General Purpose Elastomers: Structure, Chemistry, Physics and Performance

Robert A. Shanks and Ing Kong

Abstract Elastomers are unique to polymers and exhibit extraordinary reversible extension with low hysteresis and minimal permanent set. They are the ideal polymers relieved of molecular interactions, crystallinity and chain rigidity constraints. The common elastomers have characteristic low modulus, though with poor abrasion and chemical resistance. Theoretical concepts have been established for their thermodynamics and kinetics and this knowledge has been applied to extending their properties by design of chemical and molecular structures, or by modification by control of crosslinking, blending or additions of fillers. This chapter reviews elastomer theory and the demanding range of properties expected. Natural rubber is the starting material for introduction of chemistries that introduce damping, abrasion resistance and higher modulus through copolymerization and interacting functional groups. Heteroatoms such as fluorine, silicon, oxygen and nitrogen are shown to extend properties and give chemical resistance. Thermoplastic elastomers move beyond typical cured systems due to formation of two-phase block copolymers. Finally modification by filler and blended systems is considered, followed by introduction to shape memory materials and a brief comment on the future trends. The unique and diverse properties and performance of elastomers continues to be a fascinating field for science and application.

Abbreviations

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ΔH	Enthalpy change
ΔS	Entropy change
$\Delta \gamma$	Wetting surface tension
A	Helmholtz free energy
COPA	Polyamide/elastomer block copolymer
COPE	Polyether ester/elastomer block copolymer
CR	Polychloroprene

R. A. Shanks (✉) · I. Kong
Applied Sciences, RMIT University, GPO Box 2476Melbourne VIC 3001, Australia
e-mail: robert.shanks@rmit.edu.au

DSC	Differential scanning calorimetry
EPDM	Ethylene propylene diene monomer
EPM	Ethylene-propylene random copolymer
FKM	Fluorocarbon elastomer
G	Gibbs free energy
IIR	Butyl rubber
IPN	Interpenetrating blend
iPP	Isotactic polypropylene
NBR	Acrylonitrile butadiene rubber
N_C	Critical entanglement spacing
NR	Natural rubber, poly(cis-1,4-isoprene)
PCEA	Polycarbonateesteramide
PDMS	Polydimethylsiloxane
PEA	Polyesteramides
PEEA	Polyetheresteramide
PE-b-A	Polyether-block-amide
POSS	Polyhedral oligomeric silsequioxanes
PSR	Polysulfide
PU	Polyurethane
SBC	Styrenic block copolymer
SBR	Styrene butadiene rubber, poly(butadiene-co-styrene)
SBS	Styrene-butadiene-styrene
SEBS	Styrene-ethylene/butylene-styrene
SEEPS	Styrene-ethylene/ethylene/propylene-styrene
SEPS	Styrene-ethylene/propylene-styrene
SIBS	Styrene-isobutylene-styrene
SIS	Styrene-isoprene-styrene
SR	Silicones rubber
TPE	Thermoplastic elastomer
TPO	Polyolefin blends
TPV	Dynamically vulcanized blend
U	Internal energy
W	Work done on a system
W_C	Fraction of crystallinity

1 Introduction

An elastomer is a material that can exhibit a rapid and large reversible strain in response to a stress. An elastomer is distinguished from a material that exhibits an elastic response that is characteristic of many materials. An elastic response is where the strain is proportional to stress according to Hooke's Law, though the strain may
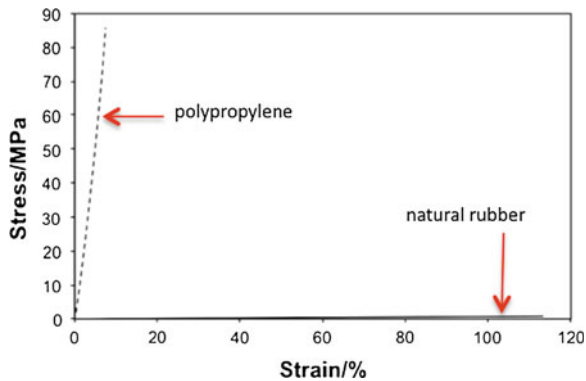
Fig. 1 The elastic stress–strain curves of a thermoplastic compared with an elastomer

only be a small amount, such as 0.001 for a silicate glass. An elastomer can exhibit a large strain of for example 5–10 and to be able to do this an elastomer must be a polymer [1]. Figure 1 shows a comparison stress–strain curve for natural rubber compared with a typical thermoplastic, polypropylene. The change in strength of polymers with similar structure due to crystallinity of polypropylene is apparent.

Elastic strain may be due to chemical bond stretching, bond angle deformation or crystal structure deformation. In an elastomer under strain bond are not elongated and bond angles not deformed. Stretch of an elastomer depends upon rotation about bonds that is changes to dihedral angles. An unstrained elastomer will exist in a random coil structure. As strain is increased the molecules will uncoil to the limiting linear structure. Therefore, to be an elastomer a substance essentially must consist of macromolecules. Large strain required very long molecules so that uncoiling can be considerable. Formation of an unstrained random coil means that the elastomer must be non-crystalline since any regular crystal structures will be unable to contribute to elastomeric properties [2]. Figure 2 illustrates a partially coiled 15 mer of poly(cis-1,4-isoprene). If linear the model would be much longer, while it would be difficult to view if in a completely coiled conformation.

The large reversible strain must be rapid which means the restraining intermolecular forces must be minimal. Elastomers will have minimal hydrogen bonding or polar functional groups that contribute to intermolecular forces. Steric hindrance to uncoiling should be minimal so that elastomers are unlikely to have bulky pendant groups or rigid intra-chain groups. This is why most common elastomers consist of simple hydrocarbon high molar mass macromolecules. An elastomer will therefore be a polymer stripped of all molecular complexity

An elastomer is theoretically a perfect polymer. Elastomers are perfect polymers to study to understand the structure and function of polymers. All other polymer attributes are aberrations on the elastomer structure. A property not addressed by the discussion to this point is strain reversibility. Crosslinking is a complexity that must be present to provide reversibility. Figure 3 shows two molecules of
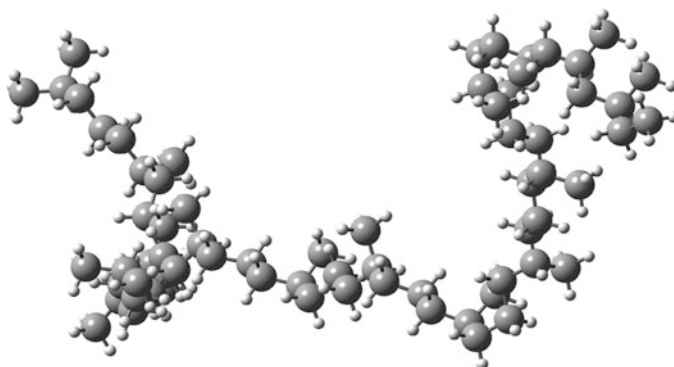
Fig. 2 A poly(cis-1,4-isoprene) random coil (with 15 monomer units)

Fig. 3 Two crosslinked 15 mers of poly(cis-1,4-isoprene)

poly(cis-1,4-isoprene linked by crosslinks that inhibit relative translational motion thereby contributing strain reversibility. This is unfortunate for studying elastomers because it means that they are insoluble, so that solution properties cannot be measured.

Solution properties contribute much to the understanding of macromolecules by virtual of hydrodynamic volume, molar mass determination, solvent swelling, theta solvent phenomenon, mean distance between chain ends, viscosity and light scattering. Solution properties of elastomers can be evaluated prior to crosslinking to characterise all of the single molecule behaviour. Crosslinking can then be performed to give the minimum crosslinks required for continuity throughout the elastomer mass that is the crosslinks must at least provide a percolation network throughout. In a solvent the elastomer will be crosslinked to or beyond the gel point. Crosslinking to a percolation network will give reversible strain. Cross-linking beyond a percolation network will decrease elastomeric performance until it is completely absent in a highly crosslinked network. Solvent swelling is a convenient method to characterise an elastomer since swelling using solvation force is analogous to straining using a physical force. Both swelling and straining are used to determine crosslink density as the molar mass between crosslinks.

The behaviour of elastomers thus far briefly introduced is why they can be described as perfect polymers. The chapter will explain the thermodynamics, structure, and polymerisation methods of these perfect molecules. The concepts will be stretched to include the less than perfect polymers that possess suitable elastomeric properties for many applications, since those perfect polymers will lack in additional properties required of elastomers in specific or harsh environments. Examples with be introduced that will include formulation and applications of commodity and advanced elastomers including blends and interpenetrating networks.

2 Thermodynamics

Application of thermodynamics to elastomers requires that the molecules rapidly equilibrate and comply with Hooke's law over the entire range of strain being considered. Such an elastomer is called an ideal elastomer. An ideal elastomer immediately causes recollection of an ideal gas. Thermodynamics of gases required consideration of deviation from idea behaviour. Gases deviate from ideality at high compression, due to contact of atomic radii limiting compression and due to non-zero intermolecular interactions. Elastomers deviate similarly at high extensions due to molecular chain approaching full extension, crosslinks becoming taut and crystallisation of elongated molecular segments. At low extensions initial uncoil of macromolecules is impeded by entanglements, some of which are permanent while others can be freed by uncoiling of loops. At high compressions, elastomers reach a limit of compressibility due to impinging molecules or a fully occupied volume [3].

Elastomer behaviour arises from cooperative segmental motions that depend upon a free volume into which segments can move. Segmental molecular motions involve cooperative pairs of bond rotations, translational motion does not occur due to the crosslinks. Translational motion occurring with creep corresponds to a permanent set or non-reversible component of creep. Recoverable creep is not elastomeric behaviour because it is time dependant, that is kinetic, while elastic behaviour is immediate and reversible that is thermodynamic.

