem.

S. Okuda, Europ. Pat. Appl. 356,167, 28 Feb 1990, to Polyplastics

T. Okuzono, M. Kifune, Jap. Pat. 001,147, 08 Jan 1975, to Mitsubishi Gas Chem.

T. Okuzono, M. Kifune, Jap. Pat. 030,255; 030,256, 11 Sept 1976, to Mitsubishi Gas Chem

J. O'Leary, S. Musgrave, PCT Int. Appl. WO 93 21,269, 28 Oct 1993, to ICI, Australia

Y. Ono, K. Iida, K. Murata, Y. Noto, Jap Pat. 03 97,756, 23 Apr 1991, to Dainippon Ink & Chem.

Y. Orikasa, S. Sakazume, Europ. Pat. Appl. 361,400, 04 Apr 1990, to Nippon Petrochem.

Y. Orikasa, S. Sakazume, Europ. Pat. Appl. 506,006, 30 Sept 1992, to Nippon Petrochem.

Y. Orikasa, S. Sakazume, U.S. Patent 5,296,538, 22 Mar 1994, to Nippon Petrochem.

Y. Orikasa, S. Sakazume, S. Nishimura, Y. Maki, Europ. Pat. Appl. 314,188, 03 May 1989, to Nippon Petrochem.

I.I. Ostromislensky, J. Russ. Phys. Chem. Soc. **44**, 204 (1911)

I.I. Ostromislensky, J. Russ. Phys. Chem. Soc. **47**, 1772, 1915, 1928 (1915)

I.I. Ostromislensky, J. Russ. Phys. Chem. Soc. **48**, 1132 (1916)

Ostromislensky, Iwan I., of New York, N. Y., Brit. Pat. 233,649, 07 May 1924; Can. Pat. 261,327, 01 June 1926; U.S. Patent 1,613,620, 11 Jan 1927; U.S. Patent 1,676,281, 10 July 1928, to Naugatuck Chem.

D.E. Overton, P.Y. Liu, Europ. Pat. Appl. 119,531, 26 Sept 1984, to General Electric Co.

D.E. Overton, P.Y. Liu, U.S. Patent 4,532,282, July 1985, to General Electric Co.

S. Pack, M. Lewin, M.H. Rafailovich, *Fire and Polymers VI: New Advances in Flame Retardant Chemistry and Science*, ACS Symposium Series, Plennm, New York, vol. 1118 (2012), American Chemical Society, Washington, DC

C.F. Paddock, U.S. Patent 4,264,747, 28 Apr 1981, to Uniroyal

M. Paleari, T. Fornasiero, Europ. Pat. Appl. 593,837, 27 Apr 1994, to W. R. Grace & Co.

C.P. Park, U.S. Patent 4,129,530, 12 Dec 1978, to Dow Chemical

C.P. Park, U.S. Patent 4,215,202, 29 July 1980, to Dow Chemical

C.P. Park, U.S. Patent 4,554,293, 19 Nov 1985, to Dow Chemical

C.P. Park, U.S. Patent 4,623,671, 18 Nov 1986a, to Dow Chemical

C.P. Park, U.S. Patent 4,567,209, 28 Jan 1986b, to Dow Chemical

C.P. Park, U.S. Patent 4,605,682, 12 Aug 1986c, to Dow Chemical

C.P. Park, U.S. Patent 4,581,383, 08 Apr 1986d, to Dow Chemical

C.P. Park, U.S. Patent 4,652,588, 24 Mar 1987, to Dow Chemical

C.P. Park, U.S. Patent 4,722,972, 02 Feb 1988, to Dow Chemical

C.P. Park, U.S. Patent 5,469,818, 24 Oct 1995, to Dow Chemical

C.L. Parker, U.S. Patent 2,539,385, 30 Jan 1951, to Radio Corporation of America

D.S. Parker, H.-J. Sue, J. Huang, A.F. Yee, Polymer **31**, 2267 (1992)

A. Parkes, Brit. Pat. 1,147, 25 Mar 1846; Brit. Pat. 1,313, 07 Nov 1865

C.E. Parks, U.S. Patent 3,975,315, 17 Aug 1976, to BFGoodrich

I.K. Partridge, in *Multicomponent Polymer Systems*, ed. by I.S. Miles, S. Rostami (Longman Scientific & Technical, Harlow, 1992)

E.F. Paschke, M.A. Stasi, E.F. Rader, U.S. Patent 4,383,084, 10 May 1983, to Standard Oil

E.E. Paschke, C.L. Myers, G.P. Desio, Europ. Pat. Appl. 572,266, 01 Dec 1993, to Amoco Corp.

E.E. Paschke, C.L. Myers, G.P. Desio, U.S. Patent 5,292,805, 08 Mar 1994, to Amoco Corp.

G.A.R. Patfoort, Belg. Pat. 833,543, 18 Mar 1976

J.C. Patrick, U.S. Patent 1,890,191, 1932, to Thiokol Chem.

J.C. Patrick, U.S. Patent 2,278,128, 31 Mar 1942, to Thiokol Chem.

T. Patton, LaMarre, Europ. Pat. Appl. 068,695, 05 Jan 1983, to Exxon

J.-R. Pauquet, F. Sitek, R. Todesco, U.S. Patent 5,298,540, 29 Mar 1994, to Ciba-Geigy Corp.

A.J. Peacock, *Handbook of Polyethylene* (Marcel Dekker, New York, 2000)

R. Pernice, C. Berto, A. Moro, R. Pipa, Europ. Pat. Appl. 528,477, 31 July 1992, to ECP Enichem Polimeri

P.J. Perron, Adv. Polymer Technol. **6**, 79 (1984)

P.J. Perron, U.S. Patent 4,782,114, 01 Nov 1988, to Dexter Corp.

P.J. Perron, K. Nangrani, E. Bourbonais, U.S. Patent 5,187,228, 16 Feb 1993, to Dexer Corp.

R.J. Petcavich, U.S. Patent 5,367,003, 22 Nov 1994.

E.N. Peters, J.A. Rock, Europ. Pat. Appl. 325,719, 02 Aug 1989, to General Electric Co.

H. Peters, F. Schuelde, Ger. Offen. 1,146,251, 28 Mar 1963, to Hoechst

P. Pfleiderer, Ger. Offen. 10,164, 1880, to Maschinenfabrik Werner und Pfleiderer

E.M. Phillips, K.E. McHugh, K. Ogale, M.B. Bradley, Kunststoffe **82**, 671 (1992)

S.U. Pickering, J. Chem. Soc. Abstr. **91–92**, 2001 (1908)

M.R. Piggott, in *Failure of Plastics*, ed. by W. Brostow, R.D. Corneliussen (Hanser, Munich, 1986)

L.Z. Pillon, L.A. Utracki, Polym. Eng. Sci. **4**, 1300 (1984)

L.Z. Pillon, L.A. Utracki, Polym. Process Eng. **24**, 375 (1986)

L. Pinchuck, Europ. Pat. Appl. 461,375, 18 Dec 1991, to Corvita Corp.

A. Plochocki, T. Bek, J. Bojarski, L. Czarnecki, L. Grabiec, J. Kepka, P. Machowski, Polish Pat. 100,160, 17 Apr 1979, to Institute Chem. Ind., Polish Academy of Sci.

