1.1 Blends

The field of polymer blends has seen vast growth in both its scientific basis and its technological and commercial development. By definition, a combination of two or more structurally different polymers or copolymers giving rise to materials with a range of properties, not delivered by any of the constituents is a polymer blend.

The rubber industry has used the concept of blending for decades. In recent years, however, there has been a resurgence of interest arising primarily from the demand for engineering plastics and speciality polymers. Development of a new polymer to meet a specific need is a costly enterprise. If the desired properties can be realized simply by mixing two or more existing polymers, there is an obvious economic advantage. The time required to develop a new blend is commercially 3-5 years, compared to 8-10 years required for new materials. Thus, reasons for using blends include attainment of specific article performance, by improving the technical properties of the original polymers, by adjusting the processing
characteristics and reducing the cost [1-6]. The major markets are automotive, electrical and electronic, packaging, building and household.

Polymer blends are either homogeneous or heterogeneous. In homogeneous blends, both blend components lose part of their identity and the final properties usually are the arithmetical average of both blend components. In heterogeneous blends, the properties of all blend components are present. Weaknesses of one polymer can to a certain extent be camouflaged by strengths of the other. In a few exceptional cases, some properties of the either homogeneous or heterogeneous blend can be better than those of the individual components. This synergism is unfortunately hard to predict. Heterogeneous blends appear in a variety of morphologies. The best known and most frequently observed morphologies are: (i) a dispersion of one polymer in the matrix of the other polymer; and (ii) a co-continuous two-phase morphology. Which type of morphology is obtained is dependent on the nature of the blend components, the viscosity and the viscosity ratio of both polymers at the blending temperature, and the blend composition [7].

1.1.1 Thermodynamics of polymer blends

Blending of two different kinds of polymers usually results in an immiscible two phase blend, because of thermodynamic reasons. The phase behaviour of polymer mixtures is generally determined by the thermodynamic parameter $\Delta G_m$, the Gibbs free energy change of mixing, which is given by the following equation:

$$\Delta G_m = \Delta H_m - T\Delta S_m \ldots ........................................(1)$$

where, $\Delta H_m = \text{enthalpy change of mixing (J)}$, $\Delta S_m = \text{entropy change of mixing (J/K)}$ and
T = absolute temperature (K).

The change in the entropy of mixing, \( \Delta S_m \), is generally very small in polymer blends due to the high molecular weights of the polymers. This fact, combined with an enthalpy change of mixing, \( \Delta H_m \), which is generally positive for most non-polar polymer, makes it unlikely to realize the necessary negative Gibbs free energy change for mixing to occur. Because of these thermodynamic aspects, the number of miscible blends is very limited. The miscibility on a molecular scale can be improved, if certain specific interactions are involved, resulting in a negative heat of mixing. Consequently, \( \Delta G_m \) will be negative despite the small entropy change. These interactions may range from strong ionic to weak non-bonding interactions, such as hydrogen bonding, ion-dipole, dipole-dipole and donor-acceptor interactions [5,8].

1.1.2 Classification of polymer blends

Polymer blends may be classified in general into two broad classes: immiscible and miscible blends. Immiscible blends are those which exist in two distinct phases, but are still very useful materials, e.g., toughened plastics. Miscible blends are those, which exist in a single homogeneous phase and may exhibit synergistic properties, different from the pure components. Apart from these two, there exists a third category of blends, often known as technologically compatible blends or alloys. Alloys are those, which exist in two or more different phases on a micro-scale, but exhibit macroscopic properties akin to that of a single-phase material [7,8]. Rubber-thermoplastic blends can be classified broadly into three types:

1. Impact resistant rubber-toughened thermoplastics;
2) Blends of vulcanisable rubbers, which contain various amounts of resins that can act as reinforcing or stiffening agents and

3) Blends showing thermoplastic elastomeric behaviour, commonly known as thermoplastic elastomers (TPEs) [8-12].