The free energy for volume change of a gas under constant pressure is the Gibbs free energy (G):

$$\mathrm{d}G = -\mathrm{d}H - T\mathrm{d}S, \text{ while the work done on the system, } W = P\mathrm{d}V + f\mathrm{d}L \quad (1)$$

The free energy for length change of an elastomer under constant volume ($P\Delta V = 0$, assuming Poisson ratio $= 0.5$) is the Helmholtz free energy (A):

$$\mathrm{d}A = \mathrm{d}U - T\mathrm{d}S \text{ while the work done on the system, } W = F\mathrm{d}L \quad (2)$$
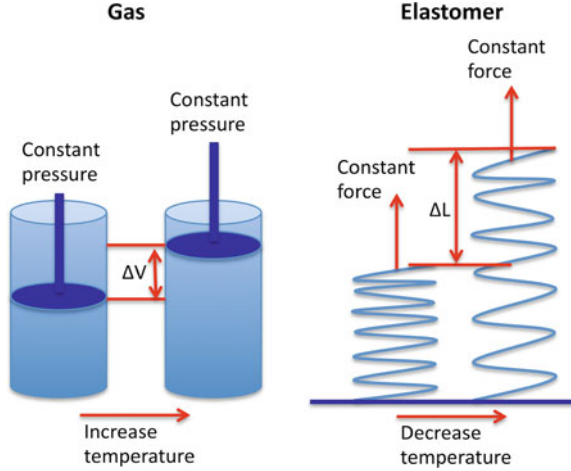
Fig. 4 Temperature volume and length relationships for a gas and elastomer

Where H = enthalpy, U = internal energy, S = entropy, T = temperature, V = volume, L = length, P = pressure, F = force. Entropy change with length is obtained from the Maxwell equation [4]:

$$\left(\frac{dS}{dL}\right)_T = \left(\frac{-dF}{dT}\right)_L \tag{3}$$

The entropy of a gas is the disorder that is increased by expansion since there are more states that the gas molecules can occupy, while as a gas is compressed the number of states becomes limited by lack of available free volume and the entropy is decreased. The entropy of an elastomer is the disorder that is increased as the elastomer is contracted since the number of possible conformations of each macromolecule approaches infinity, while as an elastomer is elongated the macromolecules become linear and the number of conformations approaches one, a completely linear macromolecule and the entropy is at a minimum. While the thermodynamics of gases leads to an engine driven by pressure and volume change (PdV), the thermodynamics of elastomers leads to an engine driven by force and length change (FdL).

The thermodynamics of gases predicts that as a gas is heated under constant volume its pressure will increase. A consequence of the thermodynamics of elastomers is the analogous prediction that if a stretched elastomer is heated its length will decrease. Alternatively is a compressed gas is allowed to expand its temperature will decrease. The same is true for a stretched elastomer that is allowed to contract its temperature will decrease. If a gas is compressed its temperature will increase, while if an elastomer is stretched its temperature will increase (Fig. 4) [5].
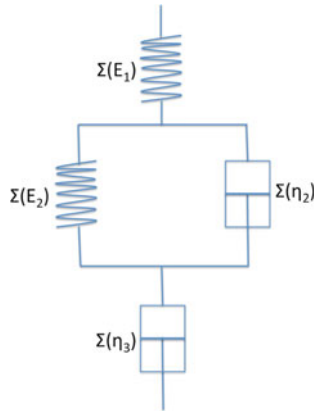
Fig. 5 Elastic, viscoelastic and viscous component models

Like most gasses, most elastomers are not ideal. Non-ideal or real elastomers do not behave completely reversibly. Real elastomers display some time dependence, where elastomeric behaviour is accompanied by creep (viscoelastic and flow) upon stretching and viscoelastic recovery and permanent set on contraction (Fig. 5). Elastomers display hysteresis upon stretching or relaxation. This additional real behaviour produces hysteresis in the stress–strain curves, that is the elongation and contraction curves do not coincide. The area between the elongation and contraction curves is the energy lost during each cycle. The energy loss is manifest as heat.

Hysteresis is demonstrated by a cyclic stress–strain experiment. Hysteresis is the area between the increasing and decreasing stress–strain curves. The solid lines in Fig. 6 illustrate the low hysteresis of lightly crosslinked natural rubber. Repetitive cyclic stress shows that subsequent stress–strain curves differ from the first curve. This phenomenon is known as the Mullins effect. During the first straining some entanglements can be removed thus decreasing slightly the stress required for subsequent cycles. This can be described as strain softening, in contrast to strain hardening observed with a polyurethane elastomer. The time response curves in Fig. 6 show the response of NR to six repeated cycles. The data are replotted as stress–strain curves and the dotted curves show the second and subsequent cycles. The response was reversible after the first cycle such that the dotted curves are exactly superimposed. If the NR is allowed to relax a similar different first cycle can again be observed. This phenomenon has been called strain conditioning.

A series of six repetitive stress–strain cycles was imposed upon SBR and the results are shown in Fig. 7. The time-based chart illustrates the overall stress and strain data. The stress–strain chart illustrates the higher hysteresis of SBR compared with NR, especially for the first cycle. The stress–strain curves after the first cycle were almost exactly superimposed though not precise and with greater hysteresis than the results for NR. The difference of the first cycle to subsequent cycles, the Mullins effect, was greater with SBR than with NR. SBR is harder and
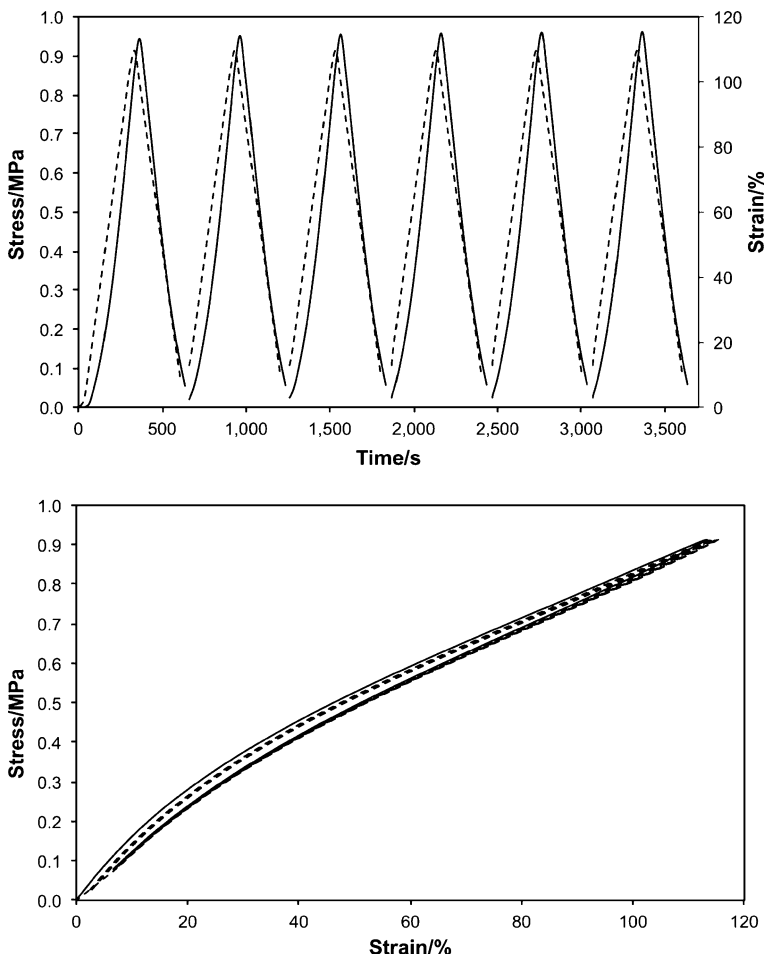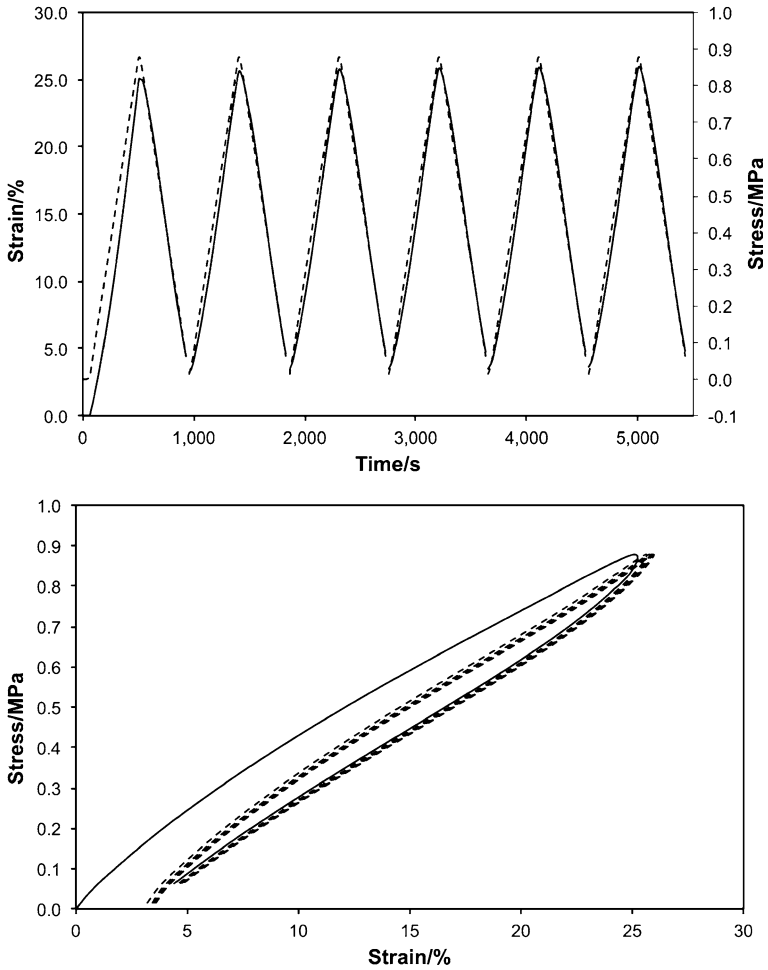
Fig. 6 Stress–strain time (*upper*) and hysteresis (*lower*) curves for poly(cis-1,4-isoprene) elastomer

more wear resistant than NR, with a consequential increased hysteresis. The energy lost by hysteresis during cyclic stress is dissipated as heat, so that high hysteresis elastomers have a disadvantageous heat build-up. This is an advantage when stress damping is required, but not when high heat build-up will cause failure of the elastomer. Damping behaviour of elastomers can be enhanced by inclusion of fillers. Typical fillers are carbon black, silica and talc.