C.J.G. Plummer, J.L. Hedrick, H.-H. Kausch, J.G. Hilborn, J. Polym. Sci. Part B Polym. Phys. **33**, 1813 (1995)

V.N. Pokrovskii, J. Exp. Theoretical Phys. **106**, 604 (2008)

M. Pontio, U.S. Patent 1,293,191, 1919

L.M. Porter, Ger. Offen. 2,156,681, 18 May 1972, to Shell

R.S. Porter, L.H. Wang, Polymer **33**, 2019 (1992)

R.S. Porter, J.M. Jonza, M. Kimura, C.R. Desper, E.R. George, Polym. Eng. Sci. **29**, 55 (1989)

M. Portugall, G. Blinne, W. Ziegler, M. Walter, H. Reimann, K. Schlichting, Ger. Offen. 3,234,174, 15 Mar 1984, to BASF

W. Posch, in *Applied Plastics Engineering Handbook*, ed. by M. Kutz (Elsevier, Amsterdam, 2011)

I. Prigogine, A. Bellemans, V. Mathot, *The Molecular Theory of Solutions* (North-Holland, Amsterdam, 1957)

M. Prillieux, P. Delbende, M. Moulin, Fr. Pat. 1,289,580, 06 Apr 1962, to Esso

E.G. Pritchett, U.S. Patent 4,228,250, 14 Oct 1980, to National Distillers & Chemical Corp.

E.G. Pritchett, U.S. Patent 4,264,746, 1981, to National Distillers & Chemical Corp.

R.C. Puydak, D.R. Hazelton, T. Ouhadi, PCT Int. Appl. WO 90 014,389, 29 Nov 1990, Oct 1992, to Exxon

R.C. Puydak, D.R. Hazelton, T. Ouhadi, U.S. Patent 5,157,081, Oct 1992, to Exxon

C.B. Quinn, U.S. Patent 4,430,484, 07 Feb 1984, to General Electric Co.

C.B. Quinn, F.F. Holub, Europ. Pat. Appl. 187,416, 16 July 1986, to General Electric Co.

C.B. Quinn, N.R. Rosenquist U.S. Patent 4,358,569, 09 Nov 1982, to General Electric Co.

M. Rabeony, D.J. Lohse, R.T. Garner, S.J. Han, W.W. Graessley, K.B. Migler, Macromolecules **31**, 6511 (1998)

P. Ramya, J. Phys. Conf. Ser. **443**, 012048 (2013)

F. Ranalli, Ital. Pat. 583,501, 14 Oct 1958, to Montecatini S. G.

R.M. Rasal, D.E. Hirt, Macromol. Mater. Eng. **295**, 204 (2010)

R.M. Rasal, A.V. Janorkar, D.E. Hirt, Progr. Polym. Sci. **35**, 338 (2010)

C. Rauwendaal, *Polymer Extrusion*, 4th edn. (Hanser, Munich, 2001)

L.S. Rayner, J.A. Bond, M. Clark, R.E. Nott, Brit. Pat. 958,079, 13 May 1964, to ICI

A. Razavi, U.S. Patent 5,278,265, 11 Jan 1994, to Fina Technology

J.E. Reardon, U.S. Patent 4,329,278, 11 May 1982, to E. I. du Pont

R.J. Reid, W.R. Conrad, U.S. Patent 2,929,795, 22 Mar 1960, to Firestone Tire & Rubber

R.J. Reid, W.R. Conrad, Belg. Pat. 617,870, 21 Nov 1962, to Firestone Tire & Rubber

H.K. Reimschussel, G.J. Dege, Ger. Offen. 1,918,499, 13 Nov 1969, to Allied Chem. Corp.

M.S. Reisch, *Chem. Eng. News*, 22–27, 15 Apr 2002

E. Reske, E. Wolters, Ger. Pat. 3,303,760; 3,303,761, 09 Aug 1984, to Hoechst

W.D. Richards, D.M. White, Europ. Pat. Appl. 592,144, 13 Apr 1994, to General Electric Co.

P.N. Richardson, Europ. Pat. Appl. 117,748, 05 Sept 1984, to E. I. du Pont

E.H. Riddle, *Monomeric Acrylic Esters* (Reinhold, New York, 1954)

B. Rieger, X. Mu, D.T. Mallin, M.D. Rausch, J.C.W. Chien, Macromolecules **23**, 3559 (1990)

R.-E. Riemann, W. Gleinser, Friedrich, *Polymer Processing Society European Meeting*, Stuttgart, 26–28 Sept 1995

M.R. Rifi, U.S. Patent 5,326,602, 05 July 1994, to Union Carbide Chem.

W. Ritter, R. Bergner, M. Schäfer, Ger. Offen. 4,121,111 A1, 07 Jan 1993, to Henkel

E.P. Rittershausen, U.S. Patent 2,489,674, 29 Nov. 1949, to Socony Vacuum Oil Co.

L.M. Robeson, Europ. Pat. Appl. 24,245, 25 Feb 1981, to Union Carbide Corp.

L.M. Robeson, U.S. Patent 4,324,869, 13 Apr 1982, to Union Carbide Corp.

L.M. Robeson, U.S. Patent 4,532,288, 30 July 1985, to Union Carbide Corp.

L.M. Robeson, PCT Int. Appl. 000,220, 14 Jan 1988, to Amoco Corp.

L.M. Robeson, *Polymer Blends* (Hanser, Munich, 2007)

L.M. Robeson, Ind. Eng. Chem. Res. **49**, 11859 (2010)

L.M. Robeson, Polym. Eng. Sci. **53**, 453 (2013)

L.M. Robeson, J.E. Harris, Europ. Pat. Appl. 133,907, 13 Mar 1985, to Union Carbide Corp.

L.M. Robeson, J.E. Harris, Europ. Pat. Appl. 176,988, 09 Apr 1986, to Union Carbide Corp.

L.M. Robeson, M. Matzner, Europ. Pat. Appl. 104,659, 04 Apr 1984, to Union Carbide Corp.

L.M. Robeson, M. Matzner, L.M. Maresca, Europ. Pat. Appl. 33,394, 12 Aug 1981, to Union Carbide Corp.

P.A. Rodgers, J. Appl. Polym. Sci. **48**, 1061 (1993)

M. Roemer, A. Schleicher, PCT Int. Pat. Appl. 002,144, 04 Feb 1993, to Hoechst

M. Roemer, A. Schleicher, Jap. Pat. 60 49,338, 22 Feb 1994, to Hoechst

K.A. Romance, U.S. Patent 4,897,448, 30 Jan 1990, to Eastman Kodak

O.V. Romankevich, S. Ya. Frenkel, Acta Polymerica, **31**, 287(1980)

F.E. Romesberg, U.S. Patent 5,051,452, 24 Sept 1991, to Dow Chemical Co.

J. Roovers, L.-L. Zhu, P.M. Toporowski, M. van der Zwan, H. Iatrou, N. Hadjichristidis, Macromolecules **26**, 4324 (1993)

J. Rösch, R. Mülhaupt, Polym. Bull. **32**, 697 (1994)

W.J. Rosenfelder, J.J. Rosen, U.S. Patent 3,046,237, 24 July 1962, to Dublon

N.R. Rosenquist, U.S. Patent 4,335,032, 15 June 1982, to General Electric Co.

