Chapter 5
Polyolefin Blends

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5.1 Introduction

Polymer blend is a very important application in the field of materials, and this has been widely investigated. The preparation of polymer blends gives the opportunity for preparing new materials with a good mix of the best properties of the component polymers in the blends. The extent to which the properties of the material are improved depends mainly on the morphology of the blend and the interaction between the different components in the blend. The best mix of properties is obtained when the polymers in the blend are completely miscible, but there are only very few polymer pairs that form completely miscible blends.

Immiscible polymer blends normally have a sea-island structure, where one polymer is dispersed as (normally spherical) 'particles' in the other polymer, which forms the matrix, or a co-continuous structure, where both polymers are equally distributed in the blend without one polymer forming a continuous phase. For the blends to have good mechanical properties, it is also important that there is good interaction between the different components in the blend. To ensure this, researchers have tried a variety of methods to compatibilize the polymers in blends. The most used method is to add a third polymer, which interacts well with the other two polymers, into the blend. Reactive blending is another well-used method, and recently, a lot of investigation went into the use of (especially clay) nanoparticles to improve the interaction between the polymer components by locating themselves on the interfaces between the polymers.

This chapter describes the recent research on the morphologies, properties and morphology–property relationships of a variety of blends having at least one

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M. Al-Ali AlMa'adeed and I. Krupa (eds.), *Polyolefin Compounds and Materials*,
Springer Series on Polymer and Composite Materials,
DOI 10.1007/978-3-319-25982-6_5

polyolefin (polypropylene or one of the polyethylenes) as a blend component. It also highlights the possible applications of polyolefin/polyolefin blends and polyolefins blended with a number of other commercial polymers.

5.2 Polyolefin/Polyolefin Blends

5.2.1 Blends with Ultra-High Molecular Weight Polyethylene (UHMWPE)

UHMWPE has excellent friction and wear characteristics, as well as good notched impact strength, energy absorption capacity at high loading rates, and very low embrittlement temperatures [1]. It is used in ballistics composite materials, bearing components, and medical materials in total joint replacement. It has a very high melt viscosity (108 Pa s), and it hardly flows above its melting point because of its high molecular weight. UHMWPE powders suspended in liquid LDPE or LLDPE, and their blends, show two-phase morphologies on the mesoscale. The mixture is therefore processable by conventional injection moulding machines and screw extruders. Due to the thick interfaces of UHMWPE/normal molecular weight polyethylene (NMWP) blends, there is no significant reduction in their excellent mechanical properties such as tensile and impact strength.

There is also interest in the development of different crystal structures in these systems. Such investigations are especially important to understand the morphology development during injection moulding. Both shish-kebabs and β-cylindrites are flow-induced crystals and are formed from stretched chains [2, 3]. A good understanding of the factors that influence the final morphologies that grow from the stretched chains provides more insights into the mechanism of flow-induced crystallization as well as valuable guidance in controlling the final morphology of products in industrial production.

Isotactic polypropylene (iPP) is among the most used polymers because of its high stiffness, excellent water and chemical resistance, low density, ease of processability, and superior performance-to-cost ratio. However, low heat distortion resistance and poor impact behaviour limit its applications. Injection-moulded samples of iPP/UHMWPE blends were prepared by a mini-injection moulding machine, which can provide high mechanical stresses to induce the formation of stretched chains, in order to investigate the coexistence of the shish-kebab and β-cylindrite structures [2, 3]. UHMWPE was added into an iPP matrix in order to enhance the flow-induced crystallization of iPP. The density of row nuclei was found to be critical for the formation of shish-kebab-like structures, β-cylindrites, and β-spherulites in mini-injection-moulded iPP/UHMWPE samples. When the row nuclei was dense enough, shish-kebab-like structures formed. As the density decreased, β-cylindrites and β-spherulites appeared. At low densities, or when no row nuclei existed, β-crystals disappeared and α-spherulites dominated. It was also found that during isothermal and non-isothermal crystallization processes, the overall crystallization rates of iPP increased with the addition of UHMWPE. Different nucleation mechanisms were observed for isothermal and non-isothermal crystallization. In non-isothermal crystallization, the primarily formed UHMWPE crystals acted as nucleating agents, largely increasing the number of heterogeneous nuclei for iPP crystallization, while during isothermal crystallization the UHMWPE in the blends was in an amorphous molten state. It was proposed that the interfaces between the iPP and the UHMWPE phase domains preferentially induced iPP crystal nuclei, which effectively enhanced the isothermal crystallization rate [4].

As already mentioned, the special composite microstructure of UHMWPE, where long, regular, and non-polar chains always connect different lamellae through the amorphous phase, gives it outstanding mechanical properties, very low friction and wear rate, excellent fatigue resistance, and recognized biocompatibility [5, 6]. UHMWPE is therefore used for load-bearing, articulating surfaces for the metal/articular pair in total joint arthroplasty. However, the use of UHMWPE implants in the case of high-stress applications such as total knee implants, especially in younger and more physically active patients, is limited. The damage to UHMWPE in vivo caused by wear debris, oxidation, or mechanical performance degradation adversely affects the long-term performance of the reconstructed joint. It is therefore important to enhance the mechanical properties of the UHMWPE implants without sacrificing the wear resistance and oxidation stability. Xu et al. [5, 6] successfully improved a number of properties of UHMWPE/low-molecular-weight polyethylene (LMWPE) blends through the formation of an interlocking shish-kebab self-reinforced superstructure by applying shear flow during the injection process. This superstructure made the PE blend samples very strong, and its rigidity improved the wear resistance along the direction of shear flow. When low-molecular-weight, low-density polyethylene (LMWPE) was solution-blended with UHMWPE and the film studied under a controlled temperature-gradient field, it was found that no clear lamellae were formed in the β-LMWPE-rich phase due to complex interactions such as solvent evaporation, crystallization, and phase separation [7]. However, the lamellae in the UHMWPE-rich phase became more disordered as the temperature was increased. The preferred orientation of the lamellae also strongly depended on the annealing temperature, and they stacked regularly and oriented parallel to the film surface at lower temperatures. However, the lamellae preferably oriented along the normal to the film surface, with a random distribution around that direction at higher temperatures. The film drawability was also influenced by this arrangement, as shown in Fig. 5.1.

When studying UHMWPE blended with low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE), it was found, using analysis of the log–additive rule, Cole–Cole plots, Han curves, and Van Gurp’s plot, that the LDPE/UHMWPE blends were miscible in the melt [8]. However, the thermal properties and morphology of the blends were not consistent with the rheological properties. The latter showed liquid–solid phase separation as a result of the different rates of crystallization of LDPE and UHMWPE. However, the rheological properties and electron microscopy images of LLDPE/UHMWPE blends showed

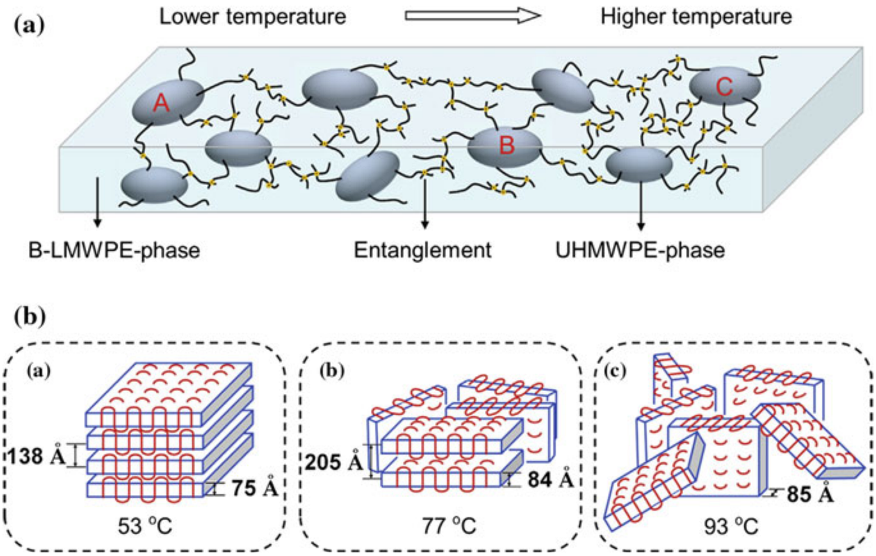


Fig. 5.1 Schematic of **a** the entanglements between UHMWPE-rich phases, where the ellipsoid represents the UHMWPE-rich phase and the nets between the ellipsoids are the entangled chains of UHMWPE, and **b** lamellae development in UHMWPE-rich phase under a T-gradient field, where *A*, *B,* and *C* correspond to the annealing temperatures 53, 77, and 93 °C, respectively [7]

partial microphase separation, with the extent of phase separation depending on the LLDPE content.

UHMWPE can also be blended with random ethylene co-polymers, but it is difficult because of a sudden decrease in the crystallinity with an increase in the incorporated monomer content [9]. This leads to a significant change in the co-polymer mechanical properties and deformation. A metallocene/methylaluminoxane (MAO) catalyst normally provides high-yield synthesis of polyolefins and olefin co-polymers, with a high incorporated α-olefin content. These catalytic systems allow one to control the structure and properties of the blend components and, therefore, to control the crystallization processes, morphology, and overall properties of the reactor blends. The precatalyst nature determines the molecular weight of the product. Ushakova et al. [10] found that the introduction of random ethylene/1-hexene co-polymers (CEHs) led to the modification of nascent reactor-blended crystalline and amorphous phases. The possibility to widely vary the composition and morphology of the co-polymer fraction from semicrystalline to completely amorphous in the polymerization with a zirconocene catalyst allowed them to change the material crystallinity and density. The tensile properties and melting indices of these blends depended on the properties of the UHMWPE fraction and the content of the CEH fraction, and on the co-polymer composition. These blends showed a high enough strength because of the presence of many interlamellar tie-molecules in the UHMWPE fraction.

5.2.2 Shape Memory Applications

Shape memory (SM) functionality is the ability of a material to fix one or more ‘temporary’ shapes after a quasi-elastic deformation and to recover its original (‘permanent’) shape through stored elastic and viscoelastic stresses that drive SM recovery after the application of an external thermal stimulus. This is normally linked to a thermal transformation like melting/crystallization or glass transition in the polymer that has a covalent or physical network. Radusch et al. [11] created SM polymers through covalently crosslinked polyolefin blends. Distinct multiple SM behaviour with high performance was obtained by blending polycyclooctene (PCO), which is thermodynamically incompatible with polyethylenes and has a low viscosity in the melt, with the polyethylenes. All the investigated materials were either quenched or slowly cooled from the melt before crosslinking. The subsequent crosslinking was performed by electron beam radiation at room temperature to fix the phase morphology, which was generated during mixing and thermal treatment. They found multiple SM behaviour only through the blending of thermodynamically incompatible materials. They also found that thermal history alone was not sufficient to improve the phase separation in thermodynamically compatible blends, which is a requirement for pronounced multiple SM behaviour. Their blends seem to have good potential for applications requiring multiple shape changes between 60 and 135 °C.

SM effects can also be induced by mixing two polymers with widely different melting points, such as LLDPE (122 °C) and PP (165 °C). A new shape memory mechanism for an LLDPE/PP/LLDPE-PP ternary SM blend was proposed [12], in which the two components that had quite different melting points both contributed to the SM performance. The PP acted as a fixed phase, the LLDPE was the reversible or switch phase, and the LLDPE-PP acted as compatibilizer to improve the compatibility of the blends. The strong interaction between the fixed and reversible phases, and appropriate blend ratios was important for the good shape memory effect of the blends. It was found that during the deformation process, the droplets of the fixed phase were unchanged, while molecular orientation occurred in the reversible phase (Fig. 5.2). Consequently, heating the material and releasing the stress reversed the shape back to the original.

Triple SMPs have one permanent shape and two temporary shapes, compared to the traditional double shape memory polymers (SMPs) that have only one permanent and one temporary shape. Triple SMPs can therefore provide more complex actuation than double SMPs. While double SMPs only need one reversible phase, triple SMPs generally need two reversible phases. Zhao et al. [13] first built a co-continuous architecture in immiscible polyethylene (PE)/polypropylene (PP) blends, and then prepared triple SMPs through chemical crosslinking of the blends. The co-continuous window of typical immiscible PE/PP blends is a volume fraction of PE of approximately 30–70 vol.%. This architecture can be stabilized by chemical crosslinking. Different initiators, 2,5-dimethyl-2,5-di(tert-butylperoxy)-hexane (DHBP), dicumylperoxide (DCP) coupled with divinylbenzene (DVB) (DCP-DVB), and their

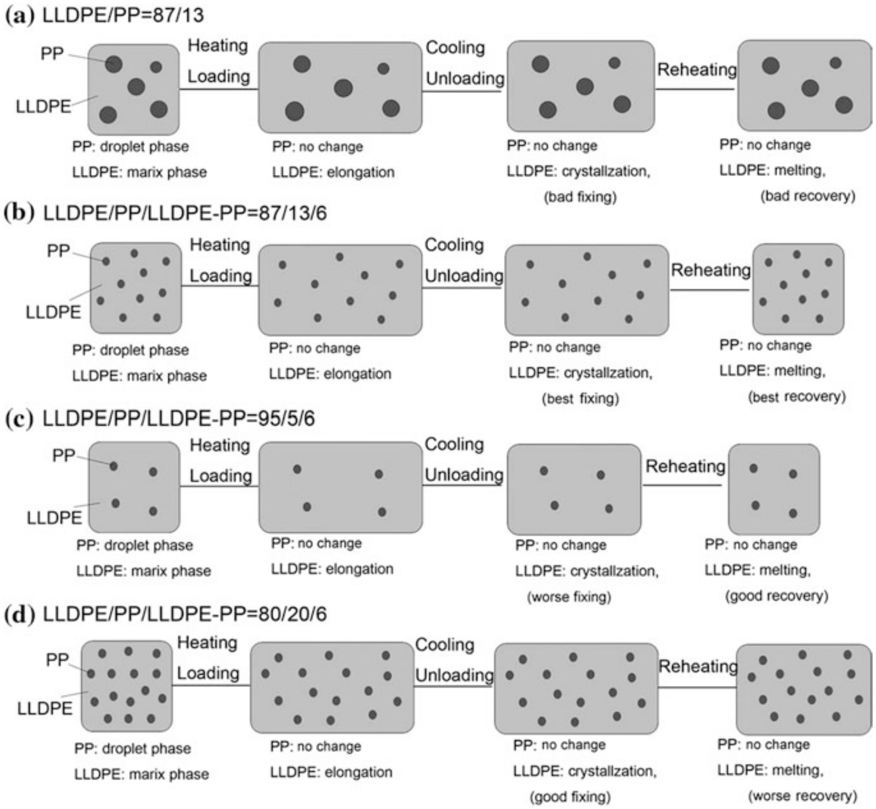


Fig. 5.2 Schematic figures of the shape memory mechanism of LLDPE/PP/LLDPE-PP blends [12]

mixture (DHBP/DCP-DVB) were used for the crosslinking. They found that DHBP produced the best crosslinking, and DCP-DVB the worst. The chemical crosslinking caused lower melting temperatures (T_m) and smaller melting enthalpies (ΔH_m). A similar investigation [14] looked at the multiple-shape memory capability of polyethylene blends that were crosslinked at the interface between a thermoplastic and an elastomer. An optimized composition containing 80 wt% ethylene octene co-polymer (EOC), 15 wt% LDPE, and 5 wt% HDPE was lightly crosslinked using DCP. The blend was found to contain finely dispersed crystalline phases, which selectively melted at distinct temperatures. The crosslinked blend was successfully programmed to a dual-, triple-, and quadruple-shape memory effect. The triple- and quadruple-shape memory showed well-defined intermediate temporary shapes (retraction < 0.5 % K^{-1}) over a significantly broad temperature range (up to 30 K), large storable strains (up to 1700 %), and nearly full recovery of all the shapes (>98.9 %).