1.1.3 Rubber-toughened thermoplastics

Impact resistance, a measure of toughness is often a deciding factor in material selection for many engineering applications. Consequently, rubber toughening was discovered to overcome the brittleness of glassy polymers such as polystyrene (PS). This led to the development of rubber modified polystyrenes (containing 5-15% rubber), the so-called *high impact polystyrenes* (HIPS). It is fabricated by dissolving the rubber in styrene monomer and then polymerizing the styrene by conventional means. The final product consists of a polystyrene matrix with inclusions of discrete rubber particles, some of which themselves contain smaller particles of polystyrene [13]. The technology of rubber toughening, which proved to be effective was extended to other commercial glassy polymers such as poly(methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC) and even polycarbonate (PC). Rubber toughening of thermoplastics depends on many factors, including size and morphology of the rubber inclusions, rubber phase volume, interfacial adhesion between the rubber and the matrix, relaxation behaviour of the rubber (modulus and T<sub>G</sub>) and the composition of the matrix [14,15].

From the morphological perspective, two types of rubber-toughened polymers can be distinguished: “disperse systems” that contain homogeneous, heterogeneous or core–shell particles, and “inclusion systems” or “network systems” that present a network arrangement of the rubber phase. Figure 1.1
shows the phase structures of high-impact PS (HIPS). During the polymerisation of PS in the presence of the dissolved rubber, phase inversion takes place, yielding rubber particles with PS inclusions, and various types of particles can be created depending on the stirring rate, ranging from core–shell particles to so-called “salami particles”.

![Figure 1.1: HIPS with rubber particles in the form of: a),b) rubber shells (core–shell) with SAN-grafted surfaces; c) “salami particles”. (Rubber selectively stained, ultrathin sections, TEM) [reproduced from (17)].](image)

1.1.3.1 Toughening Mechanism

Rubber toughening of glassy polymers involve three main micromechanical deformation mechanisms:

- Multiple crazing mechanism (e.g. in HIPS, ABS, ACS),
Multiple shear yielding mechanism (e.g. in rubber-toughened PMMA, PA, PP) and

Network (particle) yielding mechanism (e.g. in toughened PVC).

1.1.3.1.1 Multiple crazing mechanism

The polymer crazing process can be distinguished by noting that crazes are usually initiated in zones of chain segments that are weakly bonded, loosely packed, and contain structural defects under a dilatational stress field, and that craze growth gives rise to strain-softening of the craze/bulk interface and strain-hardening of craze fibrils. It was observed that the fracture of HIPS is usually preceded by an opaque whitening of the stress area. This whitening is associated with the absorption of a large amount of energy. At low TEM magnification, these stress-whitened areas exhibit many whitening bands perpendicular to the loading direction (Figure 1.2a). However, when observed at larger magnifications, these small whitening bands, are bridged by many tiny fibrils, revealing the nature of the crazes. The crazes are usually microcracks filled with voids and fibrils.
Figure 1.2(a,b): Deformation structures in HIPS: a) overview of deformation area; b) area in front of a crack tip with rubber particles (grey) in a matrix (black) with crazes (bright). (2 μm thick deformed section, for deformation direction see arrow) [reproduced from (16)].

Crazes are usually initiated at zones of stress concentration at the rubber particles, i.e. in the equatorial zones of the matrix perpendicular to the loading direction; see Figure 1.2b. When crazing occurs under well-controlled conditions, as in HIPS or ABS, it improves the material’s toughness by the mechanism of inelastic deformation. The energy dissipated by crazing can be divided up into the energy dissipated by yielding during fibril formation and the energy stored as surface energy in the matter in the craze. Figure 1.3 shows a high intensity of crazes with broad bands, propagating from one rubber particle to the next.

Figure 1.3: Broad crazes and craze bands between rubber particles in HIPS. (Semi-thin section, deformation direction horizontal, HVTEM) [reproduced from (16)].
Crazes, however, are also the precursors to cracks and, ultimately, failure. Therefore, an important additional process is needed to stop the cracking by rubber particles. The rubber particles retard the rapid propagation of cracks and prevent the premature fracture of the sample. According to the number of rubber particles, many crazes can be created in larger volumes of the sample in order to achieve increased toughness. These individual processes can be summarised in a “three-stage mechanism of toughening”, as shown in Figure 1.4.