S. Rostami, Europ. Pat. Appl. 211,604, 25 Feb 1987, to ICI

L.C. Rubens, U.S. Patent 4,604,426, 05.08.1986, to Dow Chemical

A. Rudin, H.P. Schreiber, Fr. Pat. 1,349,823, 17 Jan 1964a, to Canadian Industries Ltd. (CIL)

A. Rudin, H.P. Schreiber, Can. Pat. 688,416, 09 June 1964b, to Canadian Industries Ltd. (CIL)

N.R. Ruffing, B.A. Kozakiewicz, B.B. Cave, J.L. Amos, Belg. Pat. 632,377, 1964, to Dow Chemical

J. Rys-Sikora, U.S. Patent 4,391,923, 05 July 1983, to E. I. Du Pont

J. Rys-Sikora, U.S. Patent 4,434,253, 28 Feb 1984, to E. I. Du Pont

Z.M.O. Rzayev, Int. Rev. Chem. Eng. **3**, 153 (2011)

C. Sadrmohaghegh, G. Scott, E. Setudeh, Polym. Plast. Technol. Eng. **24**, 149 (1985)

H.R. Sailors, J.P. Hogan, in *History of Polymer Science and Technology*, ed. by R.B. Seymour (Marcel Dekker, New York, 1982)

T. Saito, Jap. Pat. 007,850, 27 Jan 1975, to Showa Denko

I. Sakai, J. Oshima, M. Yamada, Europ. Pat. Appl. 299,468; 299,469, 18 Jan 1989, to Takeda Chem.

T. Sakamoto, Kumai, K. Kenichiro, S. Gotoh, U.S. Patent 5,346,926, 13 Sept 1994, to Nippon Unicar.

S. Sakane, K. Minato, M. Takashige, Jap. Pat. 000,052, 05 Jan 1979, to Idemitsu Petrochem.

H. Sakano, A. Ito, M. Terada, Ger. Pat. 3,027,957, 12 Feb 1981, to Sumitomo-Naugatuck

H. Sakano, A. Ito, M. Terada, U.S. Patent 4,317,891, 1982, to Sumitomo-Naugatuck

H. Sakano, K. Motomatsu, I. Tsukino, I. Yoshida, T. Shima, H. Kojima, T. Yoshida, Jap. Pat. 07,757, 24 Jan 1978, to Sumitomo Naugatuck

R. Sakata, T. Kuroda, K. Masuda, Y. Nakayama, M. Tanaka, Jap. Pat. 003,964, 13 Feb 1968, to Mitsubishi Petrochem.

G. Salee, U.S. Patent 4,211,687, 08 July 1980, to Hooker Chemicals and Plastics Corp.

G. Salee, U.S. Patent 4,304,709, 08 Dec 1981, to Hooker Chemicals and Plastics Corp.

G. Salee, U.S. Patent 4,327,012, 27 Apr 1982, to Hooker Chemicals and Plastics Corp.

R.P. Saltman, PCT Int. Appl. WO 88 003,453, 19 Mar 1988, to E. I. du Pont

R.P. Saltman, U.S. Patent 4,871,810, 03 Oct 1989, to E. I. du Pont

R.P. Saltman, U.S. Patent 5,091,478, 25 Feb 1992, to E. I. du Pont

I.O. Salyer, H.P. Holladay, U.S. Patent 3,149,183, 15 Sept 1964, to Monsanto

G.J. Samuels, U.S. Patent 5,336,732, 09 Aug 1994, to AlliedSignal

I.C. Sanchez, W.M. Balaba, L.T. Stevenson, U.S. Patent 5,032,434, 16 July 1991, to Aluminum Company of America

M.A. Sanner, R.R. Gallucci, *Proc. SPE ANTEC*, 2684 (2011)

I. Sasaki, N. Yamamoto, A. Yanagase, U.S. Patent 5,011,887; Europ. Patent Appl. 332,188, 13 Sept 1989, to Mitsubishi Rayon

M.E. Sauers, B.P. Barth, Ger. Offen. 1,954,671, 06 May 1970, to Union Carbide Corp.

H. Scheckenbach, A. Schonfeld, S. Weis, U.S. Patent 5,708,041, 13 Jan 1998, to Höchst

W.M. Schilling, Brit. Pat. 975,877, 18 Nov 1964, to Hercules Powder

W.M. Schilling, U.S. Patent 3,200,173, 10 Aug 1966, to Hercules Powder

B. Schlund, L.A. Utracki, Polym. Eng. Sci. **27**, 380 (1987); ibid. **27**, 1523 (1987)

A.D. Schluter, J.P. Rabe, Angew. Chem. Int. Ed. **39**, 865 (2000)

M. Schmidt, Europ. Pat. Appl. 077,493, 27 Apr 1983, to Mobay Chemical Corp.

M. Schmidt, F.H.J. Maurer, J. Polym. Sci. Part B Polym. Phys. **36**, 1061 (1998)

E. Schmid, H. Thullen, U.S. Patent 5,288,799, 22 Feb 1994, to EMS-Inventa

J.M. Schmitt, C.H. Miller Jr., U.S. Patent 3,524,906, 18 Aug 1970, to American Cyanamid

J.M. Schmitt, L.A. Landers, J.F. Terenzi, U.S. Patent 3,354,238, 21 Nov 1967, to American Cyanamid

D.L. Schober, U.S. Patent 3,714,289, 30 Jan 1973, to Union Carbide Corp.

H.P. Schreiber, Brit. Pat. 1,037,820, 03 Aug 1966, to Canadian Industries Ltd. (CIL)

E.C. Schule, U.S. Patent 2,605,247, 29 July 1952, to Firestone Tire & Rubber

H.G. Schutze, H.C. Williams, N.P. Neureiter, D.E. Bown, U.S. Patent 3,655,718, 11 Apr 1972, to Esso

S. Seelert, P. Klaerner, A. Jung, H. Hoenl, B. Ostermayer, Ger. Pat. 4,139,627, 03 June 1993a, to BASF

S. Seelert, R. Weiss, D. Zeltner, Ger. Pat. 4,209,032, 23 Sept 1993b, to BASF

L. Segal, U.S. Patent 3,769,260, 30 Oct 1973, to Allied Chem. Corp.

N. Segrest, U.S. Patent 5,397,825, 14 Mar 1995

W.L. Semon, U.S. Patent 1,929,453, 10 Oct 1933, to B. F. Goodrich

H. Serizawa, M. Kubota, H. Sano, Europ. Pat. Appl. 468,772, 29 Jan 1992, to Polyplastics

W. Seydl, E. Strickle, U.S. Patent 3,937,757, 10 Feb 1976, to BASF

R.B. Seymour, U.S. Patent 2,574,439, 06 Nov 1951, to Monsanto Chem.

R.B. Seymour (ed.), *Pioneers in Polymer Science* (Kluwer, Boston, 1989)

R.B. Seymour, T. Cheng (eds.) *Advances in Polyolefins*, ACS Symp., Miami Beach, Spring 1985 (Plenum Press, New York, 1987)

L.W. Shacklette, G.G. Miller, C.C. Han, R.L. Elsenbaumer, PCT Int. Appl. WO 93 024,555, 09 Dec 1993, to AlliedSignal

W.J.D. Shaw, Can. Pat. Appl. 2,071,707, 20 Dec 1993, to University of Calgary

M.L. Sheer, U.S. Patent 4,317,764, 02 Mar 1982, to E. I. du Pont

M.D. Shelby, W.R. Hale, T.J. Pecorini, M.E. Rogers, S.A. Gilliam, M.D. Cliffton, M.E. Stewart, U.S. Patent 8,304,499, 6 Nov 2012 to Eastman Chemical Co.

J.S.J. Shen, U.S. Patent 5,328,962, 12 July 1994, to ICI, Ltd., Acrylics

A.M. Sherman, Europ. Pat. Appl. 027,312, 22 Apr 1981, to Mobil Oil Corp.

A.M. Sherman, U.S. Patent 4,397,988, 09 Aug 1983, to Mobil Oil Corp.

Z.H. Shi, L.A. Utracki, in *Proceedings of the Canadian Society of Chemical Engineers Annual Meeting*, Toronto, Oct 1992; Polym. Eng. Sci. **32**, 1834 (1992)

Z.H. Shi, L.A. Utracki, in *Proceedings of the Polymer Processing Society Annual Meeting*, Manchester, Apr 1993

A. Shibata, S. Nagai, M. Kobayashi, M. Kimura, H. Mimura, Europ. Pat. Appl. 500,269, 26 Aug 1992, to Mitsubishi Gas Chem.