HDPE, poly(ε-caprolactone) (PCL) (which is not a polyolefin, but is included here because of its shape memory behaviour) and binary HDPE/PCL blends containing the crosslinking agent dehydrobenzperidol peroxide (DHBP), with different mass ratios of the components, were investigated for their two-way shape memory behaviour [15]. Two-way SMEs show, on the one hand, anomalous elongation of a sample initiated by non-isothermal crystallization during cooling under load (at a constant force) and, on the other hand, the expected contraction of a sample during heating under the same load triggered by melting of the oriented crystalline phase. In contrast to irreversible one-way SMEs, invertible two-way SMEs can be reproduced repeatedly as long as the sample is loaded and the temperature change is enough to cause consecutive crystallization and melting of the sample. The SME performance of crosslinked semi-crystalline polymers therefore strongly depends on the properties of the crystalline structure and of the covalent polymer network generated in the material.

5.2.3 Compatibilization

Compatibilization of polymer blends is not a new concept, but some recent studies proposed innovative ways of compatibilizing polyolefin–polyolefin blends. Recently, the Dow Chemical Company developed a chain-shuttling catalyst technology to synthesize novel olefin block co-polymers (OBC) in a continuous process [16]. The OBC contains crystallizable ethylene/octene blocks with a very low octene content and a high melting temperature, alternating with amorphous ethylene/octene blocks with a high octene content and a low glass-transition temperature. Compared to statistically random ethylene/octene co-polymers, the OBC was much more effective in compatibilizing PP and high-density polyethylene (HDPE) blends. The adhesion of four OBCs to PP and HDPE was studied using microlayered PP/OBC/HDPE tapes [16]. Adhesive delamination occurred at the PP/OBC interface for all these OBCs. Two regimes were defined based on the tie-layer thickness. The delamination toughness increased linearly with increasing tie-layer thickness for all the OBCs in the thick tie-layer regime, which indicated that the energy was dissipated by deformation of the entire tie-layer, while the delamination toughness decreased more rapidly with decreasing tie-layer thickness in the thin tie-layer regime due to a highly fibrillated damage zone morphology.

5.2.4 Epitaxial Crystallization

Heterogeneous epitaxy is a specific interfacial crystallization between different polymer pairs due to lattice matching. Heterogeneous epitaxy at interfaces may be an active way to improve the mechanical properties of polymer blends, especially for incompatible systems. The epitaxial growth of HDPE and LLDPE on the oriented iPP lamellae, to obtain epitaxy during industrial processing and to obtain super polyolefin blends, has been clearly demonstrated, and it was shown that chain orientation induced by shearing facilitates epitaxy [17]. The crystallization of propylene-ethylene random co-polymer (PPR) is significantly promoted by flow and occurs before that of HDPE in their blends, and this sequence determines the epitaxial growth of HDPE on the PPR crystals. In a blend with HDPE as matrix, however, the epitaxial growth of HDPE under flow competes with the shear-induced formation of shish-kebabs. If shear-induced crystallization is activated, the epitaxial growth of HDPE will be suppressed and the crystallization sequence will have little effect.

Heteroepitaxy of polymers is a method to improve the mechanical properties of polymer blends, especially for incompatible systems. The epitaxy mechanism of iPP/HDPE was found to be clear [18, 19]. The epitaxially grown HDPE chains interact with rows of methyl groups that populate the iPP (010) alpha plane, since the PE chains exactly fit into the valleys formed by the methyl groups. However, well-defined epitaxial growth can only be obtained by either (a) vacuum deposition/casting film crystallization of iPP (or HDPE) onto single crystals or oriented films of HDPE (or iPP), or (b) annealing of drawn blends of iPP/HDPE and sandwiched films of iPP/HDPE. No well-defined heteroepitaxy has been achieved in polymer blends produced by traditional processing methods (such as injection moulding and extrusion). Deng et al. [18, 19] performed experiments to investigate the possible epitaxial growth between iPP and HDPE by using micro-injection moulding, which can prepare highly oriented samples, and they managed to achieve epitaxial growth at high shear and suitable temperatures. Another group [20], in a similar study, illustrated successful control of the blend superstructure via dynamic packing injection moulding. The crystalline and oriented structure in moulded bars of LLDPE/iPP blends was identified with the aid of two-dimensional wide-angle X-ray diffractometry. The iPP, which was the dominant phase, was highly oriented in the blends. The LLDPE was epitaxially crystallized on the oriented iPP and the contact planes were $(100)_{\mathrm{LLDPE}}$ and $(010)_{\mathrm{iPP}}$, resulting in an inclination of the LLDPE chains, about 50° to the iPP chain axis. Since iPP was the minor phase, it had a low level of orientation and there was no epitaxial growth between iPP and LLDPE, and the LLDPE remained oriented. The observed epitaxial growth of LLDPE on the oriented iPP was due to (1) the effect of the crystallization sequence, (2) the composition dependence of the oriented iPP structure, and (3) a 'mutual nucleation' phenomenon, where the two components acted as nucleating agents for each other.

The epitaxial growth and the formation of a shish-kebab structure were also investigated in high molecular weight iPP (HMW-iPP)/low-molecular-weight LLDPE (LMW-LLDPE) blends [21]. The formation of the initial crystallization precursor structure was investigated by using synchrotron WAXS/SAXS techniques at 130 and 140 °C. Shear was applied at temperatures above the cloud points of these blends, and therefore, the HMW-iPP chains could form a flow-induced crystalline structure in the blends only at 6 and 9 wt% of HMW-iPP; LMW-LLDPE merely served as the amorphous matrix (Fig. 5.3). When the HMW-iPP

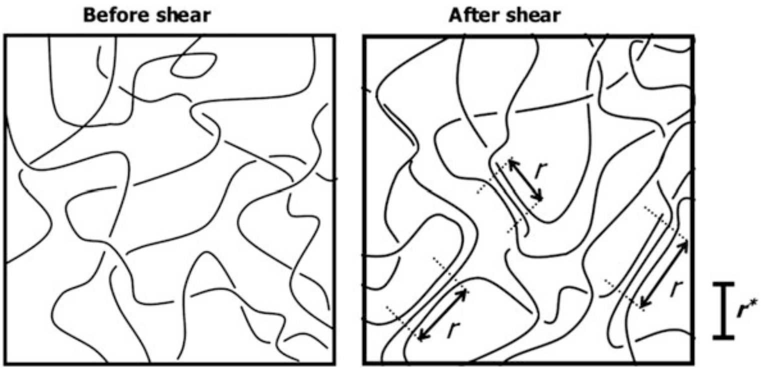


Fig. 5.3 Schematic illustration of initial crystallization precursor structure (stable critical nucleus) formation in HMW-iPP/LMW-LLDPE blends after cessation of flow. Before flow, HMW-iPP chains (*solid lines*) form a network with a given entanglement density in the LMW-LLDPE matrix (*blank area*). During shear, stretched chain segments begin to form initial crystallization precursor structure via local parallel packing. r and r^* represent the sizes of initial precursor and critical nucleus for crystallization, respectively. When $r \geq r^*$, the precursors can further develop into crystals [21]

concentration was low, no flow-induced crystallization was observed at both temperatures. When the concentration of HMW-iPP increased above 3 wt%, the flow-induced nucleation, crystallization kinetics, crystallinity, and lamellar orientation were all significantly improved.

During the extrusion of linear polyethylene (LPE) and iPP blends, the epitaxial crystallization of these blends yielded two types of epitaxial structures: (1) homoepitaxy of both components where the branches, shorter in iPP and longer in LPE, were initially oriented perpendicular to the extrusion direction, and (2) heteroepitaxy of LPE on initially crystallized iPP fibrils [22]. The positive mutual interaction of iPP and LPE was the result of the solid iPP representing a heterogeneous nucleation surface for LPE crystallization such that its lamellae were inclined ±50° to the extension direction. The limited mutual solubility of the two blend components influenced the crystallization and melting behaviour of the blend. The blend extrusion led to the iPP phase being slightly oriented towards the extrusion direction. The relatively short crystallization time resulted in a higher amorphous content and lower crystallinity, crystal size, and melting temperatures than in other highly oriented or annealed samples of iPP or LPE.

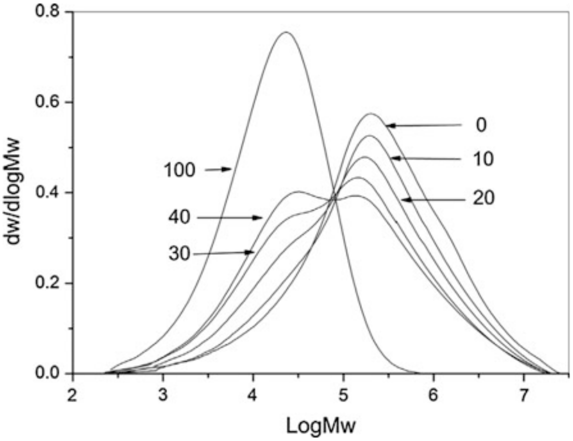
5.2.5 Other Crystallization Phenomena

As already described in the previous section, crystallization of the different components in a blend is a very important factor in determining the interaction between the different components and the blend properties. Generally, higher molecular weight will give rise to better final mechanical properties, but it also results in high melt viscosity and poor processability, which limits the application of PE [23]. Polyethylene with bimodal molecular weight distribution (defined as bimodal PE) can address this conflict between mechanical properties and processability. In bimodal PE, the low-molecular-weight fraction contributes to the stiffness and creep resistance in the crystalline state, and reduces the melt viscosity during processing. The high molecular weight fraction forms the tie-molecules that connect the crystal lamella mainly formed by the low-molecular-weight fraction, enhancing the impact strength and stress cracking resistance. Bimodal PE is produced through two methods in industry: the reactor in series configuration and the single reactor with dual site catalysts.

There was a fair amount of research into the crystallization behaviour of the low and high molecular weight components in bimodal polyolefin blends. In one such an investigation [24], differential scanning calorimetry was used to investigate the non-isothermal crystallization behaviour of blends containing low-molecular-weight polyethylene (LMWPE) and high molecular weight polyethylene (HMWPE). When LMWPE was added, the molecular weight (MW) of the blends decreased and the molecular weight distribution (MWD) broadened. Meanwhile, the low-molecular-weight fractions also increased, and the blends gradually showed obvious bimodal MWD (Fig. 5.4). The Avrami analysis modified by the Jeziorny theory and Mo's method successfully described the non-isothermal crystallization process of these bimodal PE blends, although some complicated relationships between the MW and the different analysis parameters were obtained.

In bimodal polyethylene (BPE) blends, the high molecular weight fraction with a higher degree of branching gives BPE better toughness and environmental stress crack resistance, while the low-molecular-weight fraction with a more linear chain structure ensures good processability of the material [25]. When blending an HDPE sample and an LLDPE sample with almost the same molecular weight distribution, but with a considerable difference in the short-chain-branching (SCB) content,

Fig. 5.4 MWD curves of HMWPE/LMWPE blends and their components (weight fraction of LMWPE indicated) [24]



blends with a bimodal chain branch distribution and a normal unimodal molecular weight distribution were obtained. A certain degree of co-crystallization was observed for all the blends, even after thermal fractionation, and crystal perfection was improved by the co-crystallization because the crystallizable fragments formed more prefect lamellae in the blends. The co-crystallization behaviour of this blend system effectively promotes fracture toughness, because the work of fracture (w_e) of the different blends was much higher than those of pure LLDPE and pure HDPE.

It is known that increasing MW brings good stress crack resistance and toughness to PE, but results in difficulty in processing. On the other hand, lower MW, which normally improves stiffness and ease of processing, reduces the toughness. In order to balance the relationship between processing and mechanical performance, one should simultaneously consider the MW and chain-branching parameters. With this in mind, the melt-blending of different PEs has been successfully applied in industry. However, since the crystalline phase accommodates only linear chain segments, a slight variation in the chemical structure of the PE segments that participate in the crystallization may cause these segments to be rejected by the crystalline phase, resulting in individual crystalline phases and/or segregation. In the absence of any force between the chain segments, the compatibility of different PEs depends on the accommodation of different chain segments in the crystalline phase. Analysis of the melting curves of HDPE/LLDPE blends after successive self-nucleation and annealing (SSA) treatment showed co-crystallization through a variation in the relative amount of each melting fraction [26]. When enough HDPE was added into the blends to make the number of melting peaks increase, co-crystallization occurred because the interaction between the HDPE and LLDPE molecules resulted in a new fraction forming with intermediate lamellar thickness. Once a new thermal fraction with much thicker lamella appeared through variation of the blend composition, the thickness of the original fraction slightly decreased, indicating that some long linear methylene segments were affected by the presence of HDPE and transferred from the original fraction to the newly formed fraction.