Elastomer hysteresis is where kinetics impinges upon thermodynamics. Kinetics is time dependant response, which with macromolecules is dependent upon temperature.

Fig. 7 Stress–strain time (*upper*) and hysteresis (*lower*) curves for a poly(styrene-co-butadiene) elastomer

3 Kinetics

Elastomer kinetics is a consequence of non-ideal behaviour that is shown in the previous section results in hysteresis and heat production. Another consequence of kinetics is the glass transition of amorphous polymers or amorphous regions within semi-crystalline polymers. The glass transition occurs over a temperature range defined as the glass transition temperature (Tg). When the temperature of a polymer is below Tg there is insufficient thermal energy to overcome the activation energy for segmental motions and the polymer will be glassy. When the temperature of a polymer is above Tg segmental motions will occur and the

polymer will exhibit elastomer behaviour. When the temperature is within the glass transition range the polymer will be predominately viscoelastic causing damping of forces with consequential conversion to heat. To be an effective elastomer the polymer should be well above its Tg to minimise viscoelastic behaviour. Elastomeric performance at ambient temperatures (20–25 °C) effectively requires Tg in the range −70 to −20 °C for an effective instantaneous reversible response to occur.

Creep and recovery tests were performed on NR and SBR to demonstrate that creep is almost non-existant in crosslinked elastomers, and that recovery is rapid and practically complete. After an initial instantaneous elastic strain, creep of natural rubber is low due to a network of crosslinking, while recovery was instantaneous to a strain of 1 % followed by almost complete recovery with low permanent set (Fig. 8). Similar analysis of SBR creep exhibited a slightly slower elastic response followed by greater viscoelastic creep. Recovery of SBR was rapid, though with some permanent set (Fig. 9).

Measurement of stress–strain response after a large pre-strain has been discussed under the hysteresis curves of Figs. 6 and 7, while another method is to measure the modulated stress response of an elastomer on a highly strained elastomer. Such an analysis showed that the loss modulus was independent of an underlying shear strain over most of the engineering strain range for unfilled and carbon black filled rubber compunds. These results are useful for understanding energy dissipation by strained elastomers [6].

4 Structure

The molecular structure of an elastomer consists of random coils connected by crosslinks. Irregularity is essential to prevent crystallinity. Irregularity can be due to geometric isomers where the cis configuration gives best elastomer properties even though the double bond restrains motion of the bonded carbon atoms. The trans configuration contributes to a regular planar zig–zag conformation that is crystallisable. A fully saturated hydrocarbon polymer can be elastomeric if substituents are in atactic configuration, or if it is a random copolymer where the segments cannot co-crystallise.

A statistical description of polymer elasticity is based upon a random distribution of chain links forming a random coil conformation of the macromolecules. A random coil is more thermodynamically stable compared with the fully extended chain because there are an infinite number of random coils, while there is only one fully extended chain. Random coil statistics is self-avoiding in that the model considers the excluded volume of the molecule. The assumption of a random coil conformation allows prediction of structural characteristics including end-to-end distance, radius of gyration, contour length, persistence length, characteristic ratio [7].
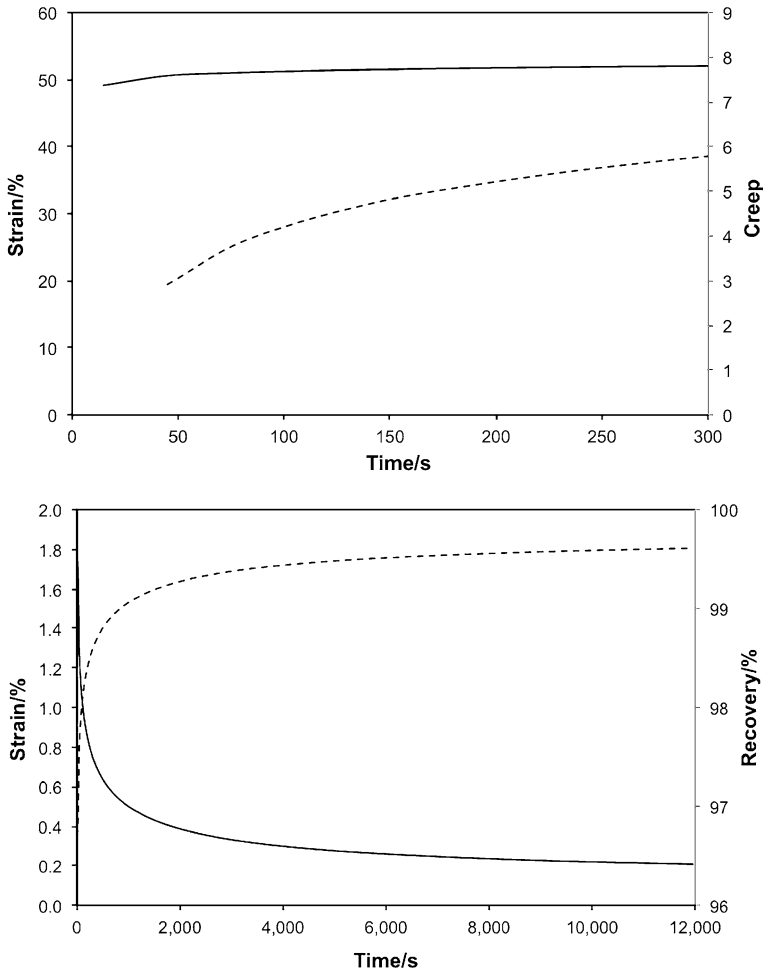
Fig. 8 Creep strain (*upper*, *creep dotted*) and recovery strain (*lower*, *recovery dotted*) response for a poly(cis-1,4-isoprene) elastomer under a tensile creep stress of 0.5 MPa followed by recovery with a minimum restraining force

Elastomer deformational reversibility requires molecular crosslinking beyond gelation so that relative molecular positions are fixed during conformational changes. Gelation occurs when crosslinked molecules extend throughout the system forming a percolation network [8]. Crosslinking covalent bonds will prevent relative translational motions that will be irreversible. Ionic crosslinks can be introduced using covalent metal ions with a polymer with anionic charges along the chain. Alternatively, physical crosslinks will be suitable for reversibility. Physical crosslinks can be due to a phase separated block copolymer structure where a disperse phase will be glassy (high Tg) or crystallise.
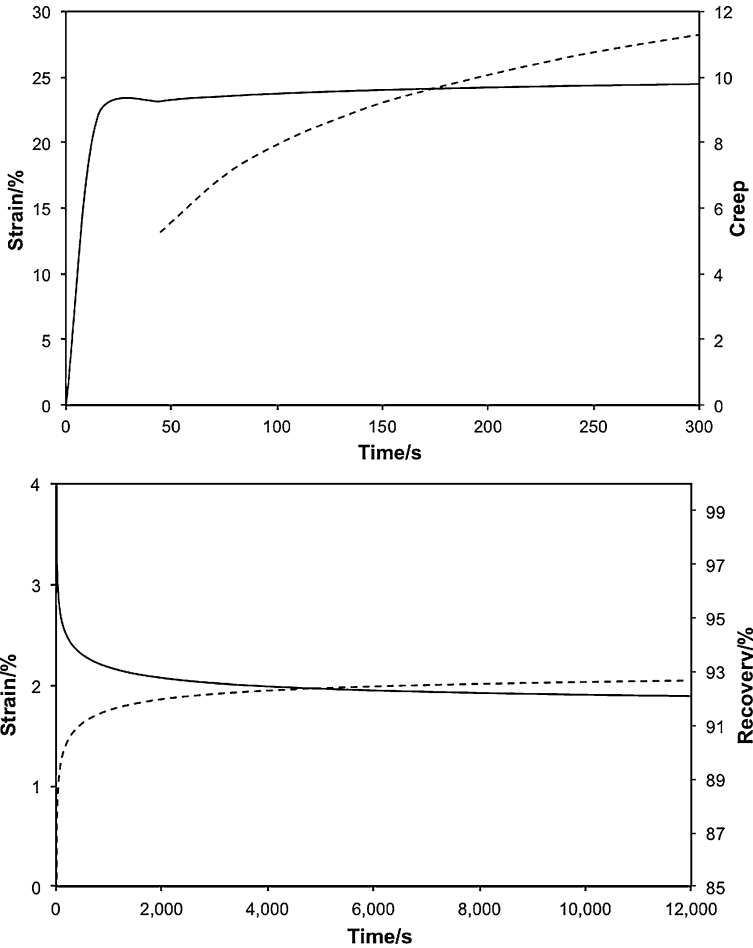
Fig. 9 Creep strain (*upper*, *creep dotted*) and recovery strain (*lower*, *recovery dotted*) response for a poly(butadiene-co-styrene) elastomer under a tensile creep stress of 1.0 MPa followed by a minimum restraining force

5 Polymerisation

Elastomers are mainly synthesised using chain growth polymerisation because high molar mass is a feature of this mechanism and high molar mass is required for high chain extension. Elastomers synthesised by the mechanism with radical initiation. Are the hydrocarbon types such as polybutadien, poly (butadiene-*co*-styrene), poly(butadiene-*co*-acrylonitrile) and the fluorocarbon elastomers. Polyisobutylene is initiated using cations. Block copolymers poly(stryene-*b*-butadiene-*b*-styrene) is initiated by anions. Poly(ethyene-*co*-propylene) and its diene terpolymers are synthesis by initiation with co-ordination metal catalysts.

Elastomers synthesised by a step growth mechanism include polyurethanes, polysulfides and the polysiloxanes or silicone elastomers. Each of the main chemical structure classes of elastomer are treated in the next section.