K. Shichijo, Europ. Pat. Appl. 593,221, 20 Apr 1994, to Mitsubishi Petrochem.

K. Shikata, K. Okamura, S. Nakamura Jap. Pat. 097,946, 13 Dec 1973, to Tokuyama Soda

K. Shimamura, Y. Suzuki, Jap Pat. 03 24,153, 01 Feb 1991, to Asahi Chem.

B.S. Shin, J.Y. Lee, D.K. Kim, S.J. Kim, S.O. Cho, U.S. Patent 5,776,993, 07 July 1998, to Korea Inst. Footwear & Leather Technology

Shin-Kobe Electric Machinery Company, Limited, Jap. Pat. 096,156, 02 June 1984

M. Shiraishi, M. Goto, Jap. Pat. 106,653, 24 May 1986, to Mitsubishi Petrochem.

T. Shiraki, Y. Hattori, U.S. Patent 5,115,035, Appl. 25 Nov 1986, to Asahi Kasei Kogyo

T. Shiraki, Y. Hattori, U.S. Patent 5,332,784, 26 July 1994, to Asahi Kasei Kogyo

T. Shiraki, S. Nakajima, M. Karaushi, Jap. Pat. 61 116,541, 04 June 1986, to Asahi Chem.

K. Shirayama, K. Iketa, Jap. Pat. 021,303; 021,305, 16 June 1971, to Sumitomo Chem.

K. Shirayama, S. Shiga, H. Watanabe, Jap Pat. 008,370, 10 Mar 1972, to Sumitomo Chem.

G.A. Short, U.S. Patent 3,354,239, 21 Nov 1967, to Shell Oil

K.K. Showa Denko, Jap. Pat. 059,242, 08 Apr 1983; Jap. Pat. 157,837, 20 Sept 1983; Jap. Pat. 176,234, 15 Oct 1983

R.S. Shue, L.E. Scoggins, U.S. Patent 4,292,416, 29 Sept 1981, to Phillips

C.B. Shulman, Europ. Pat. Appl. 116,783, 29 Aug 1984, to Exxon

R.W. Siedenstrang, A.K. Thorsrud, U.S. Patent 4,456,706, 26 June 1984, to Phillips

D.L. Siegfried, D.A. Thomas, L.H. Sperling, U.S. Patent 4,468,499, 28 Aug 1984, to Lehigh University

R.J. Signer, K.F. Beal, U.S. Patent 2,547,605, 03 Apr 1951, to Visking Corp.

R.J. Signer, K.F. Beal, U.S. Patent 2,658,050, 03 Nov 1953, to Visking Corp.

J. Silberberg, Europ. Pat. Appl. 045,875, 17 Feb 1982; U.S. Patent 4,342,846, 03 Aug 1982; U.S. Patent 4,360,636, 23 Nov 1982, to Stauffer Chemical

R. Silvestri, P. Sgarzi, Polymer **39**, 5871 (1998)

H.C. Silvis, B.A. King, V.K. Berry, J.R. Schroeder, U.S. Patent 4,968,755, 06 Nov 1990, to Dow Chemical

R. Simha, T. Somcynsky, Macromolecules **2**, 341 (1969)

W. Siol, J.-D. Fischer, T. Sufke, E. Felger, K. Frank, U.S. Patent 5,250,623, 1993a, to Rohm GmbH Chemische Fabrik

W. Siol, J.-D. Fischer, U. Terbrack, K. Koralewski, Europ. Pat. Appl. 547,481, 23 June 1993b, to Röhm GmbH Chemische Fabrik

W. Siol, J.-D. Fischer, T. Sufke, E. Felger, K. Frank, U.S. Patent 5,374,487, 20 Feb 1994, to Rohm GmbH Chemische Fabrik

W. Siol, J.-D. Fischer, U. Terbrack, K. Koralewski, U.S. Patent 5,380,797, 10 Jan 1995, to Röhm GmbH Chemische Fabrik

K.W. Small, P.A. Small, U.S. Patent 2,555,062, 29 May 1951, to ICI

A. Smith, Brit. Pat. 16,274, 1899

P.J. Smith, B.J. Cross, PCT. WO 96/00257, 04 Jan 1996, to ICI

R.R. Smith, J.R. Wilson, Europ. Pat. Appl. 105,826, 18 Apr 1984, to Goodyear Tire & Rubber

H.J.E. Smith, R. van der Meer, A.H.L. Groothuis, Europ. Pat. Appl. 369,169, 23 May 1990, to General Electric Co.

H.J.E. Smith, R. van der Meer, A.H.L. Groothuis, U.S. Patent 5,357,003, 18 Oct 1994, to General Electric Co.

G.L. Smyser, G.T. Brooks, Europ. Patent Appl. 376,347, 04 July 1990, to Amoco Corp.

H.E. Snodgrass, R.L. Lauchlan, Fr. Pat. 2,086,141, 04 Feb 1972, to Uniroyal

L.M. Soby, M.H. Lehr, E.D. Dickens Jr., M. Rajagopalan, W.S. Greenlee, U.S. Patent 5,354,812, 11 Oct 1994, to B. F. Goodrich

R.H. Somani, M.T. Shaw, Macromolecules **14**, 1549 (1981)

D. Song, W. Zhang, R.K. Gupta, E.G. Melby, Can. J. Chem. Eng. **87**, 862 (2009)

D. Song, W. Zhang, R.K. Gupta, E.G. Melby, AIChE J. **57**, 96 (2011)

R. Sonnier, V. Massardier, P. Cassagnau, Int. J. Mater. Form. (Suppl. 1), 657 (2008), Volume 1.

I.W. Sorensen, U.S. Patent 4,465,804, 14 Aug 1984, to Allied Corp.

P. Sparke (ed.), *The Plastics Age* (The Overlook Press, Woodstock, 1993)

W.J. Sparks, L.B. Turner, U.S. Patent 2,618,624, 18 Nov 1952, to Standard Oil Development Co.

L.H. Sperling, *Introduction to Physical Polymer Science*, 2nd edn. (Wiley, New York, 1992)

W.E. Sprenkle, U.S. Patent 4,207,402, 10 Jun 1980, to Monsanto

O.L. Stafford, J.J. Adams, U.S. Patent 3,642,949, 15 Feb 1972, to Dow Chemical

M. Stamm, *Polymer Surfaces and Interfaces – Characterization, Modification and Applications* (Springer, Berlin/Heidelberg, 2008)

Standard Oil Development Co., Fr. Pat. 812,490, 11 May 1937

W.J.D. Steendam, F.R. Mooijman, T.P. Kempers, Europ. Pat. Appl. 573,680, 15 Dec 1993, to General Electric Co.

R.S. Stein, M. Sethumadhavan, R.A. Gaudiana, T. Adams, D. Guarrera, S.K. Roy, J. Macromol. Sci. Pure Appl. Chem. **A29**, 517 (1992)

R.A. Steinkamp, T.J. Grail, U.S. Patent 3,953,655, 27 Apr 1976, to Exxon

R. Steller, D. Zuchowska, J. Appl. Polym. Sci. **41**, 1595 (1990)

J.C. Stevens, F.J. Timmers, D.R. Wilson, G.F. Schmidt, P.N. Nickias, R.K. Rosen, G.W. Knight, S. Lai, Europ. Pat. Appl. 416,815, 1991

R. Stewart, Plast. Eng. **63**, 24 (2007)

J.L. Stewart, E.T. Bell, U.S. Patent 5,382,628, 17 Jan 1995, to Eastman Chemical

M.E. Stewart, D.J. Massa, U.S. Patent 5,235,001, 10 Aug 1993, to Eastman Kodak

L.L. Stott, L.R.B. Hervey, Brit. Pat. 792,955, 09 Apr 1958, to Polymer Corp.