Liquid–liquid phase separation and crystallization are basic phase transitions in polymer blends. The interplay of these two processes to a large extent controls polymer morphologies. During isothermal crystallization, with the exception of very low-molecular-weight materials, co-crystallization also occurs between different materials. A study of the crystallization and melting behaviour of linear and branched polyethylenes, and their blends, using DSC and synchrotron SAXS techniques showed that co-crystallization occurred in a blend of linear polyethylene and branched polyethylene of 4.8 % hexene, whereas a blend of linear polyethylene and branched polyethylene of 15.4 % hexene showed macroscopic liquid–liquid phase separation [27]. SAXS results indicated that a large decrease in the long period in the initial stage of crystallization occurred during cooling, which gradually levelled off in the final stage. This has been explained by the lamellar insertion model, where additional thin lamellae are inserted into the thicker primary stack yielding a significant decrease in the long spacing (d_{ac}) of average lamellar stacks, and the average lamellar thickness (d_c).

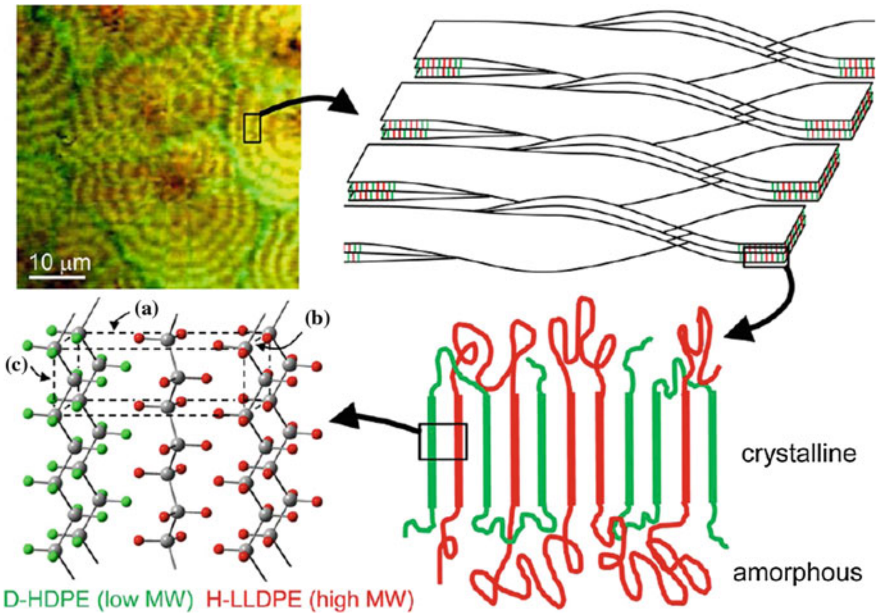


Fig. 5.5 Schematic hierarchy of microscopic structure of PE blend spherulites consisting of semicrystalline lamellar ribbons. *Green* in the composite image indicates D-HDPE, and *red* indicates H-LLDPE. The *dotted rectangular box* in the molecular structure indicates the unit cell of crystalline PE, with the unit cell parameters (*a*, *b*, *c*) as indicated [28]

The actual crystalline structure of polyolefin blends can be investigated through broadband coherent Raman (CARS) microscopy, which is a 3-D chemical imaging technique with high efficiency, developed to acquire simultaneous compositional and orientational images of multicomponent biological and materials systems [28]. CARS microscopy can simultaneously be an image of chemical composition and molecular orientation of the high and medium MW chains in a polyethylene semicrystalline blend. It was found that there was a gradual exclusion of the medium MW chains from the spherulite centre and its amorphous characteristics, a higher degree of crystallinity of the medium MW chains in the ring banding, and a filling of the interstack amorphous regions by medium MW chains (Fig. 5.5).

5.2.6 Waste and Recycling

Blending of polyolefins is increasingly used to produce usable materials from polymer waste, to improve the processing and to retain the good thermal and mechanical properties. Blend prepared from virgin and/or recycled components is a well-established strategy to handle post-consumer and post-industrial polymeric wastes. HDPE and PP constitute a significant portion of post-consumer waste [29].

PP is widely used for carpeting, packaging, and other applications, while HDPE is mostly used in the packaging of consumer and industrial products. Their occurrence in mixed scraps is likely to occur, and a complete separation of these two polyolefins is costly and almost impossible because of their close densities and similarity of other physical properties. PP shows a relatively low modulus, yield strength, and resistance to creep that limits its applications, but these properties can be improved by mechanical blending with PE.

Fang et al. [30] blended waste PP and investigated the mechanical and thermal properties of this binary blend. They wanted to improve the compatibilization of the binary blend through adding different compatibilizers (EPDM and PE-g-MAH) and a montmorillonite nanofiller, and comparing the different compatibilization effects. They blended the waste PP and PE with the different compatibilizers in a twin-screw extruder. The tensile and impact strength of the uncompatibilized blends showed a slight improvement, but the compatibilizer improved only the impact strength. The waste PP reduced the thermal stability of the blends. When the amount of waste PP was 60 wt%, the thermal stability almost reached the level of pure waste PE, but the presence of the O-MMT improved the thermal stability. EPDM had a better compatibilization effect than PE-g-MAH, but the PE-g-MAH more significantly improved the mechanical properties. Crosslinking through electron beam irradiation was also used to compatibilize waste polymers in a blend [31]. It was found that blending of waste PE with virgin HDPE and LDPE, and irradiated with an electron beam, increased the crystallinity and induced crosslinking in the blends.

5.2.7 Rheological Properties

LDPE, produced by radical polymerization at a high temperature and pressure, having a broad molecular weight distribution and long-chain branches, shows good foaming, blow-moulding, film-blowing, and extrusion coating processability. The melt elasticity of LDPE is normally enhanced by blending with LLDPE or HDPE, although both LLDPE and HDPE normally have a narrow molecular weight distribution and no long-chain branches. Mieda et al. [32] investigated the flow instability at capillary extrusion of blends composed of LDPE, as a long-chain-branched polyethylene, and three types of linear polyethylenes having different molecular weights. The effect of shear viscosity of the linear polyethylenes, which plays an important role in anomalous behaviour, on the flow instability at capillary extrusion was studied in detail. The blends containing linear PE with a high shear viscosity showed a synergetic effect, i.e. an enhanced zero-shear viscosity and marked strain-hardening. The blends showing an anomalous rheological response exhibited shark-skin failure at low shear stress, which was explained by the high Deborah number for the blends. The blends showed severe melt fracture compared to branched PE. Increased strain-hardening in elongational viscosity and a large entrance angle at the die entry were found to be responsible for this observation.

Rheological measurements were also used to detect subtle viscoelastic changes in two metallocene polyolefin co-polymers, poly(ethylene-co-hexene) (PEH), poly (ethylene-co-butene) (PEB) and their 50/50 w/w blend, by changing the moulding conditions [33]. A low level of long-chain branching (LCB) was detected in the PEB component (with higher short-chain branching (SCB) level), because of the active tertiary carbon atoms on its backbone. Since the relaxation and diffusion of polymer chains can be significantly retarded by LCB, this structure is expected to further affect the phase separation kinetics of these blends. Since PEB is less stable than PEH for moulding at temperatures above 100 °C, thermal oxidation-induced LCB was detected on PEB and the blend by rheological measurements that were more sensitive to detect the low level of LCB than other methods such as FTIR, gel extraction, and GPC. Gel extraction and GPC results indicated that there was no crosslinking for all the PEB and blend samples, which indicated that the slight LCB retarded the development of phase separation. Once LCB was beyond a certain level, the readily formed LCB entanglements prevented chain diffusion of PEB, and then phase separation could hardly occur.

Another investigation looked at the influence of different LDPE dispersed phases on the linear viscoelastic behaviour and elongation in the melt of LLDPE/LDPE blends [34]. In the case of blends of Ziegler–Natta LLDPE with LDPE, the linear viscoelastic spectrum showed an additional contribution, which could not be explained by the assumption of a simple dispersion of LDPE droplets in the LLDPE matrix. This contribution was not present when the matrix was a homogeneous LLDPE obtained by means of a single-site catalyst. It was therefore probably due to the existence of a thick interphase formed by a fraction of the longest linear molecules of the LLDPE matrix and the shortest, less branched molecules (rich ethylene sequences) of the LDPE minor phase. This interphase then gave rise to a long relaxation time tail, which could be explained by a viscoelastic model that includes the effect of non-isotropic interfacial effects with a significant elastic character.

5.2.8 Barrier Properties

Common routes to reduce gas permeability consist of combining materials, capable of giving higher barrier than the individual components, through lamination, coating, or co-extrusion. However, total barrier is no longer the main goal of food packaging, but rather the saving of freshness. This is the case, for example, with cheese and meat that must be consumed within a limited number of days, in contrast to the bakery products that are supposed to last several months. It is therefore important to investigate the modulation of the film permeability to meet specific requirements for different foods. Taglialatela Scafati et al. [35] attained the modulation of permeability by melt-blending a commercial polymer for packaging with a high-barrier material. Melt-blending is less complicated and less costly than lamination or coating, and monolayer films based on blends are attractive alternatives to multilayer co-extruded films. An LDPE/LLDPE blend was melt-blended with an ethylene/norbornene co-polymer (COC). COCs are characterized by excellent transparency, high rigidity, good thermal stability, and resistance to acids and bases. A significant decrease in O_2 and CO_2 permeability was observed with COC content ranging from 5 to 20 wt%, and the desired value of diffusional properties was obtained by adding a proper amount of COC.

5.2.9 Polyolefin Blends as Models for High-Impact Polypropylene Co-polymers (HIPCs)

HIPCs are PE-grafted PP co-polymers made through a dual-reactor process. In this way, the toughness of the material can be improved while retaining reasonable stiffness and expanding the application temperature range. A lot of research these days is aimed at unravelling the morphology and structure of these co-polymers. In some of the research, PP/PE blends are investigated as model systems for HIPCs. One investigation of such blends concentrated on the relation between the composition and mechanical performance of a series of binary polyolefin blends [36, 37]. These model compounds were fractionated with temperature rising elution fractionation (TREF) to study the possibility of fractionating industrially relevant heterophasic polyolefin systems. The separation quality, based on molecular structures or chemical composition, was found to be good for most of the systems. However, the separation of an ethylene-propylene random co-polymer and a high-density polyethylene was difficult if not impossible. Mechanical characterization, including the determination of brittle-to-ductile transition curves, showed significant effects of modifier type and amount. Toughness effects were primarily related to the modulus differences between the modifier and matrix. Compatibility and particle size were found to have a secondary influence, but were considered for a detailed interpretation of the mechanics of the investigated systems.

5.3 Polyolefin/Ethylene Vinyl Acetate (EVA) Blends

HDPE is a thermoplastic material with unique properties, such as excellent mechanical properties, ozone resistance, good electrical properties, and chemical resistance. EVA shows high impact strength, stress crack resistance, good ageing resistance, low-temperature flexibility, improved clarity, permeability to oxygen and vapours, high moisture absorption, and good electrical resistance [38–40]. Blending these two polymers should give rise to a product with a good property mix, but which should undergo much faster degradation when being disposed of.

These blends are widely used in shrinkable films, multilayer packing, and wire and cable coating. Although PE and EVA are immiscible, the vinyl consequence in EVA gives the same crystal structure as PE and partial miscibility at the interface of PE/EVA blends. Addition of EVA to HDPE could improve transparency, environmental stress cracking resistance, capacity of filler carrying, and impact properties, but usually reduces the tensile strength.

Although PE crystallinity could reach 65 %, EVA with about 50 wt% VA is completely amorphous [38]. The polarity of EVA increases as the VA content increases because of the polar nature of the acetoxy side chain. This allows manipulation of important properties such as flexible shrink wrap, agricultural films, coatings, paints, footwear soles, hot melt and heat seal adhesives, semipermeable films, flexible toys and tubing, and crosslinked foamed tyres. The addition of EVA to PE can improve its transparency, flexibility, thermal resistivity, environmental stress cracking resistance, and loading capacity of fillers. These blends possess good thermo-shrinkage and stability when subjected to ageing, weathering, and aggressive media, and are therefore used in many applications such as high-voltage cable systems, multilayer packaging films and sheets, car parts, agricultural films, and medical tubes.

The addition of PE provides a higher rigidity to the products and at the same time improves the flowability of the melt during processing. Since EVA is more expensive than PE, blending can be an effective way for cost saving [39]. Most polymer blends have some degree of immiscibility, giving rise to a multiphase morphology, and this strongly affects the rheological behaviour and mechanical properties that depend on the type of morphology and on the interfacial interaction between the phases. On increasing the EVA content, the morphology of these blends changes from a two-phase structure, if EVA is dispersed, to a co-continuous morphology and, at large EVA content, a two-phase morphology again with LDPE dispersed as domains in the EVA. This influences the rheology of the melt and the mechanical properties of the solid state. The crystallization behaviour of these blends is also influenced by the morphology, with the crystallization behaviour depending on the composition.

DSC results showed a melting temperature depression of HDPE caused by the dilution effect of the non-crystalline EVA and the probable co-crystallization of some EVA chains with HDPE chains [38, 40]. Changes in the crystallization and melting temperatures of EVA were determined mainly by the nucleation effect of HDPE crystals and the effect of partial miscibility between these polymers. Crystallization kinetics results showed that the addition of more HDPE into an EVA matrix caused more heterogeneous nucleation, while the addition of EVA would delay the nucleation of HDPE at the beginning of the cooling process. Intermolecular interaction in the melt facilitated the crystallization of both EVA and HDPE.

SEM images of HDPE/EVA blends showed that these samples have two distinctive crack propagation zones: slow and fast [38]. The lengths of these zones were affected by the EVA content. The slow crack propagation zone length increased with increasing the EVA content, and matrix fibrillation was thick and short for blends containing a smaller amount of EVA. Increasing EVA content gave rise to thinner and longer fibrils.

A rheological study showed that PE was significantly less viscous than EVA at all the shear rates, justifying blending for reducing the viscosity [39]. The viscosity of the blends can be described by a logarithmic mixing rule $\log(\eta_{\text{blend}}) = \sum w_i \log \eta_I$, where w_i is the mass fraction and η_I is the viscosity of the pure component. At EVA contents lower than 75 %, the blends presented a negative deviation from the mixing rule. The stress–strain curves gradually passed from a plot representative of pure PE to that representative of pure EVA. On increasing the EVA fraction, the modulus data followed the behaviour of a system in series and, at EVA fractions higher than 75 %, the system was well described by the parallel model. The positive and negative deviations from the mixing rules could not be ascribed to crystallinity, because the crystalline content linearly depends on the EVA fraction. At small EVA fractions, PE-rich phases form and induce blend properties closer to those of PE. The increase in elastic modulus of the solid blends is probably due to strong interfacial interactions with the other phase, and these interactions are probably the result of co-crystallization.