6 Specific Elastomer Structure and Properties

6.1 Aliphatic and Aromatic Hydrocarbon Elastomers

Natural rubber (NR) is an elastomer with a basic monomer of cis-1,4-isoprene. It is made by processing the sap of the rubber tree (i.e., *Hevea brasiliensis*) with steam, and compounding it with vulcanizing agents, antioxidants, and fillers. Natural rubber is widely used for applications requiring abrasion or wear resistance, electric resistance and damping or shock absorbing properties such as large truck tyres, off-the-road giant tyres and aircraft tyres. It is chemically resistant to acids, alkalis and alcohol. However, it does not do well with oxidizing chemicals, atmospheric oxygen, ozone, oils, petroleum, benzene, and ketones.

Styrene-butadiene rubber (SBR) is synthetic rubber copolymer consisting of styrene and butadiene. Its chemical resistance is similar to that of natural rubber, however, it exhibits an excellent abrasion resistance than polybutadiene and natural rubber that makes styrene-butadiene rubber a suitable materials for automobile tires.

Butyl rubber (IIR) is a copolymer of isobutylene and isoprene as basic monomer units. This synthetic rubber has a very low permeability rate making it a great seal under vacuum. It also has good electrical, shock dampening properties. It is used in many applications requiring an airtight rubber. The major applications of butyl rubber are tire inner tubes and hoses.

Ethylene propylene diene monomer (EPDM) is a synthetic rubber consisting of ethylene and propylene. It has outstanding heat, ozone and weather resistance due to their stable, saturated polymer backbone structure. As non-polar elastomers, EPDM has good electrical resistivity, as well as resistance to polar solvents, such as water, acids, alkalies, phosphate esters and many ketones and alcohols (Fig. 10). It is mainly used as a standard lining material for steam hoses, automotive weather-stripping and seals, radiator, electrical insulation and roofing membrane. Properties of various hydrocarbon elastomers are shown in Table 1.

6.2 Halogen and Nitrile Substituted Elastomers

Polychloroprene (CR) was one of the first commercially successful synthetic rubbers with an annual consumption of about 3,00,000 tons worldwide (excluding former Soviet Union and PR of China). It is a chlorinated rubber material, which
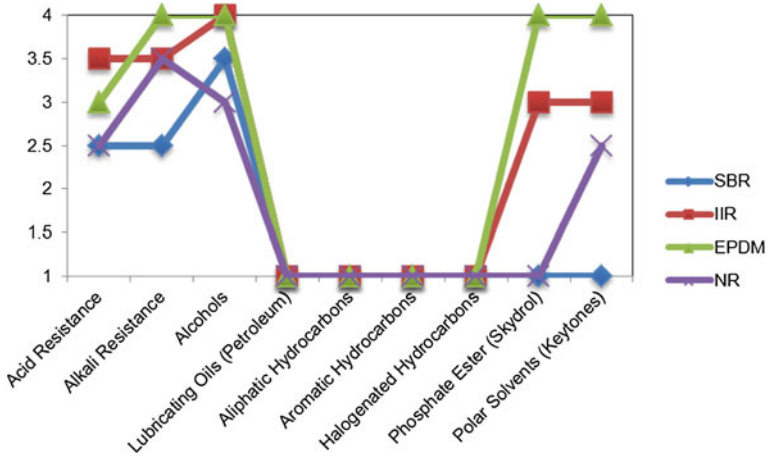
Fig. 10 Schematic representation of hydrocarbon elastomer properties (*1* Poor; *2* Fair; *3* Good; *4* Excellent)

Table 1 Relative comparison of the main hydrocarbon elastomers (*1* Poor; *2* Fair; *3* Good; *4* Excellent)

Elastomers	SBR	IIR	EPDM	NR
Economy (Cost)	1	3	1	2
Tensile strength	1.5	2	1.5	1
Resilience/rebound	2	4	2	1
Compression set	1.5	2.5	1.5	2
Adhesion to metals	1	2	2.5	1
Abrasion resistance	1.5	2.5	1.5	1
Tear resistance	2	2	1.5	1.5
Weather resistance	3	1.5	1	3.5
Ozone resistance	4	1.5	1	4
Dynamic properties	2.5	3	1.5	1
Electrical properties	2	2	2	2
Water swell resistance	1.5	1.5	1	1
Steam resistance	4	2	1	4
Flame resistance	4	4	4	4
Gas impermeability	2.5	1	2	3

was developed in 1932 by Carothers, Collins, and co-workers using emulsion polymerization techniques. In the same year DuPont began marketing the polymer first under the trade name Duprene and since 1938 as Neoprene. From the beginning up to 1960s, chloroprene was produced by acetylene process, which required expensive feedstock. The modern chloroprene process is a safer and more economical process. Chloroprene is produced in three steps from readily available butadiene: (1) chlorination, (2) isomerisation and (3) dehydrochlorination.
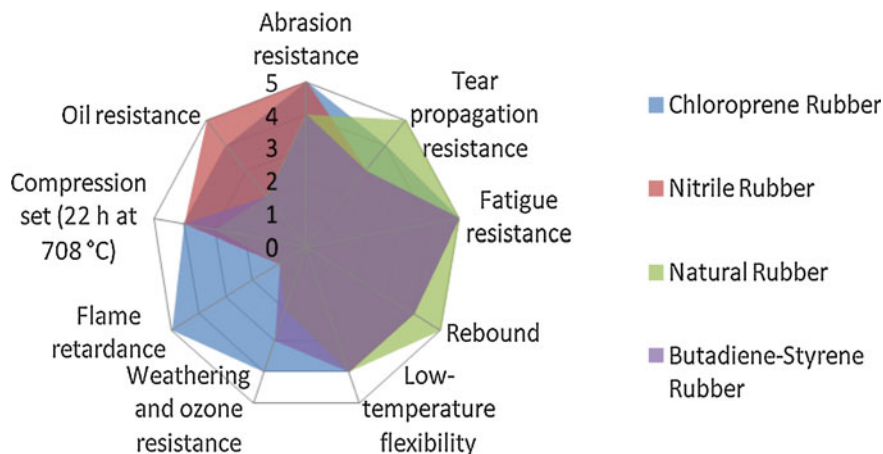
Fig. 11 Property comparison of nitrile and chloroprene elastomers (*1* Unsatisfactory; *2* Fair; *3* Good; *4* Very Good; *5* Excellent. The ratings are compound composition dependent, hence all optimum values may not be obtained simultaneously). *Source* Reference [9]

Originally developed as an oil-resistant substitute for natural rubber, CR has a good resistance towards various organic chemicals including mineral oils, gasoline, and some aromatic or halogenated solvents. It also has good aging resistance, high ozone and weather resistance. In contrast to the majority of other rubber types, CR shows a surprisingly higher level of resistance to microorganisms, such as fungi and bacteria. Moreover, it has low flammability and outstanding resistance to damage caused by flexing and twisting, an elevated toughness (Fig. 11). Therefore, its combination of unique properties makes it well-suited for many applications throughout industry. CR is commonly used as hose covers, where the hoses resistant to oil and ozone are required. In construction application, it has been used for many years as the elastomer of choice for bearings in machinery and bridges, bellows and seals. The compound is designed to have excellent low temperature, flex, ozone, and weather resistance. In the automotive industry, it serves as gaskets, seals, boots, air springs, and power transmission belts, molded and extruded goods and cellular products adhesives and sealants. Some other applications are insulating CPU sockets, to make waterproof automotive seat covers, rollers for the printing and textile industry.

Acrylonitrile butadiene rubber (NBR), also known as nitrile rubber, is a synthetic rubber produced from a copolymer of butadiene and acrylonitrile. It was invented by the chemists Eduard Tschunkur, Erich Konrad and Helmut Kleiner and a patent for this new oil-repellent rubber was awarded on April 26, 1930. The original name was Buna N and later changed to Perbunan in 1938.

The physical and chemical properties of nitrile rubber vary depending on the composition of acrylonitrile, which typically ranges from 15 to 50 %. With increasing acrylonitrile content the rubber shows higher strength, greater resistance to swelling by hydrocarbon oils, and lower permeability to gases. However, the

higher glass transition temperature makes the rubber becomes less flexible at lower temperatures.

The most common nitrile rubber with acrylonitrile content of 31–35 % withstands a temperature range of −40 to 107 °C. Nitrile rubber is considered to be the major oil, fuel, and heat resistant elastomer in the world. It is also resistant to aliphatic hydrocarbons. However, it is not resistant to aromatic hydrocarbon, ketones, ester and strong oxidizing chemicals. It has poor resistance to ozone, sunlight and weathering. Nitrile rubber is widely used in automotive industry as automotive seals and gaskets, which subject to contact with hot oils. It is used as automotive water handling applications and in fuel and oil handling hose too. In healthcare industry, its resilience makes it a perfect material for non-latex gloves. Other applications of nitrile rubber include the rolls for spreading ink in printing and hoses for oil products, as an adhesive and pigment binder.

6.3 Sulfide Elastomers

Polysulfide (PSR) is a class of chemical compounds containing chain of sulfur atoms. It was first found and patented by Joseph C. Patrick and Nathan Mnookin by accident when they were trying to invent inexpensive antifreeze. They named it Thiokol and the manufacturing began in 1929.

PSR exhibits excellent chemical resistance towards oils and greases and they have very good dielectric properties. Other unique properties of PSR including dimensional stability, flexibility, low moisture vapour transmission, low gas transmission and weatherability. These properties make them particularly useful in a variety of sealant applications.

The current types of PSR are Thiokol FA, Thiokol ST and Thiokol LP. Thiokol FA, the workhorse for specialty rollers, is a tradename for polysulfide co-polymer formed from di-2-chloroethyl formal and ethylene dichloride. With its excellent solvent resistant, it is well suited for roller applications requiring resistance to ketones, highly aromatic solvents, and some chlorinated solvents. Thiokol FA is a good choice of paint spray can gaskets and hose tubes too. Thiokol ST, a branched polysulfide formed from di-2-chloroethyl formal with about 2 % 1,2,3-trichloropropane as trifunctional branching units, designed for mechanical goods. Comparison of properties of Thiokol FA and Thiokol ST is shown in Table 2. Thiokol LP is a trade name for a range of liquid polysulfide rubbers obtained by cleavage of Thiokol FA and Thiokol ST, which is one of the most widely used mercaptan-terminated polymers. It has been used as the base polymer in sealants since the early 1950s. With more than 50 years of field experience, liquid PSR have been proven successful. The outstanding resistance of PSR to petroleum products has made them the standard sealant for virtually all aircraft integral fuel tanks and bodies. It is also used in insulating glass window sealants and construction sealants.