H. Strametz, H.J. Leuering, K. Rust, M. Engelmann, Ger. Offen. 2,417,093, 06 Nov 1975, to Hoechst

P.T. Stricharczuk, Ger. Offen. 2,644,644, 07 Apr 1977, to B. F. Goodrich

E.T. Strom, S.E. Rasmussen (eds.), *100+ Years of Plastics: Leo Baekeland and Beyond*. ACS Symposium Series (ACS, Washington, DC, 2011)

L.C.E. Struik, *Physical Ageing in Amorphous Polymers and Other Materials* (Elsevier, Amsterdam, 1978)

G.E. Stuart, Nat. Geosci. **184**(5), 88 (1993)

H. Suarez, J.W. Barlow, J. Appl. Polym. Sci. **29**, 3253 (1984)

P.M. Subramanian, Europ. Pat. Appl. 015,556, 17 Sept 1980, to E. I. du Pont

P.M. Subramanian, U.S. Patent 4,410,482, 1983, to E. I. du Pont

P.M. Subramanian, U.S. Patent 4,444,817, 24 Apr 1984, to E. I. du Pont

P.M. Subramanian, U.S. Patent 5,096,964, 17 Mar 1992, to E. I. du Pont

Y. Suenaga, T. Ishikuwa, Jap. Pat. 03 137,123, 11 June 1991, to Tosoh Corp.

M. Sugiara, S. Takayama, Jap. Pat. 88 92,663, 23 April 1988, to Fuso Kagaku Kogyo

Y. Sugimura, H. Moriyama, K. Iikura, Y. Shigemori, Jap. Pat. 020,241, 28 Sept 1972, to Teijin, Ltd.

A. Sugio, M. Masu, M. Okabe, E. Ukita, Europ. Pat. Appl. 099,231, 25 Jan 1984, to Mitsubishi Gas Chem.

A. Sugio, K. Okabe, T. Kobayashi, Jap. Pat. 010,162, 19 Jan 1987, to Mitsubishi Gas Chem.

N. Sugiyama, M. Mochizuki, Europ. Pat. Appl. 350 223, 10 Jan 1990, to Polyplastics

A.M. Sukhadia, A. Datta, D.G. Baird, Conf. Proceed. SAMPE **36**, 913 (1991); SPE Techn. Pap. **37**, 1008 (1991)

A.M. Sukhadia, A. Datta, D.G. Baird, Int. Polym. Process. **7**, 218 (1992)

Sumitomo Chem. Co., Brit. Pat. 1,114,589, 22 May 1968

Sumitomo Chem. Co., Jap. Pat. 125,253; 125,252, 04 Aug 1982

Sumitomo Chem. Co., Jap. Pat. 059,259, 08 Apr 1983

Sumitomo Chem. Co., Jap. Pat. 193,957, 02 Nov 1984

Sumitomo Chem. Co., Jap. Pat. 038,464, 28 Feb 1985

R.M. Summers, M. Kramer, D.B.G. Jaquiss, Ger. Offen. 2,229,550, 21 Dec 1972, to General Electric Co.

Sun Oil Company, Brit. Pat. 952,089, 11 Mar 1964

K. Suzuki, M. Nagahama, Jap. Pat. 004,748, 10 Jan 1987, to Toray Industries

S.B. Swartzmiller, R.J. Donald, J.E. Bonekamp, PCT Int. Appl. 013,168, 08 July 1993, to Dow Chemical

S.B. Swartzmiller, R.J. Donald, J.E. Bonekamp, U.S. Patent 5,334,657, 02 Aug 1994, to Dow Chemical
K.W. Swogger, SPE Techn. Pap. **44**, 1790 (1998)
M. Szwarc, M. Levy, R. Milkovich, J. Am. Chem. Soc. **78**, 2656 (1956)
M. Tabana, H. Maki, Jap Pat. 031,745, 031,746, 18 Mar 1976, to Sumitomo Chem.
A. Taguet, M.A. Huneault, B.D. Favis, Polymer **50**, 5733 (2009)
Y. Tajima, K. Kawaguchi, T. Nakane, 5,300,572, 05 Apr 1994, to Polyplastics
Y. Tajima, K. Miyawaki, H. Sano, Europ. Pat. Appl. 494,533, 23 Dec 1991, to Polyplastics
T. Takahashi, Ph.D. thesis, Yamagata University, Yonezawa (1996)
T. Takahashi, T. Kobayashi, PCT Int. Appl. WO 92 20,745, 26 Nov 1992, to E. I. du Pont
T. Takahashi, T. Kobayashi, PCT Int. Appl. 011,206, 10 June 1993, to E. I. du Pont
T. Takahashi, Y. Naka, J. Takimoto, K. Koyama, *Sen-i Gakkai Prep*. 67–68 (1996)
K. Takayama, T. Endo, O. Kanoto, N. Matsunaga, Jap. Pat. 03 134,050, 07 June 1991, to Polyplastics
M. Takayanagi, T. Ogata, M. Morikawa, T. Kai, J. Macromol. Sci. Phys. **B17**, 591 (1980)
K. Takayanagi, K. Nishida, K. Suzuki, U.S. Patent 5,352,721, 04 Oct 1994, to Mitsubishi Petrochem.
Takkosha Company Ltd., Jap. Pat. 010,736, 13 June, 1967
Y. Tamura, Jap. Pat. 258,253, 20 Dec 1985, to Mitsubishi Petrochem.
H. Tan, L. Li, Z. Chen, Y. Song, Q. Zheng, Polymer **10**, 3522 (2005)
M. Tanahashi, M. Kojima, Jap. Pat. 012,225, 04 May 1970, to Chisso Corp.
A. Tanaka, H. Anno, T. Kawahara, T. Hattori, Ger. Offen. 2,013,570, 07 Oct 1971a, to Japanese Geon.
H. Tanaka, M. Matsuo, N. Izawa, Jap. Pat. 005,065, 08 Feb 1971b, to Japanese Geon.
H. Tanaka, S. Futamura, K. Kato, Jap. Pat. 001,866; 001,868, 18 Jan 1971c, to Japanese Geon.
A. Tanaka, T. Hattori, H. Anno, T. Kawahara, Brit. Pat. 1,275,332, 24 May 1972, to Japanese Geon.
C. Tanaka, S. Nakajima, M. Morikawa, Jap. Pat. 040,851, 31 Mar 1979, to Toray
S. Tanaka, J. Sakai, T. Fukao, K. Wakatsuki, K. Wakamatsu, Europ. Pat. Appl. 285,414, 05 Oct 1988, to Sumitomo Chem.
T. Tanaka, H. Nakano, H. Satoh, S. Gotoh, Europ. Pat. Appl. 506,076, 30 Sept 1992, to Mitsubishi Petrochem.
T. Tang, B. Huang, Polymer **35**, 281 (1994)
H. Tashiro, H. Naito, M. Takayama, I. Yoshimura, U.S. Patent 4,384,032, 17 May 1983, to Asahi-Dow
I. Tatuhiko, O. Akira, Ger. Pat. 3,150,341, 01 July 1982, to Daicel Chem.
Teijin Chem., Jap. Pat. 082,151, 20 June 1980
Teijin Chem., Jap. Pat. 153,042, 21 Sept 1982
Teijin Chem., Jap. Pat. 017,153, 01 Feb 1983; Jap. Pat. 129,045, 01 Aug 1983
Teijin Chem., Jap. Pat. 043,053, 09 Mar 1984
B. Tekkanat, H. Faust, B.L. McKinney, Europ. Pat. Appl. 533,304, 24 Mar 1993, to Johnson Service Company, Globe-Union
B. Tekkanat, H. Faust, B.L. McKinney, U.S. Patent 5,280,066, 18 Jan 1994, to Johnson Service Company, Globe-Union
T. Teraya, S. Kikuchi, K. Yokoyama, Y. Fujita, Jap. Pat. 61 45,261, 24 May 1994, to Tonen Corp.
B.P. Thill, U.S. Patent 4,883,836, 28 Nov 1989, to The Dow Chemical
L.S. Thomas, U.S. Patent 4,335,038, 15 June 1982, to Dow Chemical
R. Timmermann, R. Dujardin, P. Orth, E. Ostlinning, H. Schulte, R. Dhein, E. Grigat, Europ. Pat. Appl. 583,595, 23 Feb 1994, to Bayer
S.P. Ting, U.S. Patent 4,892,904, 27 June 1990, to General Electric Co.
T. Tochioka, Europ. Pat. Appl. 553,846, 04 Aug 1993, to Mazda Motor Corp.
Y. Toga, I. Okamoto, Ger. Offen. 3,314,257, 20 Oct 1983, to Daicel Chem.
S. Togo, A. Amagai, Y. Kondo, T. Yamada, Europ. Pat. Appl. 268,486, 25 May 1988, to Mitsubishi Gas Chem.