1) Craze initiation: Each rubber particle generates the stress concentration in the matrix surrounding it. In general, crazes start at points of highly concentrated stress, and then propagate perpendicular to the tensile direction. In many cases, the crazes are accompanied by cavitation inside the particles, but this is not considered to be a precondition for craze initiation.

2) Superposition effect: The stress fields around rubber particles overlap when the particle content is more than 15 vol%. As a consequence, plastic strain-softening, which is characterised by a local yielding of matrix, also takes place, and is often followed by multiple crazing such as fibrillated crazes, homogeneous crazes or combinations of them.

3) Crack propagation: Once the cracks have formed within the crazes, the crack propagation can be stopped and the crack tip blunted by neighbouring rubber particles. Consequently, the strain hardening of the yield zone, a process caused by stretching the rubber phase to very high strain, also contributes to the enhanced toughness.
Maximum toughening – maximum craze formation due to the three-stage mechanism can be attributed to several parameters, such as:

- rubber particle content by volume
- rubber particle modulus
- particle size and size distribution

Figure 1.4: Three-stage mechanism of toughening (multiple crazing): a) stress concentration $\sigma_K$ at individual rubber particles; b) the superposition of stress concentration fields occurs at a larger particle volume content (>15 vol%), and the resulting increased...
stress concentration $\sigma'_{K}$ creates thicker crazes and craze bands; c) crack stop at / in rubber particles [reproduced from (17)].

- shape and internal structure of particles
- degree of grafting at and in particles
- the properties of the matrix itself.

From the morphological point of view, the particle size and the size distribution appear to be the main parameters responsible for enhanced toughness. The optimum rubber particle size is between 0.05 $\mu$m and 1 $\mu$m, especially between 0.1 and 0.5 $\mu$m, with a small size distribution. Very small modifier particles below 200 nm in size (half the wavelength of visible light) are used to prepare transparent toughened polymers such as SAN or PMMA [17].

1.1.3.1.2 Multiple shear yielding mechanism

The micrographs in Figure1.5 show deformed and elongated rubber particles as bright particles in the polyamide (PA) matrix. The material between the particles is highly deformed and appears as bright, diffuse zones. All of the material between the particles is involved in plastic deformation in the form of homogeneous yielding without internal structure or cavitation, as seen in the crazes in HIPS. In this material, the plastically deformed areas are spread over a large volume of the sample, which indicates high toughness. For such systems, it was established that a sharp brittle-to-ductile transition occurs when surface-to-surface interparticle distances become lower than a critical value $ID_{crit}$, which depends on the type of polymer matrix. Whereas $ID_{crit}$ was found to be independent of particle size and rubber volume fraction [18]. The individual steps of stress concentration, initiation of multiple yielding and crack stopping are very
similar to the three-stage mechanism as shown in Figure 1.4 [19]. A basic difference compared to the “multiple crazing” mechanism is the need for local cavitation in or at the rubber particles to enable yielding of the adjacent matrix strands. Extensive experimental studies have confirmed that microvoids form due to internal cavitation within the modifier particles or interfacial debonding at the interface between the matrix and the modifier particle.

Figure 1.5: Deformation structures of rubber-modified PA (PA-66, 22 vol% butyl acrylate): a) plastic deformation of the matrix in band-like deformation zones with highly deformed particles; b) microvoid formation inside plastically elongated particles [reproduced from (17)].

In the case of PP/EPR blends with a low concentration of ethylene in the EPR particles, the modifier particles are of a core–shell type with only one inclusion and are finely dispersed in the matrix. The shell phases consist of an amorphous ethylene–propylene block copolymer, which enhances the interfacial adhesion between the core and the matrix. At the early stage in the deformation, the modifier particles slightly deform in the tensile direction, along with the matrix. When the stress reaches a certain critical value, voids appear in the form of cavitation with or without fibrils
at the interface between the modifier particles and the matrix. This process is strongly dependent upon the inherent properties of the rubbery shell. Along with successive void formation and the continuous growth of the voids, weak shear bands form in the matrix ligaments between particles. When the polymer sample is strained still further, shear yielding is induced in the whole specimen.