It was further shown that the complex viscosity of the blends increased with increasing EVA content [38]. All the blends behaved as shear thinning materials and could be divided into two regions: (i) high shear thinning at lower frequencies and (ii) low shear thinning at higher frequencies. The viscosities of the EVA rich blends were higher than those of the neat polymers, which was due to a restriction of the molecular mobility and a reduction of the free volume induced by the addition of EVA. As the amount of EVA increased, the storage modulus, Young's modulus, and hardness decreased—all these properties are related to the crystallinity of the material which decreased with increasing EVA content.

LDPE and EVA are used in the manufacture of polymeric foams; an LDPE/EVA foam possesses higher flexibility and impact resistance [41]. Crosslinked polyethylene foams have better heat resistance than the uncrosslinked ones. Crosslinked EVA usually shows better nucleation control and the formation of cells with uniform size in the foaming of EVA. Scission and crosslinking of polyethylene molecular chains can occur simultaneously when it is subjected to irradiation by γ-rays. Chain scission occurs mainly at a low dose, and chain crosslinking at a higher dose. Crosslinking results in the formation of a three-dimensional network in the LDPE/EVA blends, leading to an increase in the melt viscosity and strength of the blend. It was found that LDPE/EVA foams irradiated to 50 kGy had the most uniform cell morphology, giving the best cell size uniformity (Fig. 5.6). The crosslinking improved the melt viscosity and strength, leading to a higher resistance to bubble expansion and an obstacle to coalescence of neighbouring cells, giving rise to smaller cell sizes and a higher cell densities in the foams. An increase in EVA content resulted in a decrease in the melt viscoelasticity of the blend. The cell expansion in the foams therefore becomes easier due to lower resistance to cell expansion. Cells can also fuse and break due to poor melt strength. After irradiation

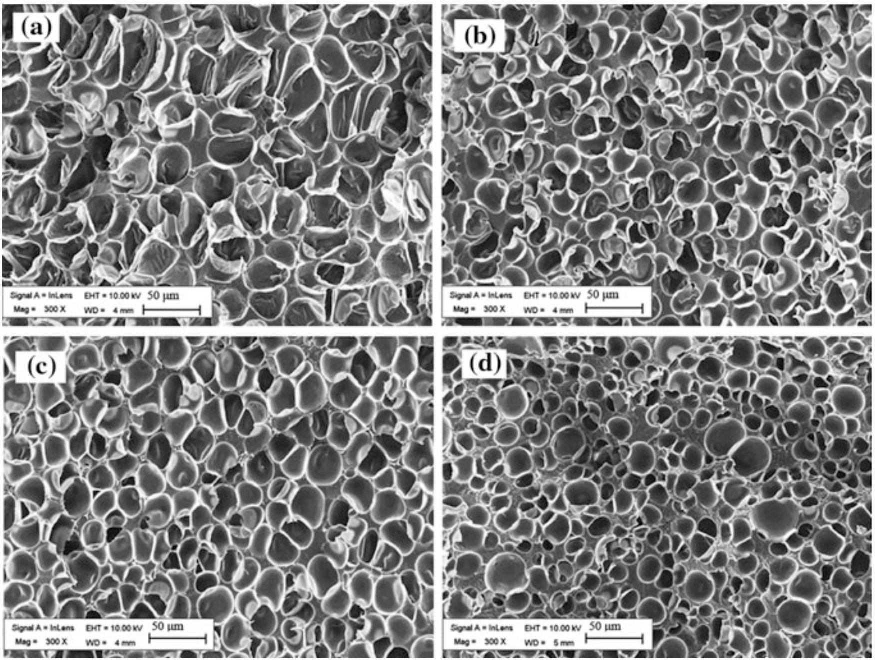


Fig. 5.6 SEM micrographs for the LDPE/EVA blend (70/30) foams produced at 105 °C and 23 MPa: **a** 25 kGy, **b** 50 kGy, **c** 75 kGy, **d** 100 kGy [41]

of the blends, the melt viscosity and strength of the blends were improved through a crosslinked network. Crosslinking gave rise to a remarkable improvement in the cell structure of the foams with higher EVA contents.

Crosslinking can improve the interfacial adhesion between two phases, giving rise to improved tensile strength but reduced elongation at break due to a decrease in molecular mobility [42]. Crosslinked polymers also have better heat resistance and mechanical properties, but poor reprocessability. The mechanical properties of crosslinked polymers are determined by their crystal structure and crosslinking degree. Properties dominated by crystallinity, such as tensile modulus and yield stress, normally decrease. It was found that for uncrosslinked HDPE/EVA blends, the tensile modulus, stress at yield, and stress at break decreased markedly, while the elongation at break only slightly decreased with increasing w_{EVA} due to the presence of the soft EVA phase [42]. The tensile modulus and yield stress did not change markedly, because the crystallinity of HDPE was little influenced by crosslinking. The impact strength is increased with increasing w_{EVA} and DCP contents. The presence of crosslinked EVA gel not only improved the toughness, but also enhanced the interfacial strength due to co-crosslinking.

5.4 Polyolefin/Paraffin Blends

Polyolefin/paraffin blends are mostly used as phase-change materials (PCM) for thermal energy storage. They are a good combination because of the paraffinic nature of their respective chains, and therefore, they are compatible but not miscible, which is a requirement to ensure stable blends with separately crystallized paraffin. Energy is stored and released through the melting and recrystallization of the paraffin, while the polyolefin matrix contains the paraffin so that it does not leak during the melting process. During the last two decades, these systems have been extensively investigated, with recent studies concentrating on the influence of thermally conductive fillers on the properties and behaviour of these blends.

Chen and Wolcott [43] investigated blends of a low molar mass paraffin with HDPE, LDPE, and LLDPE to be used in energy conservation in buildings. When the building's interior temperature approaches the melt temperature of the PCM, the PCM changes from solid to liquid and, in doing so, absorbs energy. Later, when the ambient temperature drops, the PCM begins to crystallize, releasing stored thermal energy to the building and stabilizing the interior temperature. The PCM temperature will be maintained closer to the desired temperature during each phase transition period until the phase change is complete. In this manner, the PCM decreases interior temperature fluctuations, maintaining human comfort while conserving energy through the reversible phase change. HDPE, LDPE, and LLDPE were all found to be partially miscible with the paraffin. The HDPE/paraffin blend had the lowest miscibility of the three systems. Because of the influence of miscibility on the thermal behaviour of the paraffin, it was suggested to use HDPE in PE/paraffin-form-stable PCMs to maintain the energy-saving behaviour of the paraffin in building applications for reducing interior temperature fluctuations.

In another recent investigation [44], injection moulding was proposed as a profitable method to process phase-change materials, because of the ease of processing and good properties of the final parts. Blends containing 5 to 50 vol.% of wax were extruded, and in spite of the different melting temperatures of the two components, no wax loss was detected after processing. All the prepared blends were pseudoplastic, and therefore, all of them were suitable to be injection moulded. The glass-transition temperatures of the two components in the blend were detected by dynamic mechanical analysis, confirming their immiscibility.

Ternary blends containing polyethylene and a paraffin were also investigated [45]. As a third component, dibenzylidene sorbitol (DBS) was used, which is an amphiphilic molecule derived from the sugar alcohol D-glucitol. Due to the butterfly shape and propensity to undergo intermolecular hydrogen bonding between the terminal hydroxyl group and the acetal oxygens, DBS molecules can strongly interact in the presence of an organic solvent to form a physical gel through self-assembling into a fibrillar network, with the fibrillar diameter in the nanoscale. UHMWPE and liquid paraffin (LP) have excellent affinity due to their similar chemical structures and solubility parameters. The multiple phase transitions, i.e. self-assembly of DBS, liquid–liquid phase separation between UHMWPE and LP

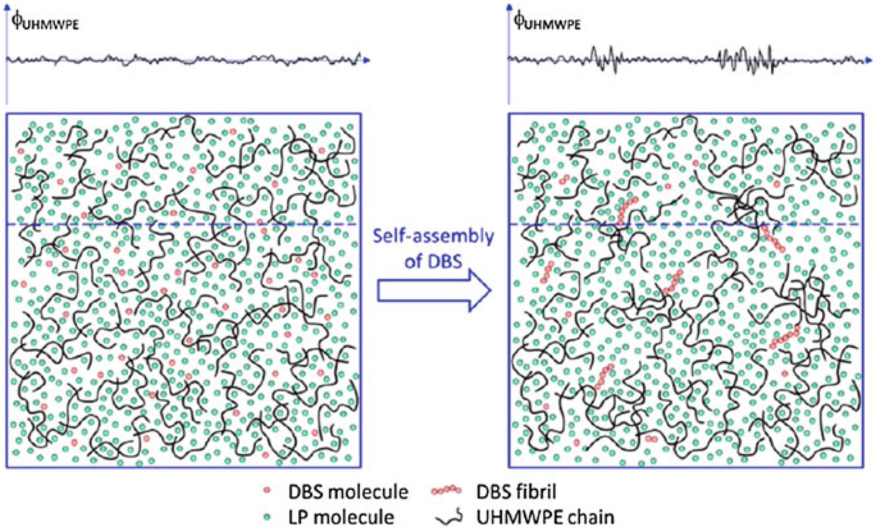


Fig. 5.7 Scheme of liquid–liquid phase separation assisted by self-assembly of DBS in the early stage [45]

assisted by the self-assembly of DBS (Fig. 5.7), and the crystallization of UHMWPE were studied. A complex relationship was found between the multiple phase transitions.

5.5 Polyolefin/Polyamide Blends

Polyolefin/polyamide blends can be used for a variety of applications where one polymer will enhance the properties of the other polymer. Research on these blends has so far been very fundamental, exploring different possibilities to compatibilize and improve the properties of otherwise very incompatible polymers.

Polyamide 6 (PA6) has good mechanical and thermal properties while LLDPE has good low-temperature flexibility and good resistance to moisture permeation. One study focused on compatibilizing an immiscible PA6/LLDPE blend through electron beam irradiation with glycidyl methacrylate (GMA) for cross-copolymerization [46]. The GMA has two reactive sites, which are an epoxy functional group and a double bond. The epoxy group can react with other functional groups in polymers during melt mixing and the double bond can be easily opened by a radical and then cross-copolymerization takes place at the interface (Fig. 5.8). GMA is also a low-molecular-weight material, which can easily diffuse to the interface during melt mixing. Another investigation on PA6/LLDPE blends looked at the use of these blends as shape memory polymers [47]. Shape memory transition temperatures were in the range of 120–130 °C, and a shape memory

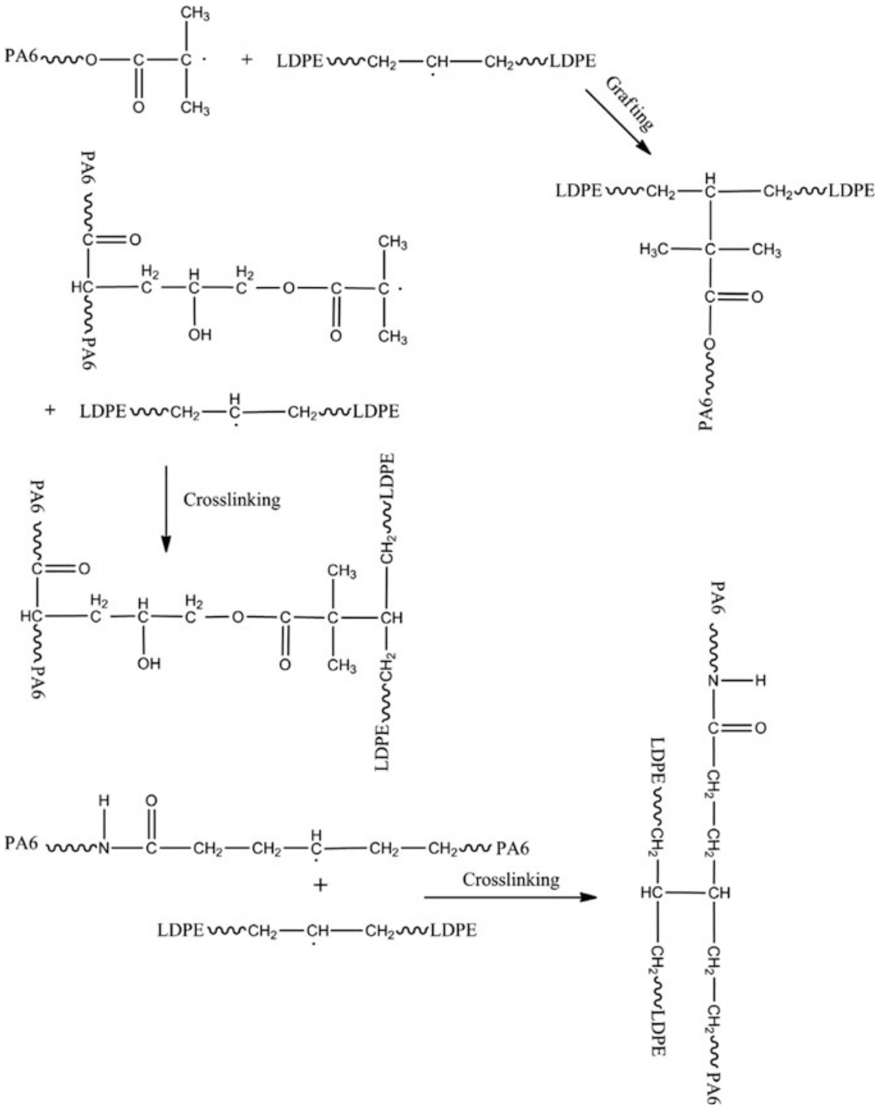


Fig. 5.8 Expected mechanisms of cross-co-polymerization at the interface between LLDPE and PA6 [46]

mechanism for this type of polymer blend SMP proposed that the LLDPE in the blend contributes to the shape memory fixing and that the PA6 in the blend with the help of PE-g-MA contributes to the shape memory recovery. The PA6 provided the stretching and recovery effects, while the LLDPE provided the fixing and unfixing effects.