Table 2 Comparison of mechanical properties of two polysulfide elastomers

| Physical properties	Thiokol FA	Thiokol ST
Shore A	65–70	65–70
Modulus at 100 %, MPa	5.1	3.7
Tensile strength, MPa	8.3	8.3
Elongation, %	380	220
Compression set 22 h at 70 °C	100	20
Gehman low temperature, 8 °C	−45	−50

Source Reference [10]

6.4 Polyurethane Elastomers

Polyurethanes (PUs) are the most well-known polymers used to make foams. The raw materials for preparing PU are polyisocyanates, polyols, diamines, catalysts, additives and blocking agents. Generally, they are formed by the reaction of a diisocyanate and a diol with either ester or ether backbone in the presence of catalysts. Ether-based PUs are used to produce flexible and rigid foams while ester-based PUs are used to produce elastomers, flexible foams and coatings.

The structure of PUs is highly influenced by intermolecular forces, such as hydrogen bonding, polarizability, van de waals forces, stiffness of the chain and crosslinking. There may be crystalline regions between flexible chains. The polymers exhibit low corrosion resistance to strong acids and alkalis, and to organic solvent. Flexible foams are used for many domestic applications, such as sofas, cushions, carpet backs and car seats, while rigid foams are used as thermal insulation materials for transportation of cryogenic fluid, and frozen food products. Some others applications of PUs are shoe soles in shoe company, dashboards, bumper covers, moldings and fenders in automobile industry.

A cyclic stress–strain response for a polyether-urethane is illustrated in Fig. 12. The time chart for the data shows the regular changes of strain with stress of six cycles. The stress–strain chart illustrates high hysteresis exhibited by the polyurthane, due to its polar structure providing intermolecular interactions that cause deviation from ideal elastomer response. The second and subsequent cycles differ from the first cycle the same as noted for NR and SBR except that strain hardening has occurred with the PUs and that the repetitive cycles are not so exactly overlayed. As the strain is increased and the random coils are elongated, intermolecular interactions become more favourably and thus the stress required for any particular strain has increased. There has been a memory of the increased interactions after the first cycle, though they remain constant for subsequent cycles.

Cyclic stress response of a PU series has been resolved into elastic and inelastic contributions. The first stress cycle difference was increase with reduced hard and soft phase separation. In subsequent cycles a Mullins effect was attributed to separation of chain segments from the dispersed hard phase to increase coupling with the soft continuous phase [11].
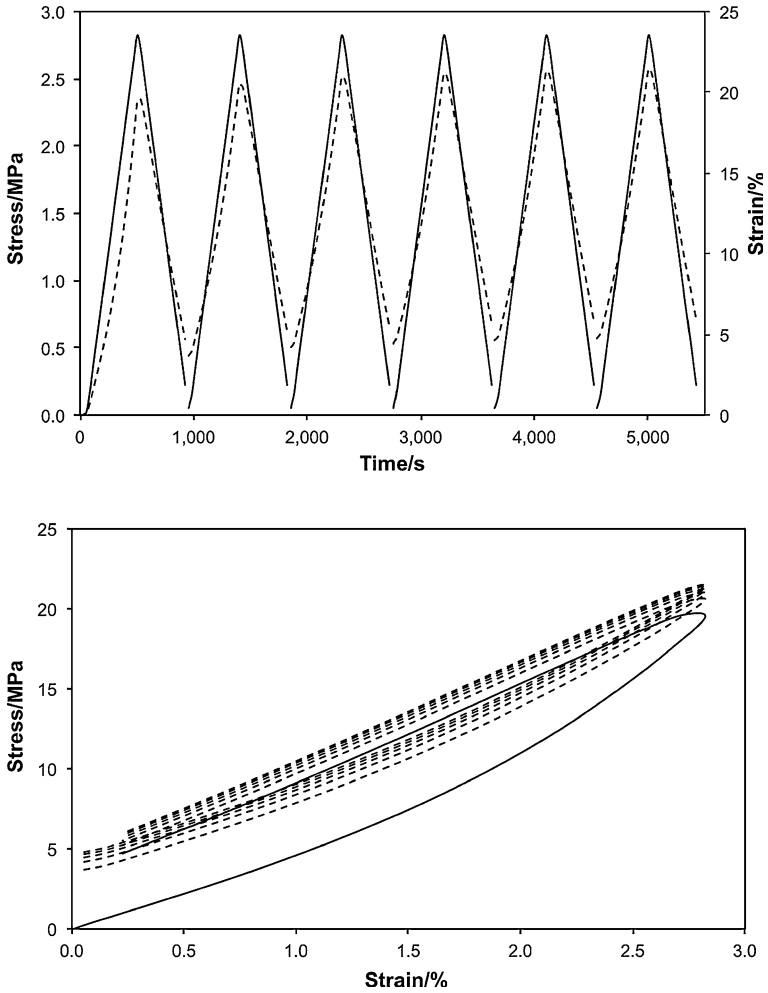
Fig. 12 Stress–strain time (*upper*) and hysteresis (*lower*) curves for a poly(ether-co-urethane) thermoplastic elastomer

Thermoplastic polyurethane elastomers are based on either polyether or polyester polyol pre-polymers. The polyesters are typically derived from succinate or adipate monomers combined with ethylene, propylene, butene or dimers thereof based diols. Succinates can be derived from sugars creating interest because of their bioorigin. The succinate and adipate polyester–polyurethane were compared and found to be similar, with slightly higher glass transition temperature, increased interaction between hard and soft phases and a slightly lower abraison resistance [14] (Tables 3, 4).

Table 3 Abbreviation and structure of elastomers

Common name	Abbreviation	Structure of repeat unit
cis-1,4-polyisoprene	NR, caoutchouc	
trans-1,4-polyisoprene	Gutta percha	
1,2-polybutadiene	BR	
cis-1,4-Polybutadiene		
trans-1,4-polybutadiene		
Butadiene styrene or styrene butadiene rubber	BS/SBR	
Butyl rubber	IIR	
cis-1,4-polychloroprene	CR	
trans-1,4-polychloroprene		
Polysulfide butadiene rubber	PSR	
Acrylonitrile butadiene rubber	NBR	
Ethylene propylene diene rubbers	EPDM	
Epichlorohydrin rubber	ECO	
Polyurethanes	PU	
Silicone rubber	SR	

R and R' = alkyl or aryl

**Table 4** Physical and mechanical properties of elastomers

Common names	Density (ρ/kg·m⁻³)	Elastic or young's modulus (E/GPa)	Ultimate tensile strength (σ_{UTS}/MPa)	Yield tensile strength (σ_{YS}/MPa)	Elongation at break (Zl%)	Shore A or D hardness	Minimum operating temperature range	Maximum operating temperature range	Glass transition temperature (T_g/°C)	Specific heat capacity (c_p/J·Kg⁻¹·K⁻¹)	Thermal conductivity (k/W·m⁻¹·K⁻¹)	Referactive index (n_D/mil)	Relative electric permitivity (@1 MHz) (ε_ρ/mil)	Electrical Resistivity (ρ/ohm·cm)
cis-1,4-polyisoprene	920–1037	3.3–5.9	29	17.1–31.7	660–850	A30–95	−56	82	−73	1,830	0.15	1.519–1.52	n.a.	2.6
trans-1,4-polyisoprene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	−58	n.a.	n.a.	1.509	n.a.	n.a.
1,2-polybutadiene	910	2.1–10.3	n.a.	13.8–17.2	450	A45–80	−100	95	n.a.	n.a.	n.a.	1.5	2.5	1.E + 15
cis-1,4-polybutadiene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	−102	n.a.	1,854	n.a.	1.52	n.a.	n.a.
trans-1,4-polybutadiene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	−58	n.a.	2,402	n.a.	1.518	n.a.	n.a.
Butadiene styrene or styrene butadiene rubber	940	2.1–10.3	21	12.4–20.7	450–500	A30–90	−60	120	n.a.	n.a.	n.a.	1.53	2.4	1.E + 14
Butyl rubber	917	0.3–3.4	17	n.a.	700–950	A30–100	−45	150	−75 to 67	1,950	0.13–0.23	1.5081	n.a.	n.a.
cis-1,4-polychloroprene	1230–1250	0.7–20.1	n.a.	3.4–24.1	100–800	A30–95	−43	107	−20	2,170	0.192	1.554–1.558	2.0–6.3	1.E + 11
trans-1,4-polychloroprene	n.a.	n.a.	n.a.	n.a	n.a.	n.a.	n.a.	−40	n.a.	n.a.	n.a.	1.5	n.a.	n.a.
Polysulfide butadiene rubber	1340	4.83–8.63	n.a	n.a	100–400	A65–70	−54	100–400	−55	n.a.	n.a.	1.6–1.7	1.3	1.E + 08
Acrylonitrile butadiene rubber	1000	n.a.	21	n.a	510	A30–90	−40	121	n.a.	n.a.	n.a.	1.52	2.5	1.E + 15
Ethylene propylene diene rubber	850	n.a.	21	n.a	100–300	A30–90	−51	150	n.a.	n.a.	2.22	1.474	2.5	n.a.
Epichlorohydrin rubber	1270	n.a.	17	n.a	400	A60–90	−46	121	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Polyurethanes	1050–1250	n.a.	29–49	n.a	10–21	n.a.	n.a.	n.a.	n.a.	1,800	0.21	n.a.	n.a.	1.E + 12
Silicone rubber	n.a.	n.a.	65	n.a	n.a.	D60A	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

Source References [12, 13]

6.5 Fluorocarbon Elastomers

Fluorocarbon elastomers (FKM) are synthetic copolymers derived by replacing some or all of the hydrogen atoms in hydrocarbons by fluorine atoms. They are typically used when other elastomers fail in hostile environments. The two main important properties of this class of elastomers are chemical resistance and heat resistance. The extraordinary chemical and heat resistance of FKM can be attributed to the high bond energy of the C–F bond and the higher bond energy of the C–C due to the presence of the most electronegative fluorine. Chemical resistance of FKM versus others elastomers are illustrated in a radar chart in Fig. 13.