In PP/EPR blend with high ethylene content in EPR, the modifier particles possess several inclusions in one rubbery shell. Void formation clearly occurs predominantly in the strongly plastically deformed EPR particles at the interface of the PE inclusions. Shear bands form in the matrix between the modifier particles in the next step. As the strain is increased, the sizes of the voids gradually increase, resulting in an acceleration of the shear flow in the matrix. As demonstrated above, the main energy absorption mechanism that occurs under loading at room temperature is shear deformation of the matrix. When the loading occurs at lower temperatures, two changes must be considered:

1) If the temperature is below the glass transition temperature of the modifier particles, the particles can no longer act as rubbery stress concentrators, the initiation of plastic deformation is lost and the materials break in a brittle manner. However, a low-temperature toughness is required for many practical applications.

2) Polypropylenes, which are commonly used as matrix materials, possess glass transition temperatures $T_g$ of about 0 °C, and it is well known that below $T_g$ the deformation mechanism changes from shear yielding to craze formation [20].
1.1.3.1.3 Network yielding mechanism

It has been well established for several decades that there is an alternative and often very effective approach to the rubber toughening of amorphous polymers – the use of “rubber networks”. This method involves embedding small particles of thermoplastic into a rubber network to form a honeycomb structure with thin layers of rubber separating the thermoplastic particles. Figure 1.6 shows a network of a rubbery ethylene vinyl acetate (EVAc) phase containing small particles of PVC. Since there are very thin network layers, the rubber content is usually kept below 10 vol% [21,22]. When this rubbery network is tensile loaded, the PVC particles start to yield and absorb energy. This results in an enhancement in the overall toughness of the system.

Figure 1.6: Rubber-toughened PVC with network structure of EVAc:
   a) total network morphology;
   b) partial network arrangement [reproduced from (16)].

Under uniaxial tensile load, the following deformation processes occur [21,23]:

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At the start of deformation, the weak rubber phase is stretched, resulting in the growth of a triaxial stress state in the whole network.

The rubber phase transfers stresses from one PVC particle to another. When the stress transfer is high enough to reach the yield stress of PVC, the particles start to deform plastically; the yielding of numerous PVC particles mainly absorbs the total fracture energy.

Through the partial rupture of the rubbery network, microvoids are generated in the specimen, yielding intense fibrillation of the network and an additional plastic yielding of the PVC particles.

One critical parameter of this mechanism is the thickness of the rubber network layers, which must be around a few tens of nanometres. Only a thin-walled network like this can generate a triaxial (hydrostatic) stress state that is high enough to reach the yield stress of PVC.

1.1.4 Dynamic vulcanisation

Dynamic vulcanisation is the procedure in which curing agents are used to crosslink an elastomer in situ during its mixing with molten plastics, which was first described by Gessler [24] in 1962 and further developed by Fisher [25], Coran and Patel [26], and Sabet [27]. The process of dynamic vulcanisation is the route to produce thermoplastic vulcanisate (TPVs), a special case of TPEs. Unlike static vulcanisation, dynamic vulcanisation is performed at a high shear rate, which leads to formation of dispersed phase morphology of the blend components [28,29]. Morphologically, the resulting TPVs are characteristic of finely dispersed,
micrometersized, crosslinked rubber particles distributed in a continuous thermoplastic matrix [31-33]. The morphology change upon dynamic vulcanisation is shown schematically in Figure 1.7. Compared with those blends comprising of uncured or slightly crosslinked components, dynamic vulcanisation possesses significantly improved mechanical properties that can be attributed to the stabilized morphology of rubber particles resulting from crosslinking. Dynamically vulcanised TPEs have been widely used because of their technical advantages in processing as well as their versatile end use properties [34]. The blends have important technical advantages in processing because of the thermoplastic nature of the melt, even though they contain a vulcanised rubber as one component.

Figure 1.7: A Schematic model showing the morphology change before and after dynamic vulcanisation of the blend.