Y. Tokai, K. Sakai, Jap. Pat. 047,942, 07 July 1973, to Teijin
E.F. Tokas, U.S. Patent 4,308,355, 29 Dec 1981, to Monsanto
M. Tokihisa, K. Yakemoto, T. Sakai, Polym. Eng. Sci. **46**, 1040 (2006)
T. Tomita, M. Ohsugi, D. Adachi, Europ. Pat. Appl. 566,149, 20 Oct 1993, to Mazda Motor Corp.
T. Tomita, M. Ohsugi, D. Adachi, Jap Pat. 60 41,444, 15 Feb 1994, to Mazda Motor Corp.
I. Tomka, Ger. Offen. 4,116,404, 19 Nov 1992, to Bio-Tec Biologische Naturverpackungen
I. Tomka, J. Meissner, R. Menard, Ger. Offen. 4,134,190, 22 Apr 1993
I. Tomka, U.S. Patent 5,705,536, 06 Jan 1998; U.S. Patent 5,844,023, 01 Dec 1998, to Bio-Tec Biologische Naturverpackungen
Toray Ind., Jap. Pat. 080,458, 17 June 1979
Toray Ind., Jap. Pat. 102,651, 06 Aug 1980
Toray Ind., Jap. Pat. 004,653, 19 Jan 1981
Toray Ind., Jap. Pat. 034,152, 24 Feb 1982
Toray Ind., Jap. Pat. 017,151, 01 Feb 1983
Toray Ind., Jap. Pat. 027,946, 14 Feb 1984
Toray Ind., Jap. Pat. 038,460, 28 Feb 1985
L.T. Toy, A.N.K. Lau, C.-W. Leong, PCT Int. Appl. WO 94 014,890, 07 July 1994, to Raychem Corp.
Y. Toyama, T. Miyaji, E. Okuya, Jap. Pat. 179,449, 13 Sept 1985, to Japan Synthetic Rubber
Toyobo Company Limited, Jap. Pat. 167,740, 23 Dec 1981
Y. Toyoda, K. Yasue, T. Okamoto, F. Ohama, Jap. Pat. 61 190,552, 25 Aug 1986, to Unitika
E. Tschunkur, W. Bock, Ger. Offen. 570,980, 1933, to I. G. Farbenindustrie
M.V. Tsebrenko, N.M. Rezanova, G.V. Vinogradov, *Nov. Reol. Polim. 11th Mater. Vses Simp. Reol.* **2**, 136 (1982)
M.V. Tsebrenko, A.V. Yudin, T.I. Ablazowa, G.V. Vinogradov, Polymer **17**, 831 (1976)
T. Tsuda, K. Azuma, Jap Pat. 03 62,853, 18 Mar 1991, to Toa Gosei Chem.
H. Tsukahara, M. Niino, Fr. Demande 2,665,904, 21 Feb 1992, to Asahi Kasei Kogyo
H. Tsukahara, M. Niino, U.S. Patent 5,354,798, 11 Oct 1994, to Asahi Kasei Kogyo
T. Tsumato, K. Asai, Y. Suzuki, Jap. Pat. 010,161, 19 Jan 1987, to Sumitomo Chem.
T. Tsumiyama, T. Shimada, Y. Akagawa, S. Nakamoto, T. Takada, Europ. Pat. Appl. 294,062, 07 Dec 1988, to Ube Ind.
K. Tsunawaki, S. Sasama, K. Watanabe, K. Nawata, Jap. Pat. 031,247, 24 Apr 1973, to Teijin
T. Tsutsumi, T. Nakakura, S. Morikawa, K. Shimamura, T. Takahashi, A. Morita, N. Koga, A. Yamaguchi, M. Ohta, Y. Gotoh, M. Amano, H. Oochi, K. Ito, U.S. Patent 5,312,866, 17 May 1994, to Mitsui Toatsu Chem.
J.A. Tyrell, O.M. Boutni, G.L. Freimiller, U.S. Patent 4,469,852, 04 Sept 1984, to General Electric Co.
Ube Ind. Ltd., Jap. Pat. 043,057, 09 Mar 1984
Ube Ind. Ltd., Jap. Pat. 69,159, 19 Apr 1985
S. Ueda, S. Sasame, Jap. Pat. 062,551, 31 Mar 1986, to Asahi Chem. Ind.
K. Ueno, T. Maruyama, Jap. Pat. 030,247, 06 Mar 1979, to Sumitomo Chem.
K. Ueno, T. Maruyama, Europ. Pat. Appl. 024,120, 25 Feb 1981, to Sumitomo Chem.
K. Ueno, T. Maruyama, U.S. Patent 4,315,086, 09 Feb 1982, to Sumitomo Chem.
K. Ueno, H. Inoue, A. Furuta, S. Ebisu, Europ. Pat. Appl. 052,854, 02 June 1982a; Jap. Pat. 108,153, 06 July 1982b, to Sumitomo Chem.
Union Carbide Corp., Neth. Pat. Appl. 6,604,731, 10 Oct 1966
Uniroyal Incorporated, Brit. Pat., 1,128,121, 25 Sept 1968
Unitika Ltd., Jap. Pat. 115,452, 17 July 1982
Unitika Ltd., Jap. Pat. 067,749, 22 Apr 1983
Unitika Ltd., Jap Pat. 112,929, 23 Jan 1984
H. Urabe, I. Ikuhara, Europ. Pat. Appl. 341,623, 15 Nov 1989, to Mitsubishi Kasei Corp.
S. Usami, Y. Ochiai, Jap. Pat. 034,941, 25 Mar 1976, to Kureha Chem.
L.A. Utracki, J. Rheol. **30**, 829 (1986)

L.A. Utracki, in *Current Topics in Polymer Science*, ed. by R.M. Ottenbrite, L.A. Utracki, S. Inoue (Hanser, Munich, 1987)

L.A. Utracki, in *Rheological Measurements*, ed. by A.A. Collyer, D.W. Clegg (Elsevier, London, 1988)

L.A. Utracki, *Polymer Alloys and Blends* (Hanser V, Munich, 1989a) [Japanese translation Tokyo Kagaku Dozin Co. Ltd., Tokyo (1991)]

L.A. Utracki, in *Multiphase Polymers: Blends and Ionomers*, ed. by L.A. Utracki, R.A. Weiss. ACS Symposium Series, vol. 395 (American Chemical Society, Washington, DC, 1989b)

L.A. Utracki (ed.), *Two-Phase Polymer Systems* (Hanser V, Munich, 1991a)

L.A. Utracki, J. Rheol. **35**, 1615 (1991b)

L.A. Utracki, in *Frontiers of Materials Research, Electronic and Materials Research*, ed. by M. Kong, L. Huang (Elsevier, Amsterdam, 1991c)

L.A. Utracki (ed.), *Encyclopaedic Dictionary of Commercial Polymer Blends* (ChemTec, Toronto, 1994)