Fluorocarbon elastomers are used widely in the harsh environment in automotive and aerospace industry (Fig. 14). In automotive industry, these materials have been designed into a number of items, such as shaft seals, valve stem seals, O-rings, engine head gaskets, filter casing gaskets, diaphragms for fuel pumps, water pump gaskets, fuel hoses, seals for exhaust gas and pollution control equipment, bellows for turbo-charger, lubricating circuits, etc. Aerospace and military uses are for shaft seals, hydraulic hoses, O-rings, electrical connectors, gaskets for firewalls, traps for hot engine lubricants, fuel tanks, heat-shrinkable tubing for wire insulation, etc. chemical and petrochemical plants utilize O-rings, expansion joints, diaphragms, blow-out preventers, valve seats, gaskets, hoses, safety clothes and gloves, stack and duct coatings, and tank lining.
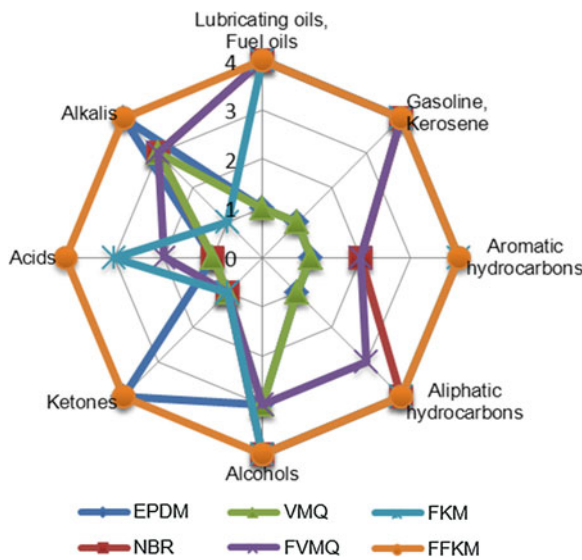
Fig. 13 Comparison of chemical resistance of elastomers with fluorocarbon elastomers. *Source* Reference [15]
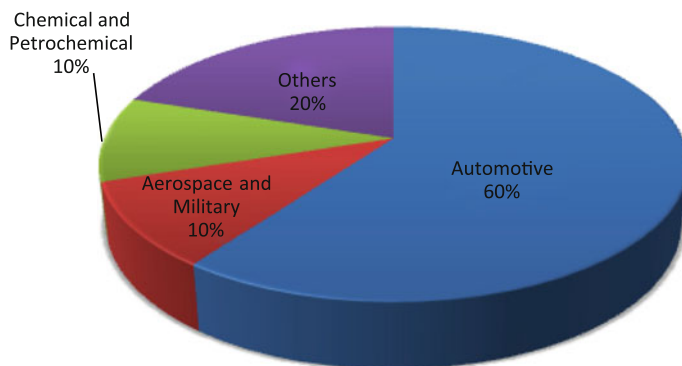
Fig. 14 Comparative market segments of fluorocarbon elastomers showing specialty automotive dominance. *Source* Reference [16]

6.6 Polysiloxane Elastomers

Polysiloxanes are mixed inorganic–organic polymers, which are well known under the common name of silicones rubber (SR). Instead of the organic carbon chain skeleton, these materials are based on a silicon and oxygen backbone (Si–O). Berzelius discovered the silicon, the basis of silicones in 1824 from the reduction of silicon tetrafluoride with potassium. In 1940s, F.S. Kipping, the father of silicone science, achieved extensive synthesis of silicone compounds and coined the name 'silicones'.

The most common siloxane is polydimethylsiloxane (PDMS). It can be prepared from the hydrolysis of dimethyl dichlorosilane that yields a silanol. The resultant silanol immediately undergo polycondensation. The mechanism of hydrolysis and the composition of silane mixture control the size of the polysiloxane molecules. Generally, silicones have an excellent resistance to heat and cold, ranging from −60 to +250 °C. They show hydrophobic properties which enable them to act as release agents for tacky substances. Silicones are also resistant to ozone and radiation. The low modulus of elasticity and a high mechanical dissipation factor make them an excellent medium for shock and sound absorption. In the cosmetic area, silicones are widely used in many skin-care products, hair products, shaving products and personal lubricants because of their high compatibility with skin, their water-repellent effect and the pleasant touch. In the automotive industry, silicones are used as a lubricant for the brake components, gaskets in automotive engines and for airbags as coatings and sealants. Transparent tubes processed from silicones are used for the food industry and medical applications and cable insulation for application at high temperature.

7 Thermoplastic Elastomer Structure and Properties

Thermoplastic elastomers (TPEs) are unique synthetic compounds that combine some of the properties of rubber with the processing advantages of thermoplastics. Generally, they can be categorized into two groups: multi-block copolymers and blends. The first group is copolymers consist of soft elastomers and hard thermoplastic blocks, such as styrenic block copolymers (SBCs), polyamide—elastomer block copolymers (COPAs), polyether ester—elastomer block copolymers (COPEs) and polyurethane—elastomer block copolymers (TPUs). TPE blends can be divided into polyolefin blends (TPOs) and dynamically vulcanized blends (TPVs). The world TPEs demand by types of TPE and by regions in year 2004, 2009 and 2014 are shown in Fig. 15.
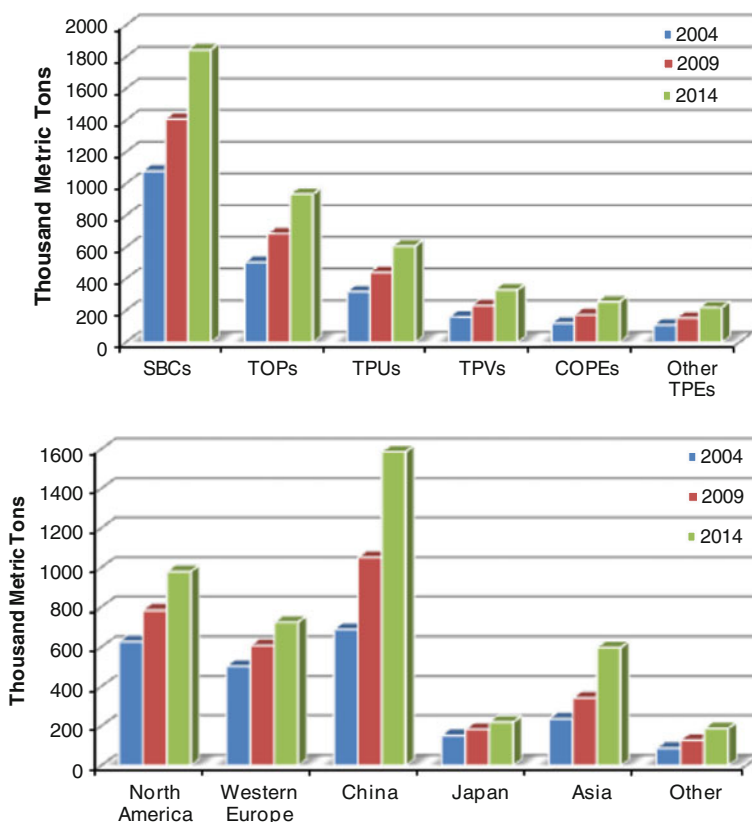
Fig. 15 World thermoplastic elastomers demand in 2004, 2009 and 2014 by types of TPEs and by regions. *Source* Reference [17]

7.1 Styrenic Block Copolymer

Styrenic block copolymers (SBCs) are the largest volume and lowest priced category of thermoplastic elastomers. SBCs are based on simple molecules (A-B-A type) that consist of at least three blocks, namely two hard polystyrene end blocks and one soft, elastomeric midblock. The midblock is typically a polydiene, either polybutadiene or polyisoprene, resulting in the well-known family of styrene–butadiene–styrene (SBS) and styrene–isoprene-styrene (SIS). Other SBCs which have been commercially successful include ethylene—butylene (SEBS), ethylene—propylene (SEPS), polyisobutylene (SIBS) and ethylene—ethylene—propylene (SEEPS). The structure of SBCs is shown schematically in Fig. 16.

It is essential that the hard and soft blocks are immiscible, so that, on a microscopic scale, the polystyrene blocks form separate domains. These domains are attached to the ends of elastomeric chains and form multifunctional junction points, thereby providing physical cross links to the rubber. When they are heated, the polystyrene domains soften and the SBCs become processable as thermoplastics. When solidified, SBCs exhibit good elastomeric properties as the polystyrene domains reform and strength returns.

Tensile strength of SBCs is much higher than those measured on unreinforced vulcanized rubbers. Most of the SBCs have elongation at break ranges over 800 % and resilience is comparable to that of vulcanized rubbers. SBCs exhibit non-Newtonian flow behavior because of their extreme segmental incompatibility. The melt viscosity is much higher than those of polybutadienes, polyisoprene and random copolymers of styrene and butadiene. SBCs are seldom used as pure materials. Most of them can be readily mixed with other polymers, oil, fillers, resins, colorants and processing aids to meet the required physical and mechanical properties [17].
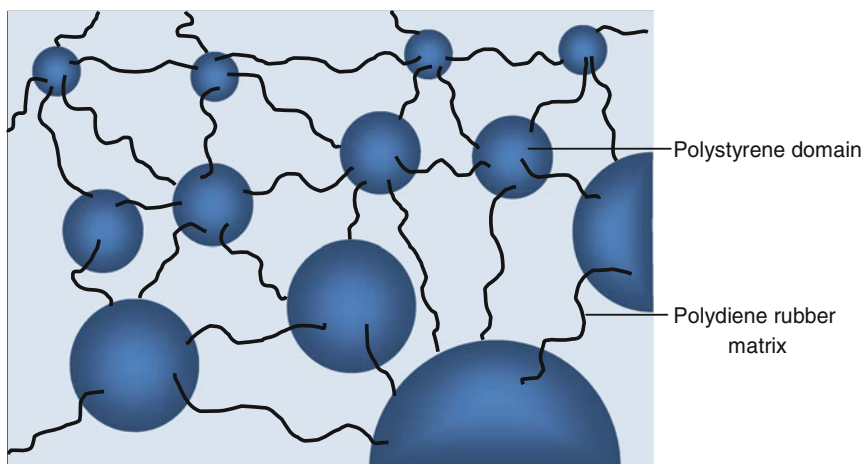
Fig. 16 Schematic of a styrene-diene-styrene block copolymer

The major applications for SBCs are footwear and adhesives and sealants. They are also used in modifying the performance of asphalt for roofing and roads, particularly under extreme weather conditions. SBS block copolymers are among the most commonly modifiers for this application [18]. Recently, it is proven that SEBS acts as a better modifier than SBS in improving the asphalts rutting resistance due to its double bond saturation which makes the SEBS more rigid than SBS [19]. SBCs can also be compounded to produce materials that enhance grip, feel, and appearance in applications such as toys, automotive, personal hygiene and packaging.