A series of extensive studies on dynamically vulcanised TPEs were carried out by Coran and Patel in the early 1980s [35-39]. Compositions containing all possible combinations of selected types of rubber with selected types of thermoplastics were prepared. The rubbers included butyl rubber (IIR), EPDM, natural rubber (NR), butadiene rubber (BR), styrene-butadiene-rubber (SBR), ethylene vinyl acetate (EVAc), acrylate rubber (ACM), chlorinated polyethylene (CPE), polychloroprene (CR) and nitrile
rubber (NBR). The thermoplastics included polypropylene (PP), polyethylene (PE), polystyrene (PS), acrylonitrile-butadiene-styrene (ABS), styrene-acrylonitrile (SAN), polymethyl methacrylate (PMMA), polybutylene terephthalate (PBT), polyamide (PA) and polycarbonate (PC) [40]. Only a few of them were commercialized, because of the fact that most of these blends were not technologically compatible and hence required one or more steps to make them compatible. Commercialized dynamic vulcanisates are commonly based on blends of unsaturated EPDM rubber and polypropylene, and to a lesser extent on a combination of butyl rubber [41], natural rubber [42-44], or nitrile rubber [9,39] with polypropylene.

Though several crosslinking agents have been employed to crosslink the elastomer phase in TPVs, the phenolic resin, peroxide and silane crosslinking systems have gained considerable commercial importance. Phenolic resin gained considerable commercial importance but still the formation of black specks motivates the development of other potential crosslinking systems [33]. Peroxides can crosslink both saturated and unsaturated polymers without any reversion characteristics. The formation of strong C-C bonds provides substantial heat resistance and good compression set property without any discoloration. However, the activity of peroxide depends on the type of polymer and presence of other ingredients in the system [45,46]. PP/EPDM blend can also be crosslinked by silane grafting in presence of a small amount of catalyst. Grafting, hydrolysis and condensation crosslinking reactions are carried out in a single stage process.

However, only few work has been carried out on the dynamic vulcanisation of rubber-toughened thermoplastics. Crosslinking of rubber raises the shear modulus, making them more difficult to cavitate. In the
more ductile polymers such as PC, this may not present problems. Crosslinking has a similar effect to a reduction in particle size, in that it shifts cavitation of the rubber to higher stresses where dilatational yielding can take place immediately. If the level of crosslinking is excessive, it will delay cavitation so much that the material fails by crazing and fracture from external surfaces before significant yielding has taken place.

Once cavitated, homogeneous rubber particles exercise only a limited influence on the subsequent yielding and fracture of the glassy polymer, because they are unable to form effective orientation-hardened bridges across shear bands, crazes and cracks [47]. The effects of crosslinking in rubber phase are seen most clearly in HIPS and ABS, where multiple crazing is the main mechanism of toughening. Crosslinking of the particles raises tensile yield stresses and depresses impact strength [48-51]. In order to optimize energy absorption in these materials, the rubber should have ideally a low level of crosslinking, allowing early cavitation of the particles and maximum extension of the rubber fibrils, but it should also form a graft or block copolymer with the glassy polymer to provide anchor points for the fibrils.

Excessive crosslinking of the rubber, introduced either deliberately during manufacture or through subsequent oxidation, can lead to a marked reduction in impact strength. Significant levels of crosslinking are also produced simply by prolonged heating at high temperatures. In extreme cases, the $T_g$ of the rubber is shifted to much higher temperatures. However, studies on both irradiated and vulcanised HIPS have shown that tensile elongation and impact energy absorption are adversely affected even when the upward shift in the rubber $T_g$ is only a few degree [52]. The rubber
remains rubbery throughout these crosslinking reactions, and the changes in
toughness are solely due to its higher shear modulus.

1.2 Composites

Composites are defined as materials consisting of two or more distinct
phases with an interface between them. The constituent that is continuous and
is often but not always, present in the greater quantity in the composite is
termed the matrix. Composites consist of one or more discontinuous phases
embedded in the continuous phase. The discontinuous phase, which is harder
and stronger than matrix, is called reinforcement or reinforcing material.
Properties of the composites are strongly influenced by the properties of their
constituent materials, their distribution and the interaction among them.
Composite properties may be either the sum of the properties of the distinct
phases, or the property resulting from the synergistic action of the constituents.
The strengthening mechanism of composites strongly depends on the
geometry of the reinforcement. Based on the geometry of the reinforcement,
composite materials may be classified as shown in Figure 1.8.