L.A. Utracki, in *Rheological Fundamentals of Polymer Processing*, ed. by J.A. Covas (Kluver Academic, Dordrecht, 1995)

L.A. Utracki, *Commercial Polymer Blends* (Chapman & Hall, London, 1998a)

L.A. Utracki, *Foaming Polymer Blends, NRCC/IMI Internal report*, Boucherville, 1998b

L.A. Utracki, in *Encyclopedia of Polymer Blends*, ed. by A.I. Isayev (Wiley, Weinheim, 2011)

L.A. Utracki, M.M. Dumoulin, in *Polypropylene: Structure, Blends and Composites*, ed. by J. Karger-Kocsis (Chapman & Hall, London, 1995)

L.A. Utracki, A. Luciani, Can. Pat Appl., Sept 1996a

L.A. Utracki, A. Luciani, Intl. Plast. Eng. Technol. **2**, 37 (1996b)

L. A. Utracki, P. Sammut, *VAMAS TWP-PB Meeting*, Berlin, 13 Apr 1987

L.A. Utracki, P. Sammut, Polym. Eng. Sci. **30**, 1019 (1990)

L.A. Utracki, P. Sammut, Plast. Rubber Compos. Process. Appl. **16**, 221 (1991)

L.A. Utracki, P. Sammut, Polym. Networks Blends **2**, 23 (1992); ibid. **2**, 85 (1992)

L.A. Utracki, B. Schlund, Polym. Eng. Sci. **27**, 367 (1987); ibid **27**, 380 (1987); ibid. **27**, 1512 (1987); SPE Techn. Papers **33**, 1002 (1987)

L.A. Utracki, Z.H. Shi, Polym. Eng. Sci. **32**, 1824 (1992)

L.A. Utracki, M.M. Dumoulin, P. Toma, Polym. Eng Sci **26**, 37 (1986)

L.A. Utracki, M.R. Kamal, N.M. Al-Bastaki, SPE-Techn. Pap. **30**, 417 (1984)

U.R. Vaidya, M. Bhattacharya, U.S. Patent 5,321,064, 14 June 1994, to University of Minnesota

R. Van Cleve, D. H. Mullins, U.S. Patent 3,062,778, 06 Nov 1962, to Union Carbide Corp.

R. Van der Meer, J.B. Yates III, PCT Int. Appl. 000,540, 29 Jan 1987, to General Electric Co.

R. Van der Meer, R. de Jong, R. Avakian, J. M. Heuschen, Europ. Pat. Appl. 300 178, 25 Jan 1989, to General Electric Co.

C.T.E. Van Nuffel, H. T. Pham, S. Namhata, J. Eiffler, U.S. Patent 5,804,673, 08 Sept 1998, to Dow Chemical

C. P. Van Sluijs, J. F. Repin, P. J. Van Asperen, W. G. M. Bruls, Europ. Pat. Appl. 481,558, 22 Apr 1992, to DSM

J.M. Vaughan, U.S. Patent 4,524,179, 18 June 1985, to Borg-Warner Chem.

J. Vermant, S. Vandebril, C. Dewitte, P. Moldenaers, Rheol. Acta **47**, 835 (2008)

T. Vestberg, I. Lehtiniemi, U.S. Patent 5,300,578, 05 Apr 1994, to Neste Oy

S.J. Vicik, U.S. Patent 5,344,679, 06 Sept 1994, to Viskase Corp.

S. Vilasagar, H.S. Rawlings, U.S. Patent 5,302,646, 12 Apr 1994, to General Electric Co.

O. Vogl, E.H. Immergut, *Polymer Science in the Next Decade: Trends, Opportunities, Promises* (Wiley, New York, 1987)

A. Voss, Dickhäuser, Ger. Offen. 540,101, 26 June 1930, to I. G. Farbenindustrie

A. Voss, Dickhäuser, Ger. Offen. 579,048, 20 June 1933; Ger. Offen. 579,254, 22 June 1933, to I. G. Farbenindustrie

A. Voss, Dickhäuser, U.S. Patent 2,012,177, 20 Aug 1935, to I. G. Farbenindustrie

A. Voss, Dickhäuser, U.S. Patent 2,041,502, 19 May 1936; U.S. Patent 2,047,398, 14 July 1936, to I. G. Farbenindustrie

P.S. Walia, R.K. Gupta, C.T. Kiang, Polym. Eng. Sci. **39**, 2431 (1999)
A.D. Wambach, R.L. Dieck, PCT Intl. Appl. 001,276, 26 June 1980, to General Electric Co.
Y. Wang, D.C. Gale, B. Huang, U.S. Patent 8,262,723, 11 Sept 2012, to Abbott, Inc.
G.F. Ward, U.S. Patent 3,548,032, 15 Dec 1970, to Shell Oil
K. Watanabe, A. Inozuka, Europ. Pat. Appl. 409,152, 23 Jan 1991, to Daicel Chem.
K. Watanabe, M. Ozaki, J. Hara, Jap. Pat. 007,700, 29 Mar 1967, to Toyo Koatsu
M. Watanabe, T. Tazaki, S. Machida, N. Ishihara, *4th SPSJ International Polymer Conference*, Yokohama, 1992, pp. 11.29–12.03
C.A. Waugaman, J.C. Taylor, J.C. Anthony, Belg. Pat. 626,029, 13 June 1963, to B. F. Goodrich Co.
E.P. Weaver, Ger. Offen. 2,154,445, 04 May 1972, to Uniroyal
E.P. Weaver, Europ. Pat. Appl. 086,069, 17 Aug 1983; Europ. Pat. Appl. 086,069, 17 Aug 1983, to Uniroyal
E.P. Weaver, U.S. Patent 4,529,776, 16 July 1985, to Uniroyal
A. Webb, A.W. Carlson, T.J. Galvin, PCT Int. Appl. 001,733, 06 Feb 1992, to ICI
H. Weber, E. Nintz, M. Walter, D. Ballweber, B. Ostermayer, U.S. Patent 4,927,859, 22 May 1990, to BASF
M. Weber, K. Muehlbach, Ger. Offen. 4,121,705, 07 Jan 1993; Europ. Pat. Appl. 561,197, 22 Sept 1993; Ger. Pat. 4,208,339, 23 Sept 1993, to BASF
M. Weber, F. Seitz, A. Jung, N. Guentherberg, Ger. Pat. 4,227,742, 24 Feb 1994; Europ. Pat. Appl. 586,898, 16 Mar 1994; Jap. Pat. 61 72,595, 21 June 1994, to BASF
J.M. Wefer, Europ. Pat. Appl. 107,303, 02 May 1984; U.S. Patent 4,485,212, 27 Nov 1984, to Uniroyal Chem.
J.M. Wefer, U.S. Patent 4,493,921, 15 Jan 1985, to Uniroyal Chem.
J.M. Wefer, Europ. Pat. Appl. 287,207, 19 Oct 1988, to Uniroyal Chem.
G. Wegner, *4th SPSJ International Polymer Conference*, Yokohama, 1992, pp. 11.29–12.03.
K. Weyer, L. Bottenbruch, D. Neuray, W. Stix, Ger. Offen. 3,227,028, 26 Jan 1984; Ger. Offen. 3,227,029, 26 Jan 1984, to Bayer
D.M. White, R. van der Meer, PCT Int. Appl. 000,179, 12 Jan 1989, to General Electric Co.
R.J. White, S. Krishnan, U.S. Patent 4,837,243, 06 June 1989, to Mobay Corp.
R.P. White, J.E.G. Lipson, Macromolecules **45**, 1076 (2012)
M.V. Wiener, U.S. Patent 3,466,348, 09 Sept 1969, to Goodyear Tire and Rubber
D.L. Wilfong, R.J. Rolando, Europ. Pat. Appl. 547,834, 23 June 1993, to 3M Co.
J.D. Wilkey, U.S. Patent 5,288,800, 22 Feb 1994, to Shell Oil
E.S. Wilks, J. Chem. Inf. Comput. Sci. **37**, 171 (1997a); ibid. **193** (1997b); ibid. **209** (1997c); ibid. **224** (1997d)
J.L. Willett, U.S. Patent 5,087,650, 11 Feb 1992, to Fully Comp. Plastics
D.R. Williams, C.S. Ilenda, Europ. Pat. Appl. 560,496, 15 Sept 1993, to Rohm & Haas
M.L. Williams, R.F. Landel, J.D. Ferry, J. Am. Chem. Soc. **77**, 3701 (1955)
M.C.K. Willott, Brit. Pat. 1,118,545, 03 July 1968, to ICI
A. Winter, B. Bachmann, V. Dolle, Europ. Pat. Appl. 552,681, 28 July 1993, to Hoechst
K.F. Wissbrun, R.H. Ball, P.J. Rossello, Belg. Pat. 614,282, 22 Aug 1962, to Celanese Corp.
K.F. Wissbrun, R.H. Ball, P.J. Rossello, Brit. Pat. 994,376, 10 June 1965, to Celanese Corp.
C.P. Wong, U.S. Patent 5,124,184, 11 Oct 1990, to 3M Co.
C.P. Wong, U.S. Patent 5,330,697, 19 July 1994, to 3M Co.
S. Wu, Polymer **26**, 1855 (1985)
S. Wu, Polym. Eng. Sci. **27**, 225 (1987)
S. Wu, J. Appl. Polym. Sci. **35**, 549 (1988)
S. Wu, Polym. Eng. Sci. **30**, 753 (1990)
G. Wu, J.A. Cuculo, Polymer **40**, 1011 (1998)
A. Wurtz, Compt. Rend. **49**, 813 (1859)
A. Wurtz, Compt. Rend. **50**, 1195 (1860)
A. Yahata, H. Kitada, S. Tanaka, Jap. Pat. 040,756, 02 Dec 1971; Jap. Pat. 041,103, 04 Dec 1971, to Sanyo Kako