PA6/HDPE blends have been widely investigated. PA6 shows good tensile strength and barrier properties, while HDPE shows good impact resistance and low-temperature flexibility. PA6/HDPE blends are thermodynamically immiscible and generally have poor ultimate mechanical properties. When these immiscible blends are subjected to stress, the stress concentrates at the interface of the immiscible blends and serves as failure initiation points. An investigation on twin-screw extruded 50/50 w/w PA6/HDPE blends containing different amounts of functionalized multiwalled carbon nanotubes (FMWCNTs) showed that, at relatively low FMWCNT contents (0.5 and 1.0 wt%), the addition of FMWCNTs had no influence on the phase morphology of the blend [48]. The PA6 still formed the continuous phase while the HDPE formed the dispersed phase. At moderate FMWCNT contents (2.0 and 5.0 wt%), the nanocomposites showed typical co-continuous morphology, and at high FMWCNT contents (10 wt%), the PA6 formed the dispersed phase and HDPE formed the continuous phase, indicating the occurrence of phase inversion. Further results showed that the FMWCNTs selectively distributed in the PA6 phase due to the lower interfacial tension between the PA6 and the FMWCNTs. As a consequence, the crystallization behaviour of the PA6 component changed. Rheological measurements showed the formation of an FMWCNT network structure, which was the main reason for the formation of the co-continuous morphology. It was also found that the incorporation of FMWCNTs significantly improved the ductility of the immiscible blend. The FMWCNTs induced a change in the crystallization behaviour of the PA6 component and a two-step crystallization process occurred, while the crystalline structures of both the HDPE matrix and the PA6 dispersed particles were varied insignificantly. The much improved interfacial adhesion was ascribed to a nanobridge effect of the FMWCNTs on the interfaces, which prevented crack initiation and propagation along the interfaces under stress.

Argoud et al. [49] investigated the morphologies of these blends, but they used MA-g-HDPE as reactive compatibilizer. They observed two characteristic sizes. At the larger scale, the characteristic domain sizes varied from 10 μm down to ~1 μm, specifically in case of co-continuous morphologies, depending on the compatibilizer/HDPE ratio. The composition (the PE/PA6 volume ratio) was the predominant system parameter which determined the type of morphology, and the morphology depended very little on the amount of compatibilizer (for a compatibilizer structure which does not induce a strong curvature at the interface). As expected, by increasing the compatibilizer amount, the characteristic size became smaller. The compatibilizer also suppressed coalescence and stabilized the micrometer scale morphologies. Under load, a crack usually initiates and propagates along the interface, leading to failure of the materials [50]. The minor phase of the blend forms dispersed particles with large diameters. This is unfavourable for the improvement of the mechanical properties of the blend. Improvement of the interfacial strength and decreasing the diameter of the dispersed particles are the key issues to obtain materials with excellent mechanical properties. The presence of clay did not seem to improve the interfacial adhesion, and the main reason for the improvement in mechanical properties was the change in the morphology. For an immiscible HDPE/PA6 blend containing both clay and HDPE-g-MA compatibilizer, the blend morphology was determined by a competition between and/or synergistic effects of the clay and the compatibilizer. The most acceptable model is that the clay functions first, decreasing the average diameters of the dispersed particles and stabilizing the morphologies of the blends. The compatibilizer effect then follows, strengthening the interfacial adhesion between the dispersed particles and the matrix.

Instead of using a reactive compatibilizer, silane grafting can also be used with nanoclay to improve the morphology of HDPE/PA6 blends [51]. Both these modifications play a significant role in the morphology of the HDPE/PA6 blends, where nanoclay acts as a nucleating agent and/or barrier to coalescence of PA6 droplets, and silane grafting along with the location of the clay at the interface mediates the polarity between the two phases and causes improved interfacial adhesion. The presence of organoclay and/or PA6 reduced the gas permeability of the samples. Silane grafting of the HDPE enhanced the barrier properties of the blends because of its compatibilizing effect, which caused a finer blend morphology or more delaminated clay in the nanocomposites. These blends exhibited excellent permeation resistance to both cyclohexane and oxygen.

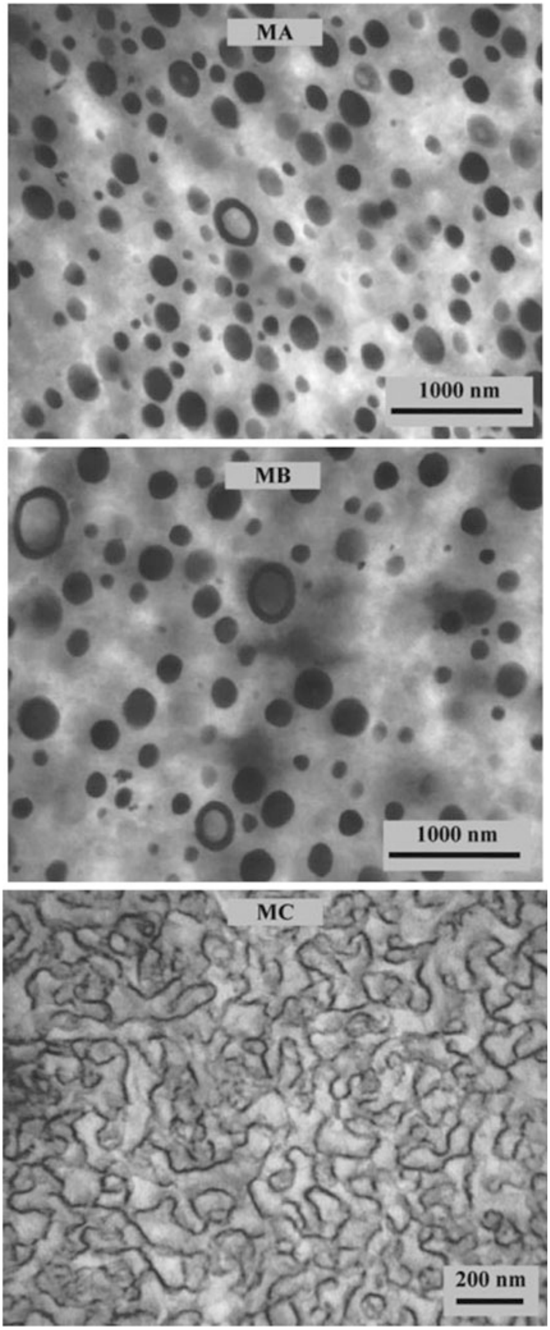
Neutralization of acrylic acid, methacrylic acid, and/or maleic anhydride (MAH) functional groups with a metal salt or alkaline bases forms ionomers from polyethylene. Ionomers are an attractive way of compatibilizing PA6 and PE, because the amide functional groups in PA6 can interact with the ionomer via hydrogen bonding, ion–dipole interaction, and/or metal ion coordination during melt-blending. Charoenpongpool et al. [52] studied the effect of zinc neutralization of hydrolysed anhydride acid groups in MAH-grafted HDPE (MAH-g-HDPE) on the efficiency of compatibilization. When using zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) as the neutralizing agent, they found that the dispersed phase sizes decreased with added compatibilizer and with increasing compatibilizer content. Compatibilization improved the mechanical properties, and significantly improved the melt viscosity of the high PA6 content blend.

An in-depth study [53] focused on the compatibilization mechanism of clay particles on the PE/PA interface. The clay-filled PE/PA blends exhibited an interphase composed of clay particles intercalated by PA chains. No emulsifying effect was obtained if the degree of exfoliation of the clay particles was too high, which was shown to happen (i) when a high viscosity polyamide was used, favouring the presence of the clay particles in the PA nodules and (ii) when a low-viscosity polyethylene was used, making deformation and break-up of the PA nodules more difficult. These results highlighted the role played by the molecular characteristics of both polyamide and polyethylene chains in the structure and properties of the intercalated PA/clay interphase. The viscoelastic properties of the PE/PA blends were significantly influenced by clay addition and content, through various mechanisms that involve changes in (i) dispersed phase interfacial area, (ii) blend morphology, (iii) clay localization, and (iv) interphase structure.

It was also found that orientation during film blowing can significantly change the ductility of the PE/PA6 blends [54]. The elongation at break in the machine direction significantly increased compared to the anisotropic value, but it tended to decrease with increased degrees of orientation. The sample, however, remained brittle in the transverse direction. The ductility was interpreted in terms of the orientation of the matrix macromolecules and the dispersed phase particles, which gave a morphology with reduced defects in the orientation direction. In an investigation of the morphologies of injection-moulded PE/PA6 blends [55], it was found that the physical properties of a water-assisted injection-moulded part can be strongly influenced by its microstructure such as molecular orientation and morphology. The microstructure is formed by a complex thermal and deformation history that a polymer has undergone during the moulding process, and it varies depending on the location in a moulded part and on the moulding conditions. Distinct skin layers, core regions, and channel layers were observed across the thickness in both gas- and water-assisted injection-moulded tubes. The shape and size of the dispersed phase depended on the position across the part thickness and along the flow direction. Small and large particles coexisted in the skin and channel layers, indicating that both coalescence and disintegration of the dispersed phase occurred in these layers. Water-moulded parts exhibited a smaller polyamide particle distribution than gas-moulded parts, and high water pressures were found to mould parts with smaller polyamide phase domains.

Grafting and crystallization effects play a very important role in the compatibility of PE and PA and the resultant mechanical properties. By an appropriate choice of the molecular parameters of the two functionalized polymers, it is possible to control the grafting reaction at the interface and thus the amount of graft co-polymer [56]. Various morphologies can be obtained, from sub-micrometer dispersion for a low graft co-polymer content to a co-continuous nanostructured morphology for a high graft co-polymer content. A co-continuous blend constituted of functionalized PE (the majority component) and PA (the minority component) showed outstanding mechanical properties at low and high temperatures. It is possible, through morphology control provided by reactive blending, to produce stable co-continuous morphologies and also sub-micrometer droplet dispersions in PE/PA blends (Fig. 5.9). Since both blend components can crystallize, there should be an influence on the nucleation and overall crystallization kinetics of the blend, depending on which component crystallizes first. The nucleation and crystallization of PA chains strongly depend on the surrounding environment. When they are in the bulk state, they nucleate heterogeneously and crystallize at low supercoolings. When they are confined with functionalized PE in a sub-micrometer co-continuous morphology (and compatibilized by a graft co-polymer between the phases), their crystallization rate is depressed and larger supercoolings are needed for their crystallization. There was a correlation between the Avrami index and the confinement of the PA chains. As the confinement increased (on going from the bulk state to a co-continuous phase to dispersed sub-micrometer particles), the Avrami index decreased.

Fig. 5.9 TEM micrographs for the three PE/PA blends prepared by reactive extrusion [56]



5.6 Polyolefin/Rubber Blends

Thermoplastic elastomeric materials based on blends of ethylene propylene diene terpolymer (EPDM) and polyolefins combine the processing advantages of thermoplastics with the excellent physical properties of elastomers, giving rise to materials with excellent properties for use in the automotive industry, extruded profiles for windows, electrical cables and wires, packing materials, and footwear [57–60]. Car parts remain the largest market for thermoplastic elastomer compositions. EPDM exhibits excellent resistance to weather, ozone, acids, and alkalis while accommodating high volume fractions of filler and liquid plasticizers and retaining desirable physical and mechanical properties. The blending of EPDM with HDPE was found to improve the physical and mechanical properties of EPDM.

Stelescu et al. [57] found an increase in elongation at break and tear strength values of EPDM/HDPE blends, compared to the uncompatibilized sample. Incorporation of PE-g-MA or dynamic vulcanization led to an increase in contact angle, indicating an increase in the hydrophobicity of the composite surface. Addition of PE-g-MA or an increase in PE content determined the increase in the percentage crystallization in EPDM/HDPE blends. Solvent vapour permeation is an energy-saving process to remove volatile organic components (VOC) from contaminated air streams, and it is much more effective than classical VOC control processes such as incineration, oxidation, and active carbon absorption. Analysis of the equilibrium sorption of a vapour by an HDPE/EPDM blend can provide information regarding polymer–polymer interactions [58–60]. The amount of sorbed vapour is related to its interactions with the blend. It was found that the permeability and sorption coefficients increased with an increase in the EPDM concentration, and the permeation rate decreased with an increase in the molar mass of the penetrants, and as the degree of crosslinking increased, the permeability decreased (Fig. 5.10).

Thermoplastic elastomers have a large number of applications due to their unique combination of mechanical properties and processability [61]. The modulus values, from low temperatures near the glass transition of the rubber to higher temperatures around the softening point of the plastic, are comparable with those of reinforced-vulcanized rubbers. During processing, thermoplastic elastomers are in the molten state and they can be processed with plastic processing equipment. Non-irradiated LDPE blends in different compositions with SEBS and SEBS-g-MA block co-polymers showed better mechanical, thermal, and volume resistivity properties than pure LDPE. The improvement in the properties of the non-irradiated blends by using SEBS-g-MA was more significant than when using SEBS. The mechanical, thermal, and electrical properties were further improved after electron beam irradiation.

Polyethylene can also be blended with a number of other rubbers. When ozonolysed natural rubber is blended with polyethylene and cured, it was found that sulphur dynamic vulcanization was better than peroxide curing, with a higher crosslink density resulting in a change in the LDPE crystallization behaviour [62].