A composite whose reinforcement is a particle, which is non-fibrous
and have dimensions approximately equal in all directions is called
particulate composite. The shape of the reinforcing particles may be
spherical, cubic, platelet or any regular or irregular geometry. Particle
fillers are widely used to improve the properties of matrix materials such as
to modify the thermal and electrical conductivities, improve performance at
elevated temperatures, reduce friction, increase surface hardness and reduce
shrinkage. In many cases, they are simply used to reduce cost.
Fibre reinforced composites contain reinforcements which is characterized by its length being much greater than its cross-sectional dimension. However, the ratio of the length to the cross-sectional dimension, known as the aspect ratio, can vary considerably. In fibrous composites, the matrix serves to bind the fibres together, transfer loads to the fibres, and protect them against environmental attack and damage due to handling. Reinforcing fibres in a single-layer composite may be short or long compared to its overall dimensions.
Figure 1.8: Classification of composites.
Introduction

Composites with long fibres are called continuous-fibre-reinforced composites and those with short fibres, discontinuous-fibre-reinforced composites. Another distinction is that in discontinuous-fibre composites, the fibre length affects the properties of the composites [53].

Natural and man-made fibres are used as reinforcements in fibrous composites. Cellulose [54], jute [55-60], sisal [61,62], coconut fibre [63-66], banana fibre [67,68], hemp [69], flax [70-72], kenaf [73-75], agave [76,77], oil palm fibre [78-81], sugar palm fibre [82-84], etc are examples of natural fibre. All natural fibres except silk are short or staple fibres. Man-made fibres include carbon [85-88], aramid [89-93], polyester [94], Nylon [177-181], glass [95-98] etc. The natural fibres have many attractive characteristics like low density, less abrasiveness, low cost, biodegradability, and renewability over traditional glass and organic fibres. However, the major drawback of the natural fibre-polymer composites is the inherent incompatibility between the hydrophilic fibres and the hydrophobic polymer matrix.

1.2.1 Short fibre polymer composites

In short fibre composites, the length of short fibre is neither too high to allow individual fibres to entangle with each other nor too small for the fibres to lose their fibrous nature. The reinforcement is uniform in the case of composites containing well dispersed short fibres. Short fibre reinforced composites can be processed in a manner similar to the matrix. The properties are strongly dependent on the fibre volume fraction and the fibre orientation distribution [99]. By adding suitable fibres and by controlling factors such as the aspect ratio, the dispersion and orientation of fibres, and the fibre-matrix adhesion, significant improvement in property can be achieved with thermoplastic, thermosetting and rubbery polymers. Typical
advantages of short fibre composites are design flexibility, high low-strain modulus, anisotropy in technical properties and stiffness, good damping, ease in processing and production economy.

1.2.2 Reinforcing Mechanism of short fibres

In composites, loads are not directly applied on the fibres but are applied to the matrix material and transferred to the fibres through the fibre ends and also through the cylindrical surface of the fibre near the ends. In the case of short-fibre composites, the effects associated with fibre ends cannot be neglected and the composite properties are a function of fibre length. The end effects significantly influence the behaviour of and reinforcing effects in short-fibre composites. Early studies concerning variation of stresses along the length of a fibre were performed by Cox [100] and Outwater [101]. Probably the most often quoted theory of stress transfer is the shear-lag analysis applied by Rosen [102], who modified an earlier analysis of Dow [103].

1.2.3 Stress and strain distribution at fibres

On considering a single fibre of length $l$ embedded in a matrix of lower modulus and aligned with the loading direction, the stress applied to the matrix will be transferred to the fibre across the interface if the fibre is well bonded to the matrix. The matrix and the fibre will experience different tensile strains because of their different moduli; in the region of the fibre ends the strain in the fibre will be less than that in the matrix, as indicated in Figure 1.9. As a result of this strain difference, shear stresses are induced around the fibres in the direction of the fibre axis, and the fibre is stressed in tension. The shear strength of the fibre-matrix interface is relatively low. However, the surface
area of the fibre is large, so that, given sufficient length, the fibre can carry a significant load, even up to the fibre fracture load.