S. Yamada, Ger. Offen. 1,569,448, 04 July 1963, to Teijin Chem. Co.

N. Yamamoto, A. Nakata, A. Koshiari, A. Yanagase, Europ. Pat. Appl. 488,263, 03 June 1992, to Mitsubishi Rayon

N. Yamamoto, A. Yanagase, A. Nakata, A. Koshirai, T. Yanai, U.S. Patent 5,334,656, 02 Aug 1994, to Mitsubishi Rayon Co.

S. Yamamoto, H. Shimizu, Jap. Pat. 038,347, 22 Mar 1979, to Teijin

S. Yamamoto, A. Toyota, Europ. Pat. Appl. 489,437, 10 June 1992, to Mitsui Petrochem.

S. Yamamoto, S. Honda, H. Shimizu, Jap. Pat. 043,470, 23 Dec 1971, to Sekisui Chem.

M. Yamauchi, T. Magome, A. Takahara, T. Kajiyama, Reports Prog. Polym. Phys. Japan **34**, 229 (1991)

S. Yamauchi, K. Yasuno, S. Kitamura, Jap. Pat. 013,855, 03 Apr 1974, to Sumitomo Chem

I. Yamazaki, T. Fujimaki, Jap. Pat. 007,627, 03 Mar 1970, to Showa Denko

I. Yamazaki, T. Fujimaki, Jap. Pat. 007,141, 29 Feb 1972, to Showa Denko

W.Y. Yang, Europ. Pat. Appl. 212,449, 04 Mar 1987, to B. F. Goodrich

S. Yao, E. Kamei, Nihon Reor. Gakk. **23**, 103 (1995)

K. Yasue, T. Marutani, Y. Fukushima, T. Ida, Europ. Pat. Appl. 301,663, 01 Feb 1989, to Stamicarbon

J.B. Yates III, G.F. Lee Jr., Europ. Pat. Appl. 349,747, 10 Jan 1990, to General Electric Co.

J.B. Yates III, PCT Int. Appl. 005,311, 11 Sept 1987, to General Electric Co.

J.B. Yates III, Europ. Pat. Appl. 303,077, 15 Feb 1989, to General Electric Co.

J.B. Yates III, Europ. Pat. Appl. 550,208, 07 July 1993, to General Electric Co.

Y.-C. Ye, F.P. La Mantia, A. Valenza, V. Citta, U. Pedretti, A. Roggero, Europ. Polym. J. **27**, 723 (1991)

A.F. Yee, Y. Shi, SPE Techn. Pap. **41**, 2642 (1995)

S.-K. Yeh, S. Agarwal, R.K. Gupta, Comp. Sci. Technol. **69**, 2225 (2009)

J.K. Yeo, J.M. Oh, S.K. Chang, E.S.H. Lee, U.S. Patent 4,829.125, 09 May 1989, to Lucky

C. Yeung, R.C. Desai, J. Noolandi, Macromolecules **27**, 55 (1994)

Y. Yoga, I. Okamoto, K. Watanabe, Ger. Offen. 3,313,442, 27 Oct 1983, to Daicel Chem.

E. Yonemitsu, A. Sugio, M. Masu, T. Kawaki, Y. Sasaki, Jap. Pat. 057,754, 20 May 1976, to Mitsubishi Gas-Chem.

K. Yonetani, S. Nakamura, S. Inoue, Jap. Pat. 121,757; 121,760, 03 June 1987, to Toray

Y. Yoo, R.R. Tiwari, Y.-T. Yoo, D.R. Paul, Polymer **51**, 4907 (2010)

Y. Yoshihara, Europ. Pat. Appl. 397,531, 14 Nov 1990, to Mitsui Petrochem

T. Yoshitake, T. Tasaka, R. Sato, Jap. Pat. 050,254; 050,264, 08 May 1978, to Kuraray

S.H.P. Yu, Europ. Pat. Appl. 282,985, 21 Sept 1988; Jap. Pat. 63 314,261, 22 Dec 1988, to B. F. Goodrich

M.C.C. Yu, W.H. Beever, Europ. Pat. Appl. 473,038, 04 Mar 1992, to Phillips

L. Yu, K. Dean, L. Li, Prog. Polym. Sci. **31**, 576 (2006)

L. Yu, E. Petinakis, K. Dean, H. Liu, in *Poly (Lactic Acid)*, ed. by R. Auras, L.-T. Lim, S.E.M. Selke, H. Tsuji (Wiley, Hoboken, 2010)

H. Yui, T. Kakizaki, H. Sano, Jap. Pat. 014,752, 09 Feb 1978, to Mitsubishi Petrochem.

O. Yuichi, S. Suehiro, Europ. Pat. Appl. 304,041, 22 Feb 1989, to Nippon Petrochem.

S. Yukioka, T. Inoue, Polymer **34**, 1256 (1993)

S. Yukioka, T. Inoue, Polymer **35**, 1182 (1994)

P.C. Yung, H.C. Linstid III, U.S. Patent 5,418,281, 23 May 1995, to Hoechst Celanese Corp.

G.R. Zeichner, P.D. Patel, *Second World Congress of Chemical Engineering*, Montreal, 1981, vol. 6, p. 333

G. Zeitler, H. Mueller-Tamm, U.S. Patent 4,020.025, 26 Apr 1977, to BASF

J. Zimmerman, E.M. Pearce, I.K. Miller, J.A. Muzzio, I.G. Epstein, E.A. Hosegood, J. Appl. Polym. Sci. **17**, 849 (1973)

A. Zletz, U.S. Patent 2,692,257, 19 Oct 1954, to Standard Oil of Indiana