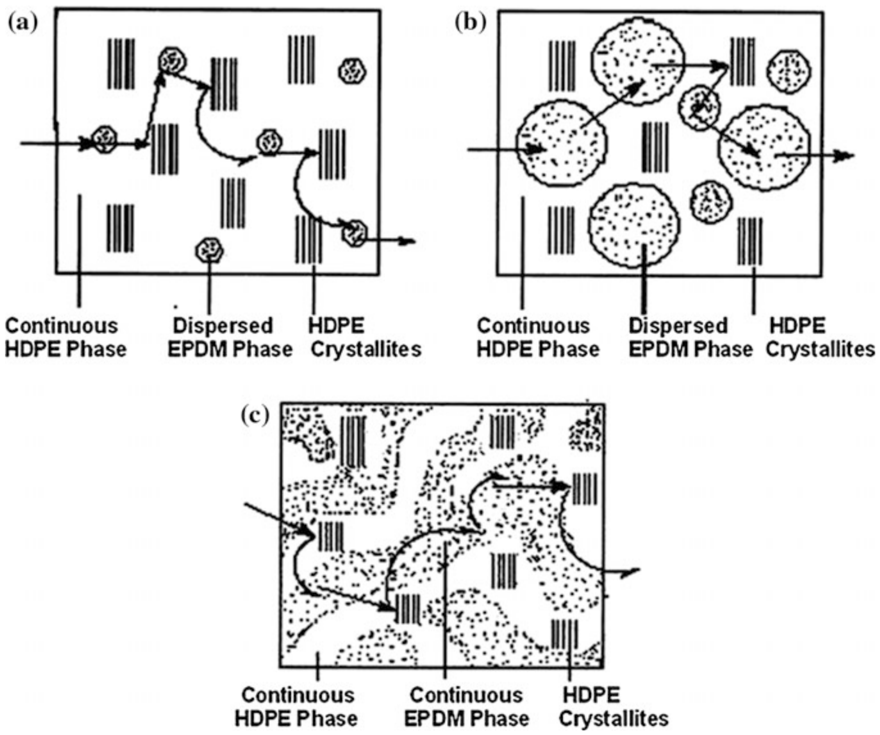


Fig. 5.10 Schematic representation of the tortuous path exhibited by the crystalline HDPE phase to the transport of solvent [60]

The α-temperature of LDPE shifted when the ozonolysed NR loading reached 50 % w/w for peroxide curing and 40 % w/w for sulphur vulcanization. The tensile strength and elongation at break of the peroxide-cured blends were much better than those after sulphur curing. The tensile strength and elongation at break of the peroxide-cured blends significantly increased with the ozonolysed NR content in the blends.

When a radiation-crosslinked semicrystalline polymer is stretched, the molecules are oriented in the stretching direction gets frozen in its extended form. If the stretched sample is heated (without any mechanical force), the material shrinks. Such heat-shrinkable polymers find applications in the packaging and cable industries and in heat-shrinkable tube production. When nitrile butadiene rubber (NBR) was mixed with HDPE, the tensile modulus increased with increasing HDPE content and increasing radiation dose [63]. Radiation dose had little effect on the elongation at break at high HDPE contents, but this property decreased with increasing radiation dose up to 150 kGy at high NBR contents. The hardness increased significantly with HDPE content, but only slightly with increasing radiation dose. Permanent set decreased with increasing HDPE content and radiation dose.

It was also found that the addition of up to ~30 wt% SBR delayed nucleation, but accelerated the rate of crystallization of HDPE [64]. An SBR amounts >30 wt% in the blends delayed the crystallization of the matrix polymer. The presence of small rubber particles, dynamically crosslinked, accelerated the crystallization of the matrix, and this was attributed to the formation of more nuclei. The nucleation effect caused an increase in the overall crystallization rate. However, due to the increased rigidity of the crosslinked amorphous component, it was unable to diffuse into the spherulitic growth sites, thereby obstructing spherulitic growth. Another rubber used for heat-shrinkable materials is bromobutyl rubber (BIIR). An investigation into LDPE/BIIR blends cured through γ-irradiation showed that (i) crosslinking was induced in all the samples by the irradiation, and the extent of crosslinking increased with increasing irradiation dose and LDPE content in the blend, (ii) blending of LDPE with small amounts of BIIR gave better mechanical properties than BIIR alone, but the improvement in properties depended on the irradiation dose, (iii) the heat shrinkability increased significantly when the blend was crosslinked by gamma irradiation, and (iv) an increase in the elastomer content in the blend improved the heat-shrinkable properties [65].

5.7 Polyolefin/Natural Polymer Blends

The degradation of polyolefins involves two stages: oxidative degradation (oxo-degradation) and biodegradation [66]. Oxo-degradation incorporates oxygen into the carbon chain, which results in the formation of oxygen containing functional groups. This process can be accelerated by ultraviolet (UV) light or heating. When the molar mass of a polymer is reduced to a certain level through oxo-degradation, the oxidation products can be biodegraded by microorganisms that consume the oxidized carbon backbone fragments to form CO_2, H_2O, and biomass. This is one of the main reasons for investigating blends of polyolefins with natural polymers.

5.7.1 Starch

Starch is a natural carbohydrate storage material accumulated by green plants in granular form and is composed of amylose (linear molecules) and amylopectin (branched molecules). It is a renewable, inexpensive natural polymer that can be blended with synthetic polymers to decrease their relative amount and to lower the cost of the final product [67]. It is possible to improve their compatibility through the addition of a suitable interfacial modifier. It has been considered as a partial substituent for synthetic polymers in packaging, agricultural mulch, and other low-cost applications. The crystalline structure of starch can be disrupted through gelatinization, during which the starch is first mixed with water and subsequently stirred and heated, resulting in the formation of hydrogen bonds between the water molecules and the free hydroxyl groups of starch. Gelatinized starch, which can flow, can then be plasticized by the addition of a suitable plasticizer such as glycerol. Thermoplastic starch (TPS) can flow at high temperatures and shows good ductility, making it suitable for melt-processing. Blends of TPS and polyolefins have relatively high interfacial tensions because of the high incompatibility between the non-polar polyolefin and the highly polar TPS.

LDPE–starch blends are biodegradable because the starch moiety is a carbon source that is consumable by microorganisms [68, 69], and it is considered a feeding stimulant for insects possessing specific amylase digestive enzymes. Subsequently, the remaining synthetic polymer matrix is more easily attacked by natural elements such as thermal oxidation and ultraviolet photodegradation. PE–starch materials are suitable for the manufacturing of any kind of home and light industrial plastic containers, bottles, dishes, glasses, and cups through injection moulding. There should, however, be a specific starch concentration for each application because there are specific needs in terms of the mechanical, thermal, and water resistance properties. Weight loss during exposure normally increases with starch content and time. It is expected that about 12 years are required for the complete degradation of a sample containing 40 % starch. Even though this is a long time for biodegradable materials, it is realistic for end products with possible applications that need a longer lifetime.

Various pro-degradants have been developed to accelerate the oxidation of polyolefin under UV light [66]. A pro-degradant can be divided into two groups: (1) transition metal systems such as transition metal salts, ferrocene, and metal oxides; (2) metal-free systems such as ketone co-polymers, chemicals containing oxo-hydroxy groups, peroxides, and unsaturated alcohols or esters. Yu et al. [66] investigated the influence of the distribution of Fe- and Co-based pro-degradants in the different phases of PE/starch blends on the ultraviolet (UV) photo-oxidative degradation. The distribution in the different phases was varied by a dual step process using a side-feed on a reactive extruder. They found that the mechanical properties varied more when the pro-degradants were distributed in the PE phase, the concentration of the carbonyl groups increased as a function of UV exposure, and the concentration of carbonyl groups was higher when the pro-degradants were distributed in the PE phase.

Another investigated blend system is TPS/HDPE/NR compatibilized with PE-g-MA [70–76]. A blend of thermoplastic natural rubber (TPNR) and HDPE gives rise to a new material that exhibits good tensile properties and improved impact resistance. Incorporation of starch into TPNR should also enhance the biodegradability of the blend. Kahar et al. [70, 71] observed the occurrence of covalent bonding between the functional groups of PE-g-MA and the hydroxyl groups of starch, which confirmed reactions between these two polymers. The compatibilized blends showed better tensile properties and improved surface morphology, while the compatibilized blends with 5 and 10 % TPS showed significant improvements in tensile strength. This was attributed to better interaction at the interphase between TPS and HDPE/NR, allowing stress transfer between the phases. Another compatibilization method used for this system is dynamic sulphur vulcanization [72, 73]. Morphology studies showed that the TPS particles were homogeneously dispersed and well-embedded in the vulcanized HDPE/NR matrix, and that the tensile strength improved significantly, which was attributed to the crosslinking reactions in the NR phase. Compatibilization in these systems was also achieved through citric acid modification of starch (TPSCA) [74]. Starch hydrolysis and acetylation between the starch and citric acid were observed. The modified TPS blends showed better tensile properties and surface morphology than HDPE/NR/TPS, and the blends with 5 and 10 % TPSCA loading showed tensile strength almost the same as that of the HDPE/NR blend. This was attributed to the low viscosity of TPS, which allowed it to easily disperse when blended with the HDPE/NR matrix. The blends with TPSCA showed better dispersion of the starch in the HDPE/NR matrix.

Starch can also be propylated and blended with polyolefins. Propylated starch–LDPE blend films were prepared and the effect of the degree of substitution (DS) and starch concentration on the mechanical properties, morphology, water absorption capacity, and biodegradability of the blend films was investigated [75]. The tensile strength, elongation, and melt flow index of the propylated starch blend films were higher than those of the corresponding native starch blend film, and these properties improved with an increase in DS from 1.56 to 2.51. The propylated starch blend films were thermally more stable than the native starch blend films, and the water absorption capacity decreased for the films containing propylated starch at high DS. The biodegradability of the films increased with an increase in the starch concentration, but decreased with an increase in the DS (Fig. 5.11). LDPE-g-MA was also used as compatibilizer in corn starch (TPCS)–LDPE blends [76]. The tensile properties and impact strength of the samples decreased with increasing the TPCS concentration, but addition of up to 25 wt% TPSC gave rise to similar mechanical properties than those of pure LDPE. A linear relation was found between the reduction in melt flow index and the starch content in the blends. The

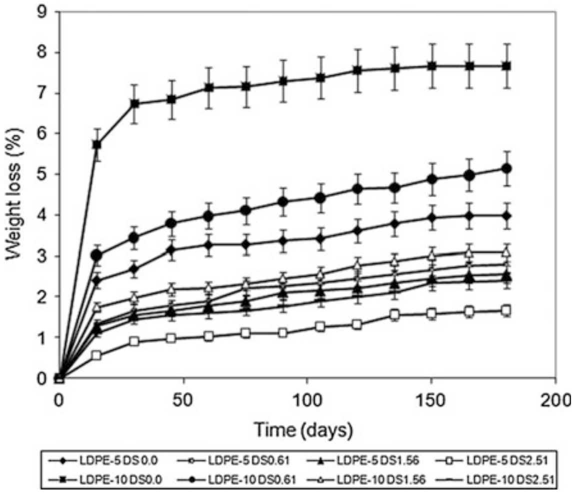


Fig. 5.11 Weight loss of starch–LDPE films during soil burial test [75]

apparent viscosity of the blends increased by increasing the starch concentration and by decreasing the shear rate.

As was the case of some previously described blends, nanofiller was included into PE–starch blends to improve the compatibility of the different components in the blends and the mechanical properties of the blends. Recently, Zeolite 5A [77] and sepiolite [78] were used for this purpose, and improved properties were generally observed.

Glycerol has mainly been used as plasticizer in TPS, but glycerol is very hydrophilic, has a low thermal stability, and it migrates to the surface with time, especially in thin films. TPS formulations, with diglycerol and polyglycerol plasticizers, were blended with HDPE at a concentration of 20/80 w/w TPS/HDPE and a range of interfacial modifier contents via a one-step extrusion process [79]. The emulsification curves of the blends that track the volume and number average diameter of the dispersed TPS as a function of per cent interfacial modifier showed significantly different profiles. The addition of small amounts of interfacial modifier to the blends gave rise to TPS droplets in the order of 200–300 nm coexisting with droplets of 5–7 μm. This wide polydispersity is indicative of an erosion-type droplet formation mechanism, where small parts of the TPS droplet break off the surface of the droplet. Blends prepared with glycerol-TPS and sorbitol-TPS did not show this behaviour. Dynamic mechanical analysis showed miscible behaviour for diglycerol-TPS and polyglycerol-TPS, and partially miscible behaviour for glycerol-TPS. This was attributed to the presence of ether bonds in the chemical structure of diglycerol and polyglycerol. The increased chain flexibility and lower cohesive energy forces of diglycerol and polyglycerol led to a more homogeneous TPS phase and to the erosion-type compatibilization at the interface. The mechanical properties of the blends prepared with polyglycerol and diglycerol showed a similar overall behaviour to that of glycerol.

5.7.2 Chitosan

Polyolefin/chitosan blends have not been investigated as extensively as polyolefin/starch blends. Chitosan is a polysaccharide more commonly found in nature, and its films can be used as packaging material because of their antimicrobial activity, non-toxicity, and biodegradability [80, 81]. The mixing of chitosan, a biodegradable polysaccharide, with LDPE decreases the fluidity of the molten polymer [80]. Mixing of PE-g-MA into this blend allows easy processing of the polyethylene/chitosan mixtures into films in standard extrusion equipment. It is therefore possible to obtain films with a maximum content of 20 wt% chitosan. The use of an anhydride-based coupling agent, extensively used to compatibilize polymer blends, was effective in improving the mechanical properties of the chitosan composites, especially the deformation at break, which makes these compositions suitable for the preparation of biodegradable films and other biodegradable items intended for short-term applications. PE films containing

15 wt% of chitosan were severely degraded in less than 6 months of exposure to natural weathering [81]. The oxidative degradation produced a significant increase in the content of carbonyl groups, and the exposure also led to the formation of microfractures and polymer embrittlement with the concomitant variation in mechanical properties. The extremely high temperatures and radiance recorded in the weathering location during the test period, and the use of PE-g-MA as a compatibilizer, accelerated the degradation rate of the films.

5.7.3 Poly(Lactic Acid) (PLA)

Although not strictly a natural polymer, PLA is a biodegradable polymer derived from natural resources. PLA is a linear aliphatic polyester derived from the fermentation of plant starches and can be bio-degraded into environmentally manageable compounds [82–84]. It has some unique properties such as good strength and stiffness, and resistance to fats and oil. Applications of PLA are limited in the commodity industries due to its brittleness, poor thermal resistance, low viscosity, high moisture sensitivity, medium gas barrier properties, high cost, and low solvent resistance compared to those of non-biodegradable polymers such as polyolefins, polyethylene terephthalate, polycarbonate, and nylon. So far PLA, because of its non-toxicity, biodegradability, and biocompatibility, has been used in biomedical and pharmaceutical applications such as implants, drug delivery carriers, and scaffolds for tissue engineering. Polyolefin/PLA blends have mainly been investigated with the aim of producing materials that have acceptable properties, but that have at least one biodegradable component. This has become necessary because of the huge plastics waste problem the world currently facing.