Figure 1.9: Effect of deformation on the strain around a fibre in a low modulus matrix: a) continuous fibre, b) short fibre.

The stress distribution along a fibre aligned parallel to the loading direction of the matrix may be represented as in Figure 1.10. The tensile stress is zero at the fibre ends, and a maximum at the centre of the fibre. Conversely, the shear stress around the fibre is a maximum at fibre ends, and for a sufficiently long fibre falls to zero in the centre. It is this variation
Chapter 1

of shear stress (shear effect) that causes the build-up of tensile stress in the fibre.

Figure 1.10: Variation of tensile stress in a fibre and shear stress at the interface.

The reinforcing efficiency of fibres also depends on interface strength since load transfer requires a strong interfacial bond. The large shear stresses at fibre ends can produce undesirable effects such as

1) interfacial shear debonding
2) cohesive failure of matrix or fibre, and
3) matrix yielding

1.2.4 Critical fibre length and average fibre stress

The maximum strain that can be achieved in a fibre is that applied to the matrix, $\varepsilon_m$, then the tensile stress in the fibre, $\sigma_f$, is given by
\[ \sigma_f = \varepsilon_m E_f \] .................................................................(2)

where \( E_f \) is the Young’s modulus of the fibre.

When the applied load is increased then \( \varepsilon_m \) will be larger resulting in a higher stress in the fibre, the maximum stress which can be obtained in the fibre is the fracture stress \( \sigma_{fu} \). In order to achieve this level of stress in the fibre, the fibre length must be equal to a critical value \( l_c \) known as the critical fibre length. \( l_c \) may be defined as the minimum fibre length for a given diameter which will allow tensile failure of the fibre rather than shear failure of the interface, i.e., the minimum length of fibre required for the stress to reach the fracture stress of the fibre. The critical fibre length may be determined by considering a force balance in the fibre when the fibre stress is \( \sigma_{fu} \).

\[
\text{tensile force in fibre} = \frac{\sigma_{fu} \pi D^2}{4} \] ..........................................................(3)

\[
\text{shear force at interface} = \frac{\tau_s \pi D l_c}{2} \] ..........................................................(4)

Equating (3) and (4)

\[
\frac{l_c}{D} = \frac{\sigma_{fu}}{2\tau_s} \] ..........................................................(5)

The value of the average stress depends on the stress distribution in the ends of the fibres and upon the fibre length.

a) At \( l < l_c \)
The stress never reaches that sufficient to break the fibre and other mechanisms such as matrix failure and fibre pull-out will occur. The peak stress occurs at the centre of the fibre.

The average fibre stress $\bar{\sigma}_f = \frac{\tau l}{D}$ ...........................................................(6)

b) At $l = l_c$
The peak stress may just reach the fibre stress.
The average fibre stress $\bar{\sigma}_f = \frac{\tau l_c}{D}$ ...........................................................(7)

c) At $l > l_c$
The peak stress applies over the central portion of the fibre.
The average fibre stress $\bar{\sigma}_f = \left[1 - \left(\frac{l_c}{2l}\right)\right] \sigma_{fu}$ .............................................(8)

To obtain an average fibre stress close to the maximum fibre stress, the fibre must be considerably longer than the critical length [104].

1.2.5 Parameters influencing the characteristics of short fibre-polymer composites

1.2.5.1 Type and fibre breakage

Several researchers have studied the importance of fibre length and its influence on the properties of the composites [53,105-107]. In a composite material, fibre length is a critical factor which should not be too long so that they entangle with each other causing problems of dispersion. But a very small length of fibre does not offer sufficient stress transfer from the matrix to the fibre and give poor reinforcement. The severity of fibre breakage mainly depends on two factors: i) the type of fibre and its initial
aspect ratio and ii) the magnitude of the shear force generated during mixing. Fibres like glass and carbon are brittle and they possess a low bending strength than Nylon fibre which are more flexible and resistant to bending. There exists a certain aspect ratio for each type of fibre, below which no further breakage can occur depending on its resistance to bending. If the mix viscosity is high, more shear will be generated during mixing thus exceeding the critical bending stress of the fibre which eventually results in severe breakage. The breakage of fibre during mixing has been reported by O’Connar [108]. Murthy and De [109] reported that the breakage of the fibre is due to the buckling effect. Considerable fibre breakage occurred during mixing of fibres with high aspects ratio (as high as 500) resulting in reduction in aspects ratio [110]. Noguchi et al. [111] suggested that short PET fibres did not break up during the milling process and they are well dispersed, but carbon fibres did break up during milling, the fibre length being reduced to about 150 μm. Kutty et al. [112,113] has reported that significant breakage of short Kevlar fibres occurs during mixing in Brabender plasticorder in TPU matrix.