7.2 Thermoplastic Elastomers Based on Polyamide

Thermoplastic polyamide elastomers (COPAs) belong to the group of segmented block copolymer. They consist of multiblock copolymer structure with repeating hard and soft segments. The hard segments are polyamides which serve as virtual cross-links reducing chain slippage and the viscous flow of copolymer, whilst the soft segments are either polyethers or polyesters which contribute to the flexibility and extensibility of elastomers. Both segments are connected by amide linkages. The important members of COPAs are polyesteramides (PEAs), polyetheresteramides (PEEAs), polycarbonateesteramides (PCEAs) and polyether-block-amides (PE-b-As).

The properties of COPAs may vary according to such factors as the proportion of the hard and soft segments in the copolymer, chemical composition, molecular weight distribution, the method of preparation, and the thermal history of the sample that affects the degree of phase separation and domain formation. The hard segment controls the degree of crystallinity, crystalline melting point and mechanical strength while the soft segments determines the thermal oxidative stability, hydrolytic stability, chemical resistance and low temperature flexibility.

Most of the COPAs exhibit higher resistance to elevated temperature than any other commercial TPEs. They are also higher resistant to long-term dry heat aging without adding any heat stabilizers. Abrasion resistance of COPAs is comparable to that of TPUs [20]. COPAs have excellent abrasion resistance, which is comparable to that of TPUs. The hardness is in the range from Shore 80A to Shore 70D by varying the content of hard and soft segments [21]. The good insulation properties of COPAs make them suitable for low voltage applications and for jacketing. Other application areas for this material include conveyor and drive belt, footwear such as ski boots and sport shoes, automotive applications, electronics, hot melt adhesives, powder coatings for metals and impact modifiers for engineering thermoplastics [22].

Polyester amides constitute a peculiar of biodegradable family, due to the presence of both ester and amide groups that guaranties degradability. These biodegradable polymers are receiving great attention and are currently being

developed for a great number of biomedical applications such as controlled drug delivery systems, hydrogels, tissue engineering, and other uses [23, 24] .

7.3 Thermoplastic Polyether Ester Elastomers

The polyether ester elastomers or copolyesters (COPEs) consist of sequence of hard and soft segments. The high melting blocks (hard segments) are formed by the crystalline polyester segments which are capable of crystallization and the rubbery soft segments are formed by the amorphous polyether segments with a relatively low glass transition temperature. At useful service temperature, the polyester blocks form crystalline domains embedded in rubbery polyether continuous phase. These crystalline domains act as physical cross-links. At elevated temperatures, the crystallites break down to yield a polymer melt, thus facilitating the thermoplastic processing.

COPEs are considered engineering thermoplastic elastomers because of their unusual combination of strength, elasticity and dynamic properties. They have a wide useful temperature range between the glass transition temperature (around $-50\ °C$) and melting point (around $200\ °C$) [25]. These materials are elastic but their recoverable elasticity is limited to low strains. They have excellent dynamic performance and show resistance to creep. COPEs can be used in electrical applications for voltages 600 V and less. COPEs are resistant to oils, aliphatics and aromatic hydrocarbons, alcohols, ketones, esters and hydraulic fluids [26].

These materials, because of their high modulus and stiffness, have been used to replace some convention rubbers, PVC and other plastics in many applications. Uses of COPEs are reported in fuel tanks, quiet running gear wheels, hydraulic hoses, tubing, seals, gaskets, flexible couplings, wire and cable jacketing.

7.4 Polyolefin-Based Thermoplastic Elastomers

Polyolefin thermoplastic elastomers (TPOs) are an important part of the TPEs, which consist of polyolefin semi-crystalline thermoplastic and amorphous elastomeric components. TPOs are co-continuous phase system with the hard phase providing the strength and the soft phase providing the flexibility. The two most important processing methods of TPOs are injection moulding and extrusion. Others processing methods include calendaring, thermoforming, negative thermoforming and blow molding. TPOs ingredients generally include ethylene-propylene random copolymer (EPM), isotactic polypropylene (iPP), and the addition of other fillers and additives.

TPOs share with all TPEs the fundamental characteristics of having elastomeric properties, yet they process like a thermoplastic material. They are available in the hardness range from 60 Shore A to 70 Shore D. Their flexural modulus can range

from 1,000 to 2,50,000 psi (6.9–1,725 MPa). TPOs containing high amounts of elastomers are quite rubbery with high elongation at break values while TPOs containing high amounts of polyolefin undergo a yiled at low elongation and there is little recovery after drawing. Most TPOs are resistant to ozone, unaffected by water or aqueous solutions of chemicals. TPOs are excellent electrical insulating materials with the dielectric strength of 500 V/mil and the volume resistivity at 23 °C and 50 % RH is 1.6 × 1016 [27].

Hard TPOs compound is often used for injection molded automotive interior or exterior fascia. Soft TPOs compound can be extruded into a sheet and thermoformed for large automotive part such as interior skin [28].

7.5 Thermoplastic Elastomers Prepared by Dynamic Vulcanization

Dynamic vulcanization is a widely used method to prepare thermoplastic elastomers comprising partially or fully cross-linked elastomer particles in melt-processable thermoplastic matrix. The thermoplastic elastomers prepared by this method are referred to thermoplastic vulcanizates (TPVs). The difference between the TPOs and TPVs is that both the elastomeric and polyolefin phases in TPOs are co-continuous phases while in the TPVs the polyolefin phase is continuous and surrounds the cross-linked and discontinuous elastomeric phase. A two-dimensional representation of TPOs and TPVs are shown in Figure 17.

Thermoplastic vulcanizates can be processed using processing and fabrication techniques common to thermoplastics, such as extrusion, injection molding, compression molding, blow molding, thermoforming, calendaring and extrusion foaming [29]. Commercialized TPVs are commonly based on dynamically vulcanized EPDM rubber blend with a polyolefin resin. However, it is possible to make TPVs with a variety of thermoplastics and elastomers. Some that have been used are diene rubbers and polyolefins, butyl and halobutyl rubbers and polyolefin
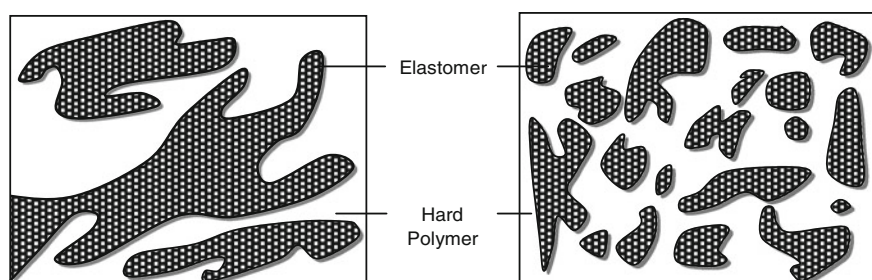
Fig. 17 Development of morphology in a thermoplastic vulcanizates from a co-continuous phase to dispersed phase

resins, polyacrylate rubber and polyolefins [30] and butadiene-acrylonitrile rubber and polyvinyl chloride [31].

The ratio of both elastomeric and thermoplastic components in the systems is crucial for the main physical properties (Young modulus, modulus at 100 % elongation, etc.) and its influence on final properties (tensile strength, elongation at break, tear strength and resilience, etc.). There are three decisive characteristics in order to obtain TPVs with good balance of properties: the wetting surface tensions ($\Delta\gamma$) of the elastomeric and thermoplastic components, the fraction of crystallinity (W_C) of the thermoplastic and the critical entanglement spacing (N_C) of the elastomer macromolecules [32]. A decrease of both tensile strength and elongation at break has been found with an increase in $\Delta\gamma$ and N_C and a decrease in W_C [33].

At the beginning, TPVs were used to substitute existing applications of elastomers now they are also opening new fields of application due to their processing potential. As the second largest group of soft TPEs after styrenic-based block copolymers, TPVs play an important role in under-the-hood applications in automotive industry as vacuum tubing, body plugs, seals, air conditioning hose cover, emission tubing and fuel line hose cover. They are used widely in electrical applications as wire and cables insulation and jacketing, connectors and terminal ends too. Furthermore, TPVs can also be used mechanical rubber goods applications such as convoluted bellows, mount, bumpers, housings, oil-well injection lines, etc.

8 Elastomer–Filler Compositions

Elastomer formulations required for applications requiring extended performance include fillers, the most common being carbon black. Fillers such as silica, kaolin, talc and calcium carbonate are often used. Recently organomodified clays, nanoparticulate synthetic inorganic compounds and carbon nanotubes have been introduced. Filler elastomers exhibit changed beyond those expected from volume fraction theories and much has been discussed about filler distribution and interactions. Fractal nanostructure was used to interpret heterogeneous deformation where filler aggregates vary with increases in strain [34]. SBR and NR subjected to large pre-strains of 100 % showed storage and loss modulus behaviour independent upon the pre-strain when filled with 25 pph carbon black while at higher filler content to 50 pph the loss modulus increased with pre-strain. The influence of pre-strain on higher carbon black filled elastomers was interpreted as due to molecular slippage at the filler interface [35].

Dispersibility of nano-fillers in elastomers is dependent upon surface treatments to decrease filler–filler interactions while increasing compatibility between filler and elastomer. Relative interaction between filler and elastomer has been estimated from surface energies and polarity and derived work of adhesion [36].