In an investigation of single-screw-extruded LDPE/PLA blends, it was found that the stress at break and Young's modulus values were below the mixing rule line, which is typical for incompatible polymer blends [82]. Rheological results showed that these blends were pseudoplastic in nature; their viscosity decreased with increasing shear rate similar to most polymer melts. The true viscosity of PLA decreased sharply with increasing temperature, whereas the true viscosity of LDPE varied only slightly with temperature. The true viscosity of the blends decreased with increasing PLA content, and this was attributed to the low viscosity of PLA. Adding acrylonitrile–butadiene–styrene as compatibilizers in these blends gave rise to similar observations [83]. Jiang et al. [84] did a similar investigation by using a single-screw extruder with different screw elements. They found that the different screw configurations gave rise to different morphologies, different rheological properties, and different crystallinities.

It was proposed [85] that PLA could improve the properties of PP/HDPE/EVA blends. The mechanical properties showed that the polymer blend had optimum tensile and burst strengths at 4 wt% PLA incorporated into the PP/HDPE/EVA blend. The tear strength decreased with increasing PLA content in both the machine and the transverse directions. The friction coefficient was found to be the lowest at 4 wt% PLA loading in the blend, probably because of better PLA dispersion at this loading. The modification of PP/HDPE/EVA blends with PLA caused a gradual increase in haze.

When adding an ethylene–glycidyl methacrylate–vinyl acetate co-polymer as compatibilizer into a metallocene polyethylene elastomer co-polymer (mPE)/PLA blend, the results from SEM, FTIR, and rheological studies revealed that the interaction between the mPE matrix and the dispersed PLA was enhanced with the addition of the compatibilizer [86]. The addition of the compatibilizer completely hindered the cold crystallization and rearrangement crystallization of PLA, even though the additional annealing effect of mPE/PLA blends in the injection moulder tended to increase the crystallization of PLA. The synergistic effect of compatibilization and annealing treatment significantly improved the tensile strength and Young's modulus of the blends.

In a study of ternary LDPE/PLA/poly(ethylene-co-glycidyl methacrylate) (EGMA) blends [87], it was found that there was a reaction between the epoxy groups of GMA and the functional groups (hydroxyl and carbonyl) of the PLA, which led to a good compatibilization of the blend. The SEM results supported the FTIR results and showed that the incorporation of EGMA in a 60/40 w/w LDPE/PLA blend, at a level higher than 7 phr, led to further connections between the blend phases giving rise to almost indistinguishable component domains. The uncompatibilized blends showed the typical behaviour of immiscible blends with a sharp drop in the tensile and impact properties. However, the 60/40 w/w LDPE/PLA blend containing 15 phr of EGMA showed very good mechanical strengths (Fig. 5.12). The micro-hardness characteristics of the different blends were in good agreement with the macroscopic mechanical properties such as yield stress, Young's modulus, and impact strength. Similar observations were made in the case of HDPE/PLA blends compatibilized with maleic anhydride-grafted PE [88].

The mechanical and physical properties of PLA are severely degraded when subjected to electron beam irradiation [89], because the dissipated energy from the irradiation easily causes chain scission of the backbone chain of PLA and forms free radicals. Additional additives, such as a crosslinking agent, are therefore

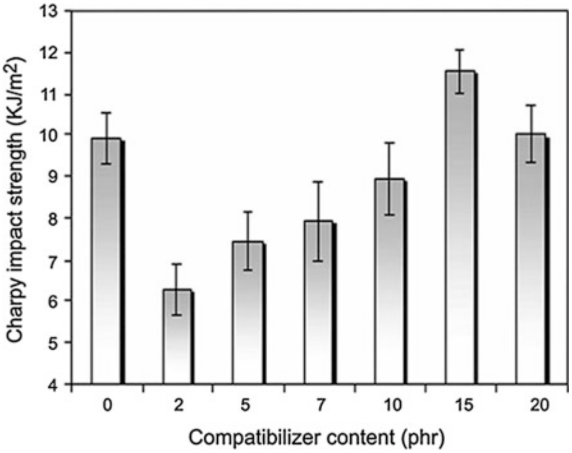


Fig. 5.12 Effect of the compatibilizer content on Charpy impact strength of 60/40 (LDPE/PLA) blend [87]

necessary to promote irradiation-induced crosslinking in PLA. LDPE is widely used in various applications due to its excellent electrical insulation, good mechanical properties and processability, and resistance to chemicals and irradiation. It tends to crosslink when exposed to high-energy electron beam irradiation and is able to withstand the application of an electron beam radiation dosage of up to 300 kGy without undergoing degradation. When the percentage of LDPE added to PLA was gradually increased, the gel content of the irradiated PLA/LDPE blends significantly increased compared to that of pristine PLA. Increasing amounts of LDPE marginally increased the crystallinity of the PLA/LDPE blend by introducing new crystalline structures to PLA. The application of irradiation significantly increased the crystallinity of these blends because of the formation of crosslinked networks that acted to converge the random structures into a highly ordered arrangement.

Poly(L-lactic acid) (PLLA) is environmentally biodegradable through a two-step process that begins with the high molecular weight polyester chains hydrolysing to lower molecular weight oligomers in an appropriate temperature and moisture environment. Microorganisms then convert these lower molecular weight components to carbon dioxide, water, and humus. LLDPE and PLLA were melt-blended in an extrusion mixer with a post-extrusion blown film attachment, with and without LDPE-g-MA [90]. Varying degrees of property modifications were achieved by blending these polymers. The most important observation was a significant increase in biodegradability of these blends, especially at higher pH values. Singh et al. [91] reported similar observations.

5.7.4 Other Biodegradable Polymers

Poly(vinyl alcohol) PVA and poly(hydroxyl butyrate-co-valerate) (PHBV) are also not natural polymers, but they are biodegradable and useful for various applications in packaging such as for foods, pharmaceuticals, chemicals, detergents, cosmetics, compost bags, grocery bags, shipping bags, cutlery, plates, and toys [92, 93]. Polymers such as polyethylene (PE), polyvinyl chloride (PVC), polypropylene (PP), polyethylene terephthalate (PET), polystyrene (PS), and polyvinyl alcohol (PVA) are most frequently used for packaging because of their excellent thermal and mechanical properties, but they persist in the environment even after many years of disposal, contributing to the waste disposal management problem. Within the PE family, LLDPE is widely utilized in packaging applications, but its resistance to biodegradation causes serious problems. Poly(vinyl alcohol) (PVA) is a water soluble polymer which is also widely used in packaging applications because of its strength and biodegradability. The packaging applications of PVA are potentially limited because of its low resistance to humidity and its poor processability [92]. These problems can be solved by blending these two polymers with in situ silane crosslinking. Biodegradable plastics like poly(hydroxybutyrate-co-valerate) (PHBV) can be used to improve the gas barrier properties of PE without sacrificing the other properties (Fig. 5.13) [93].

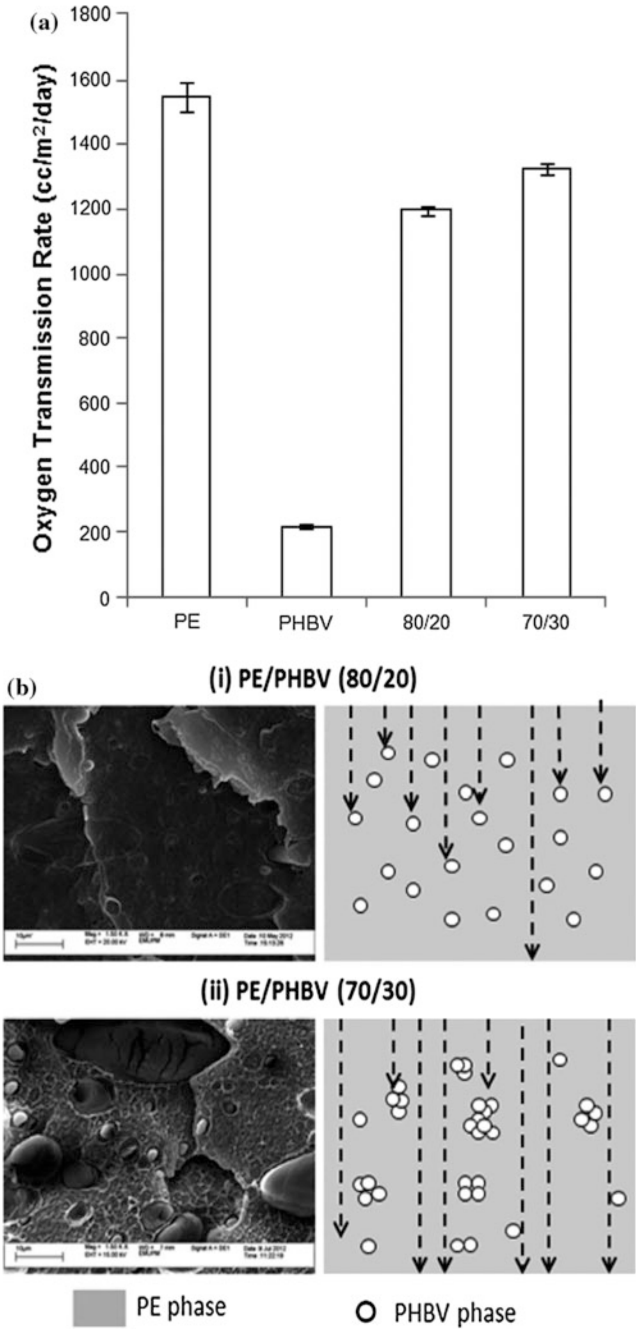


Fig. 5.13 **a** Oxygen transmission rate (cm^3 per m^2 per day) of PE, PHBV, and PE/PHBV blends (20 and 30 wt% PHBV). **b** PHBV distribution within the polymer matrix at different PHBV compositions and its effect on oxygen transmission rate [93]

Poly(butylene succinate) (PBS) is another biodegradable polymer which is not commonly blended with polyolefins. However, Yang et al. [94] investigated the effect of PBS content, extrusion rate, and extensional strain rate on the melt strength and extensional viscosity of LDPE/PBS blends using a melt-spinning technique, and developed extensional master curves. Based on both the extensional master curve and a neural network method, they compared the predicted extensional viscosities with the experimental data of the LDPE/PBS blends.

5.8 Polyolefins Blended with Other Polymers

A number of other polymers have been blended with polyolefins for a number of applications. Space does not allow one to give too many details about work done on these systems. This section will therefore summarize the proposed applications for these systems, and some very interesting observations will be included.

5.8.1 Polyaniline (PANI)

Active food-packaging systems contain agents such as antioxidants or antimicrobials, either in sachets, functionalized on the surface or incorporated directly in the packaging matrices [95, 96]. These systems do not simply provide an inert barrier to external elements, but can interact dynamically with the products or their immediate environment to enhance product shelf life. PANI, an intrinsically conducting polymer, also has antimicrobial and free radical scavenging properties. It is also relatively cheap and easy to prepare [97]. It can exist in a continuum of oxidation states and can be easily switched between the reduced and the oxidized states. It has good chemical, electrical, and optical properties that are associated with its insulating and conducting forms. The oxidation of food stuff is induced by oxygen-containing radicals, and therefore, radicals scavenging can be an effective strategy to inhibit the oxidation of food stuff, because the propagation of the oxidation reaction is prevented. Incorporating PANI in polymers such as LDPE, one of the most widely used packaging materials in the food sector, can yield antioxidant and antimicrobial active packaging systems. However, PANI's insolubility in common solvents and its poor mechanical properties make its processing very difficult. Several conventional thermoplastics, such as PE, PP, nylon 12, and polystyrene, have been combined with PANI to obtain materials with a proper balance between electrical and mechanical properties. Blends of LDPE and PANI showed particularly attractive properties as antistatic materials, for gas-separation and ion-exchange membranes, as transducers in sensor devices, and for flexible electrochemical systems.

5.8.2 Thermoplastic Polyurethane (TPU)

Some of the applications, like automotive and consumer goods, where polyolefins are used, demand that the part is painted. The non-polar surfaces of polyolefins, however, lead to poor paint adhesion. In order to enhance the adhesion between a polyurethane paint and an olefin block co-polymer (OBC), TPU can be blended into OBC [98]. TPUs are an important class of materials with desirable properties such as high strength, good abrasion, tear, oil and solvent resistance, and low-temperature flexibility. The advantage of TPU over conventional PU is that it can be melt-processed in conventional melt-processing equipment such as extruders and mixers. It has already been used extensively in cars, electronics, medicine, glazing, textiles, footwear, cable sheathing, and tubing. However, extruded TPUs do not have the desired properties for applications such as transmission or hoisting belts. UHMWPE is a material with good strength, low creep, low friction coefficient, low abrasion, and reduced wear, and the incorporation of UHMWPE into TPU can improve the tribological properties, while retaining most of the mechanical properties of the matrix [99].

5.8.3 Poly(Ethylene Terephthalate) (PET)

One of the recent applications in which recycled plastics were utilized is the production of plastic lumbers that can be used in applications where treated wood was previously used [100]. Railroad cross-ties are one of these applications. The patents on this subject claim that the appropriate material for this application is a proper combination of different disposed polymers such as 'waste polyolefins', mainly HDPE, as well as polystyrene (PS) and thermoplastic polyesters (PET or PBT). Since HDPE is the main source of plastic waste and has suitable mechanical properties at a reasonable price, it is a good candidate for plastic recycling on a large scale. However, the production of PET rapidly increased with the expansion of the packaging industry [101]. The short life cycle of beverage bottles also leads to the accumulation of post-consumed PET bottles, which inevitably creates serious environmental problems. The recycling of waste PET therefore also became important, and blending of recycled PET with PE is very attractive because of their relatively low cost and excellent properties [102]. The amount of waste from post-consumer PET and PP, especially in the beverage and packaging industry, stimulated an in-depth investigation into the production of innovative new products from recycled PET and recycled PP.

The thermal degradation stability and moisture absorption characteristics of thermoplastics are not only related to their chemical composition, but also to the effect of the dispersed phase size in polymer blends. The various forms and sizes of thermoplastic raw materials, e.g. pellets, flakes, or powder, can also have an effect on their thermal degradation stability. Smaller pellets can easily absorb moisture due to their large surface area and their surface roughness. They are therefore more susceptible to hydrolysis when exposed to high temperatures, especially in the presence of O_2. However, these small pellets can dry more quickly and thoroughly than larger pellets under similar drying conditions. These considerations led to an investigation into the thermal degradation stability and moisture absorption characteristics of PET/PP blends [103]. PP/PET blends were also investigated as shape memory polymers, which were already discussed earlier in this chapter. The shape-recovery value of the PP/PET blends increased rapidly up to 98.5 % with increasing POE-g-MAH content. The recovery rate increased with increasing recovery temperature [104].