Presence of filler aggregates and formation of filler agglomerates are determinants strain and time dependant properties. Agglomerates can be disrupted by increasing strain, though they may reform over time. Elastomer entrapped within filler agglomerates increases the effective filler volume fraction since the entrapped elastomer is immobilised and does not contribute to the elastic response until the filler agglomerate is disrupted at larger deformations. Constraint of elastomer response by filler has been described as due to a tightly bound interphase attributed to a hydrodynamic effect that increases the effective filler volume fraction [37].

Changes of filled-elastomer response with strain and over time between strains have been long observed described as Payne and Mullins effects. Much attention to the interpretation of these effects has recently occurred because of advances in instrumentation and the interest in elastomer nanocomposites. Agglomeration of filler particles has been described as the rupture and re-birth of glassy interfiller bridges allowing formation of rigid clusters for finite times. Plastic deformation due to the clusters is superimposed upon the elastic response [38].

Nanofiller–elastomer composites exhibit increased thermal stability attributed to binding of elastomer molecules to the nanofiller and the tortuosity of the path for diffusion of volatile degradation products. Polyhedral oligomeric silsequioxanes (POSS) are single molecule nanofillers that have received much recent attention, for example they have been used as part of the polyol components in polyurethane elastomers. Thermogravimetry showed that POSS-polyurethane hybrids have increased thermal stability due to an influence of POSS on ther degradation mechanism [39]. Thermoplastic elasomers based on poly(ethylene-co-vinyl acetate) have been used to form nanocomposies with organo-modified layered double hydroxides (LDH) where the LDH exfoliated upon dispersion. The mechanical properties where increased while thermal degradation resistance and fire retardance improved [40].

Nano-silica particles are now included in many elastomeric products, polysiloxane being the main examples, however silca has been found to enhance hydrocarbon elastomers. Silica was included in solution polymerisaed poly(butadiene-co-styrene) and produced a non-linear stress relaxation due to the juxtaposition of an elastomer network and a silica network that both contributed to the non-linearity [41]. Nano-fillers such as silica consist of indispersible aggregates that flocculae into larger agglomerates existing as fractal arrays within the elastomer. The agglomerates can be disrupted by elastomer strain and reform upon relaxation. The agglomerates may contain occluded elastomer reulting in an artificially high apparent filler volume fraction, a phenomenon known as the Payne effect. Up to 25 %·w/w fumed silica was dispersed in poly(dimethyl siloxane) that were found by NMR to have a two phase morphology where the silica formed percolated network structures, dependent upon surface functionalisation of the silica. Microscopic network changes occurred with storage time of the poly(dimethyl siloxane)–silica composites [42].
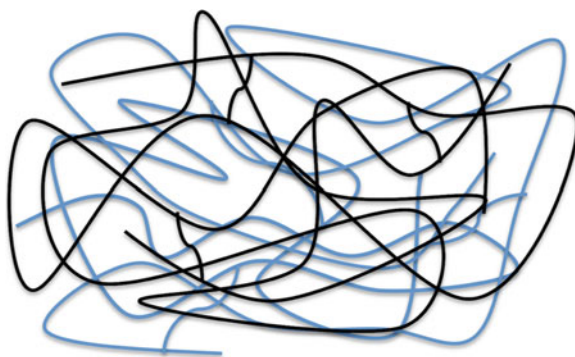
9 Elastomer Blends

Polymer blends are classified are incompatible, compatible, miscible. Polymer blends suitable for application must be compatible though they may be miscible often miscibility is not desired because properties are averaged. SBS and thermoplastic PU based upon polyether or polyester provided transparent blends due to narrow dispersed phase particle size and similar refractive index of the blended elastomers. The SBS–TPU blends showed improved thermal resistance, mechanical properties and damping at high frequency [43]. Membranes prepared from blends of nitrile rubber and epoxidized natural rubber has been prepared and their morphology, miscibility, mechanical and viscoelastic properties have been measured. Blend composition influenced homogeneity, microdomain structure and viscoelasticity [44].

Blends were prepared from natural rubber with carboxylated poly(butadiene-*co*-styrene) rubbert and composition and temperature property dependences were investigated. Two glass transitions were found and other data were consistent with a uniform two-phase system where morphology and viscoelasticity were controlled by composition [45].

10 Interpenetrating Elastomer Blends

Interpenetrating polymer/elastomer bnetworks (IPN) can be formed by simultaneous and sequential polymerisation or crosslinking to give a co-continuous network of chemically separate polymers (Fig. 18). The uncrosslinked, blended elastomer polymers or prepolymers must be initially miscible to allow the interpenetrating network to form at the molecular level. As the separate crosslinking reactions proceed, the polymers entropically phase separate forming the co-continuous networks. Both polymer could be elastomers, or one an elastomer and the other a polymer to enhance toughness. For example, an acrylate-modified polyurethane was interpenetrated with an unsaturated polyester resin to form a gradient IPN.

Fig. 18 Schematic structure for an interpenetrating polymer blend

The interpenetrated domains were found to be of nanometre dimension, with glass transitions linked such that the IPNs varied from elastomeric to brittle [46].

Blends of a poly(oxypropylene)-type epoxy resin and poly(butadiene-*b*-styrene) were prepared and simultaneously cured to form a network with three glass transitions, due to two expected phases from the poly(butadiene-*b*-styrene) and a thrid epoxy phase [47]. Interphases in a polybutadiene-natural rubber blend, a poly(methyl methacrylate)–poly(vinyl acetate) structured latex film, a poly(epichlorohydrin)–poly(vinyl acetate) bilayer film, and polystyrene–polyurethane and poly(ethyl methacrylate)–polyurethane interpenetrating polymer networks were investigated using modulated temperature differential scanning calorimetry (mT-DSC). The mT-DSC results identified glass transitions of the individual components and of interphases [48].

11 Formulation and Compounding

Elastomer formulations include additional components such as crosslinking or curing agents, initiators and accelerators for curing, stabilisers such as antioxidants, processing lubricants, plasticisers or extenders and fillers such as carbon black and silica [49]. Elastomer based adhesives are applied as contact adhesives for example. The initial adhesion requires addition of a tacifier with rosin and phenol–formaldehyde as examples. A brominated isobutylene-co-p-methylstyrene rubber tacified with a combined hydrocarbon resin and maleated hydrocarbon resin tackifier has been found to lead to better performance during bonding and de-bonding measured using a peal test and dependent on the bulk viscoelastic properties [50].

12 Shape-Memory Polymers

Shape-memory polymers are elastomers in the temperature regime where they are deformed from their equilibrium shape, however, at ambient temperatures they must retain there deformed shape. At ambient temperatures they must be below the glass transition of their elastomeric continuous phase so that they retain their deformed shape for long times until the memory is activated by heating. The glass transition temperature should be conveniently above any likely ambient temperatures, though typically low enough so that elastomeric behaviour can be activated using moderate heat such as hot water, hot air from a heated air gun such as a hair dryer and other portable heating devices. When heated into the elastomeric regime shape memory materials should have true elastomeric behaviour that is they should have rapid and reversible deformations without creep, which is irreversible and with minimal viscoelasticity since immediate return to original shape is required [51, 52]. Polyurethanes are common shape-memory materials because they exhibit elastomeric properties over temperature ranges controlled by structure and

characteristic hydrogen bonding provides restraint on conformational change and molecular motions. The shape-memory response may be electrically activated in lieu of application of a mechanical force [53]. Interaction parameters between hard and soft phases and differences in glass transition temperatures proved stronger interactions in polyester–polyurethane than in polyether polyurethane. Transparency of polyester–polyurethane was due to smaller dispersed hard phase particles giving higher physical crosslink density and strain hardening [54].

13 Future Trends

A trend with new polymers is toward specialty applications where advanced and unique properties are required. The requirements are met through improved control of molecular structure, copolymerization and formulation of existing polymer types. Elastomers follow this trend with new polymerization techniques and catalysts to control tacticity, comonomer composition, molar mass and molar mass distribution. Formulation innovation has come from polymer blends that are compatible, though not miscible when averging of properties would occur. Recent publication frequencies show that nanocomposites are the elastomers with most rapid development. Elastomers nanocomposites have always been significant in that carbon blacks and silicas used in the traditional rubber industry are nano-particulate materials. Enhnced elastomeric properties and energy damping are prime areas of new developments. In addition, resistant elastomers are in demand for chemical resistance, thermal resistance, radiation resistance, wear/abrasion resistance and weathering resistance.

A second trend is towards biomaterials, or materials derived from renewable resources. The source of monomers for elastomer synthesis has been mentioned in this review. Natural rubber has always been a biomaterial and it would be rational to continue to innovate with its use and enhancement through compounding. Natural rubber crop design is another area with potential. The rubber derived from plantations in different locations and hence climates or microclimates, as well as weather trends and seasonal variations for collection cause variation in the rubber. New plant breeds or genetic modification is likely to yield rubber with enhanced properties and of greater initial purity. These plantation improvement processes have been underway throughout the history of natural rubber, however biotechnology has recently advanced rapidly.

14 Conclusion

This chapter has described the characterisitc properties of an elastomer and that such materials must be polymeric. Elastomers are unencumbered polymers preferably of high molar mass so that random coils will form and the coils can be

extended towards an entropically unstable linear conformation. Elastomeric polymers have contributed significantly to understanding of the behaviour of macromolecules. Structural refinments are required in practice, firstly some threshold of crosslinking prevent flow thus restricting molecules to reversible uncoiling. Further modification includes chemical structures to provide resistance to harsh environments, functionality to delay some elastic response to enhance toughness and energy damping. Other mechanically active compnents include fillers and blended polymers that may be other elastomers, miscible or compatibile polymers. Elastomers find application in a huge array of products where their role may be obvious or they may contribute an important but concealed function. Natural rubber was among the first polymers used and vital to even current economies. New blends and nanofillers now refine properties. Diversified elastomers classes such as fluorocarbon polymers, polyurethanes and polyacrylates now contribute unique property combinations to specialised and diversified high technology products. The trend towards biomaterials signals a return to importance of natural rubber, however, there is opportunity for development of new hybrid bioelastomers.

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