5.8.4 Polyethylene Acrylic Acid (PEA)

PEA is well known for its use in conventional extrusion coating, co-extrusion coating, and extrusion lamination [105]. The beneficial properties of PEA, such as excellent adhesion to various substrates such as foils, paper, and films, can add value to other polymers that require these properties for specific applications. PEA/LDPE blends have many industrial uses because of their good mechanical strength, processability, and impact strength.

5.8.5 Liquid-Crystalline Polymers (LCP)

There are several reasons for the development of thermotropic LCP-modified thermoplastics [106]. LCP multicomponent mixtures with polymers such as PE, PP, PS, polycarbonate (PC), PET, poly(butylene terephthalate) (PBT), PA, poly(ether imide) (PEI), poly(ether ether ketone) (PEEK), and elastomers showed improvements in the rheological, mechanical, and barrier properties, and in the dimensional and thermal stabilities of the polymers. To effectively reduce the viscosity and hence facilitate processing, the LCP inclusions should be in the nematic state with a critical concentration oriented in the flow direction. Enhanced barrier properties are the result of the dense packing of the rigid LCP chains and the continuity and lamellar shape of the LCP phase, while the improved mechanical properties are the result of the formation of extended LCP fibrils in the matrix polymer. A self-reinforcing effect was obvious during extrusion and subsequent drawing of the compositions containing considerable amounts of LCPs.

5.8.6 Fluorothermoplastics

Blend properties are normally controlled by the morphology and phase sizes developed during the blending of two or more polymers. The polymer blend processing parameters can be controlled to a large extent by understanding the rheology of the blend. Fluorothermoplastic (THV) blends are considered a cost-effective replacement of engineering materials, especially in the fabrication of vehicle fuel tanks [107]. THV in a PE matrix has very good barrier properties that will enhance the permeability resistance of PE containers. The mechanical properties of these blends depend on the type of THV used, which determines the size and dispersion of the THV spheres in the PE matrix (Fig. 5.14).

5.8.7 Poly(3-Alkylthiophenes) (P3ATs)

Conjugated polymers and, especially, regioregular P3ATs demonstrated intriguing electrical and optical properties that led to a number of potential applications in high-performance organic thin film transistors, polymer solar cells, and chemical sensors [108]. Both the electrical and the optoelectrical properties of the P3AT-containing blends are significantly influenced by their morphology and phase behaviour. If the miscibility between P3AT and a non-conducting polymer becomes very poor, the conductivity of the blend is low. Since perfect mixing on a molecular level is not possible, a conductive network of P3AT cannot be easily formed. Poly (3-butylthiophene) (P3BT) has a limited miscibility with polyethylene, and the very small spherulites of the pure PE were changed into large, ring-banded 2D-spherulites in the thin films by blending with P3BT (Fig. 5.15). The limited miscibility created the necessary conditions for improving the growth of PE-ringed spherulites and resulted in PE lamellar twisting during crystallization with the period decreasing with increasing P3BT content.

5.8.8 Speciality Blends for Membranes and Foams

Block polymers containing an etchable block have been used as precursors for nanoporous polymers [109]. Because nanoporous polymers have large internal surface areas, large pore volumes, and uniform pore dimensions, these materials were studied as separation/purification media, battery separators, templates for nanostructured materials, low dielectric materials, and low refractive index materials. Both pore wall functionality and robustness of the matrix are important for the practical use of nanoporous polymers. As shown in Fig. 5.16, PLA was selectively etched from a blend with reactive block co-polymers to form a nanoporous material,

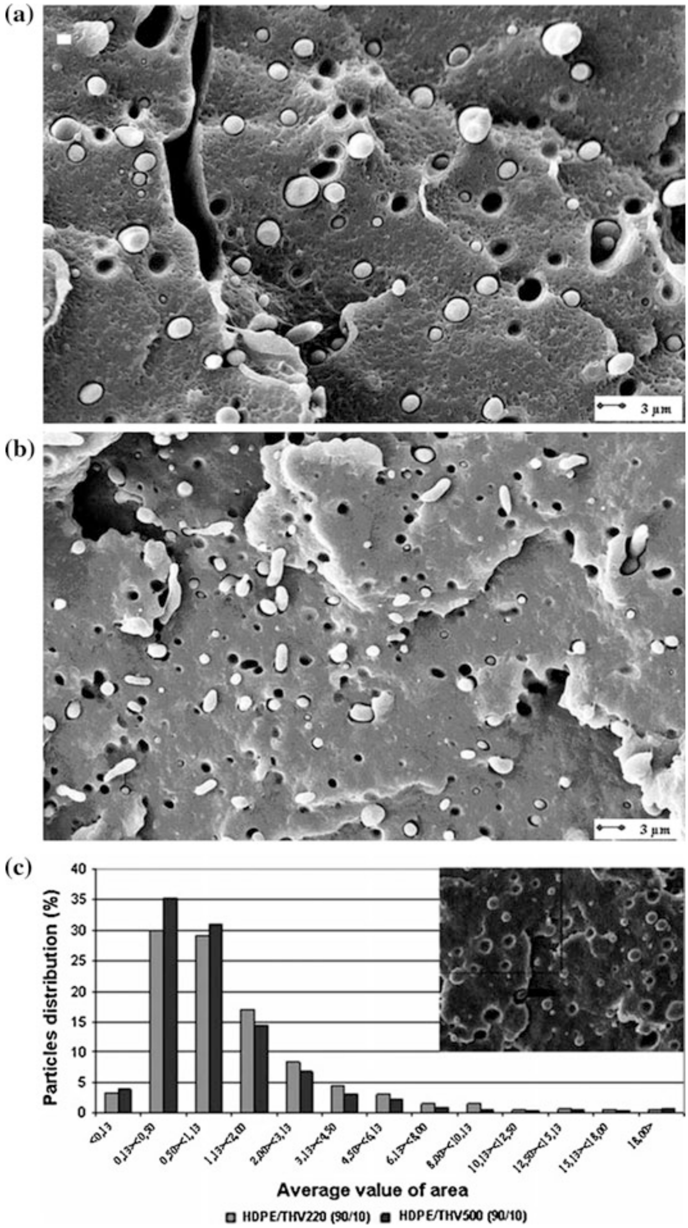


Fig. 5.14 SEM pictures of a HDPE/THV500 (90/10) blend (**a**), HDPE/THV220 (90/10) blend (**b**) and particle distribution of blends (**c**) [107]

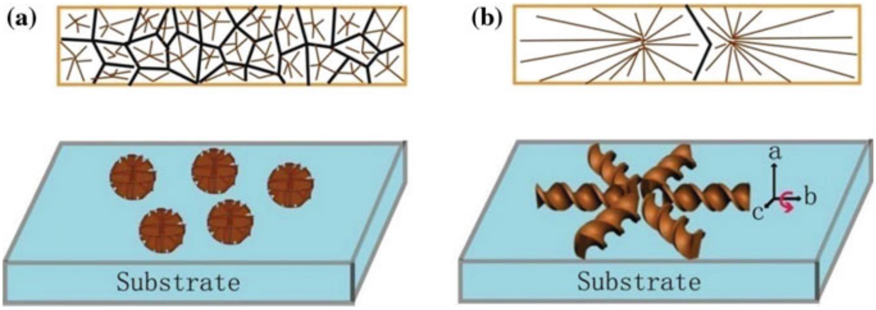


Fig. 5.15 Schematic illustration of structures of small (**a**) and large (**b**) PE spherulites in PE/P3BT blend films with 4 μm of thickness. *Top panel* cross section of surface; *bottom panel* overall view [108]

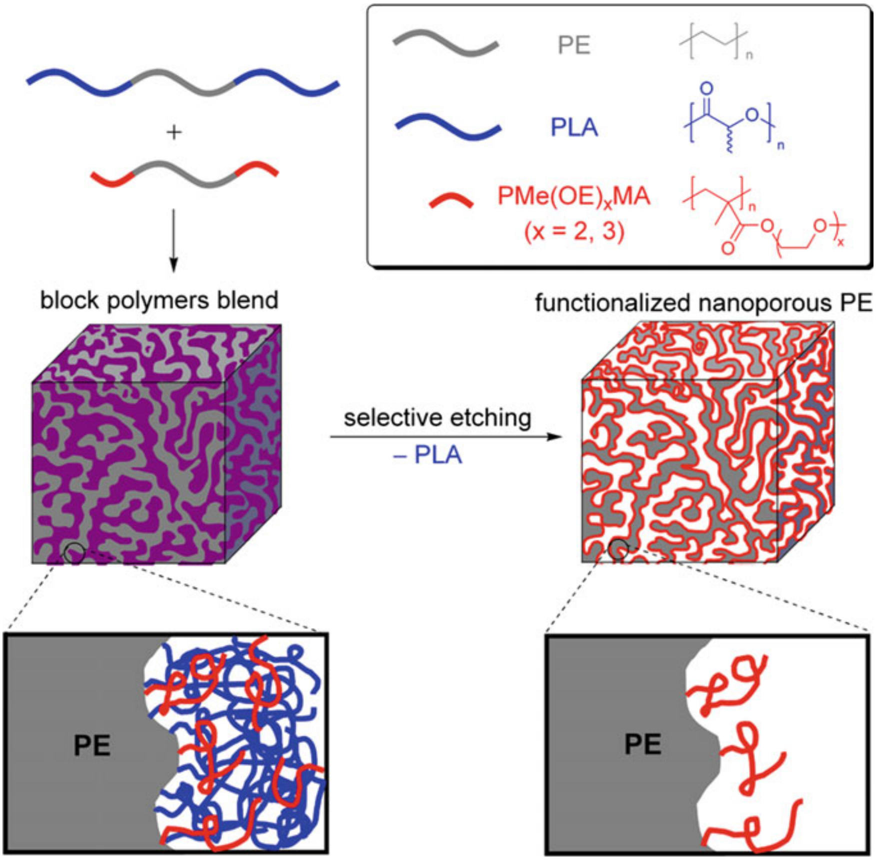


Fig. 5.16 Preparation strategy of the nanoporous polyethylene whose pore wall is lined with poly [2-(2-methoxyethoxy)ethyl methacrylate] and poly{2-[2-(2-methoxyethoxy)ethoxy]-ethyl methacrylate} PMe(OE)$_x$MA (x = 2, 3) by the PLA selective etching from the reactive block polymer blends [109]

which showed improved water uptake because of the hydrophilic PMe(OE)xMA on the pore walls.

The hydrophobic properties of polyethylene (PE) are considered to be the key factor limiting the application of PE membranes, especially for water treatment [110]. The hydrophobicity of the membrane causes (i) high energy consumption during its use, because a higher pressure is required for water to penetrate the membrane and (ii) membrane fouling which leads to a rapid decay of the flux. Hydrophilic modification is therefore an important direction for research into high-performance PE membranes. Extensive studies focused on amphiphilic co-polymers (e.g. PE-b-PEG), because the hydrophobic segments usually have good compatibility with the matrix and can act as anchors in the membrane matrix to prevent the loss of the co-polymer during the membrane preparation and operation processes. Meanwhile, the hydrophilic moiety always enriches the surface of the membrane, giving the membrane improved hydrophilicity.

A foamed plastic is called an open-cellular foam when its pores are interconnected with one another; otherwise, this plastic is called a closed-cellular foam [111]. Open-cellular plastic foams are applied in the field of acoustic insulation. Two different mechanisms of bubble nucleation exist: homogeneous and heterogeneous nucleation. Several nucleating agents have been used to enhance heterogeneous bubble nucleation. PS/PE blends with dispersed PE domains were studied to observe the effects of a dispersed domain polymer on heterogeneous bubble nucleation, as well as on cell wall opening. PS and PE are immiscible, and the interfacial tension between these polymers is higher compared to blends such as PMMA/PS or PP/PE. The viscosity difference between the dispersed domain and the matrix could be altered by changing the processing temperature and the PE grade.

5.8.9 Chlorinated Polyethylene (CPE)

CPE is a special class of elastomer prepared from polyethylene by random chlorination in an aqueous medium, and it is always available in a powder form [112]. It possesses a number of advantageous properties over other unsaturated and saturated elastomers. The saturated backbone of CPE imparts excellent weather, ozone, oxidation, chemical, and hydrocarbon oil resistance, as well as very good compression set, low-temperature flexibility, heat-ageing resistance, and very good processability. The presence of chlorine atoms in the backbone of CPE gives inherent flame retardancy. Ethylene methacrylate co-polymer (EMA) also has a saturated backbone, and therefore, it has very good age, oil, and thermal degradation resistance. It further has excellent low-temperature flexibility which is much better than that of CPE, even without any plasticizer. All halogen-containing polymers produce toxic and corrosive gases once it burns, and therefore, CPE is not always a good choice in a number of applications. Blending of EMA with CPE should reduce the adverse effect of halogen in a polymer used for wire and cable covers and jacketing, while combining the beneficial properties of the two polymers.

PVC is a widely used commodity polymer because of its excellent properties such as high stiffness, good transparency, low flammability, and favourable price [113]. PVC is recyclable, but incompatible contaminations reduce its mechanical properties. Polyethylenes, with their low glass-transition temperatures, should be good impact modifiers of PVC, but the incompatibility of these two polymers makes the preparation and application of such a blend almost impossible. The thermal stability of PVC is limited, and it requires special care during processing to prevent thermal degradation by dehydrochlorination. CPE was found to be a very good compatibilizer in PVC/polyethylene blends because it contains a broad range of different structural units on the same molecule.

5.9 Conclusions

This chapter described recent research on polyolefins blended with other polyolefins and with a variety of other polymers, including natural and biodegradable polymers. Most of the research concentrated on morphology–property relationships and on understanding the different morphologies and their influence on obtaining the required properties for specific applications. From this chapter, it is clear that polyolefin blend research during the first decade of the twenty-first century was concerned with (i) improving the usability of known polyolefin blends for certain applications, (ii) obtaining a better understanding of blending technology for recycling of polyolefins, and (iii) increasing the biodegradability of polyolefins through blending with natural or biodegradable polymers, without sacrificing the excellent properties of the polyolefins.

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