1.2.5.2 Critical fibre length and aspect ratio of fibre

The fibre ends in the short fibre reinforced composites plays a major role in the determination of ultimate properties of the composite. The concept of critical fibre length over which the stress transfer allows the fibre to be stressed to its maximum, or at which efficient fibre reinforcement can be achieved has been used to predict the strength of the composites. A theoretical analysis has been done by Broutmann and Agarwal [53] on the mechanism of stress transfer between matrix and fibre of uniform length
and radius and they have given the expression for the critical fibre length \((L_c)\) as in eq. (5).

The aspect ratio \((l/D)\) of fibres is a major parameter that controls the fibre dispersion and fibre-matrix adhesion that gives the optimum performance of short fibre polymer composites. If the aspect ratio of the fibre is lower than the critical aspect ratio, insufficient stress will be transferred and the reinforcement will be inefficient. An aspect ratio in the range of 100-200, essential for high performance fibre-rubber composites have been suggested by several researchers [114-117]. It was reported that for synthetic fibre like polyester and Nylon aspect ratios of 220 and 170, respectively give good reinforcement in natural rubber vulcanisates [118,119]. Hong Gun Kim [120] have investigated the effects of fibre aspect ratio in short fibre reinforced composites.

1.2.5.3 Fibre orientation

The preferential orientation of fibres in the matrix results in the development of anisotropy in the matrix.

When the composite undergoes shear flow, short fibres get oriented preferentially in a particular direction. The type of flow is determined by the processing techniques adopted, such as milling, extrusion and calendering. Mc Nally [121] has reviewed in detail the orientation of short fibres in polymer matrices. The effect of mill parameters such as number of passes, nip gap and mill roll speed on the fibre orientation was initially studied by Moghe who reported that nearly 60-70% fibres get oriented in the direction of the applied stress [122]. It was observed that the lower the nip gap, higher the anisotropy in tensile properties of the composites.
implying greater orientation of fibres. This is represented as anisotropy index, which reduces gradually with increasing nip gap.

During processing and subsequent fabrication of short fibre polymer composites, the fibres orient preferentially in a direction depending upon the nature of flow i.e., convergent and divergent as explained by Goettler [123]. If the flow is convergent the fibres align themselves in the longitudinal direction and if it is divergent they orient in the transverse direction. During shear flow as experienced in a Brabender Plasticorder or a capillary rheometer, the fibre alignment may be random or unidirectional depending on the rate of shear. If the flow is elongational, then the fibre orientation takes place mainly in the direction of applied stress which is experienced during sheeting through the tight nip of a mill or during calendering.

**1.2.5.4 Fibre dispersion**

The primary requirement for obtaining a high performance composite is good dispersion of fibres in the matrix. The factors that affect dispersion in polymer matrices are fibre-fibre interaction and fibre length. These factors also account for the tendency to agglomerate during mixing.

Good fibre dispersion is the ultimate objective of any mixing process. Depending on the type of fibre, mixing may be either distributive or dispersive. Distributive mixing increases the randomness of spatial distribution of the minor constituents within the major base without reducing the size of the fibre, whereas dispersive mixing serves to reduce the agglomerate size. However, both phenomena occur simultaneously. Brittle fibres such as glass, jute, Kevlar, carbon and boron break down severely during
mixing on a mixing mill and in an intensive mixer. Therefore, these fibres need more distributive mixing, whereas fibres such as cellulose, Nylon, polyester and silk require more dispersive mixing due to their tendency to agglomerate during the mixing process. Homogeneous dispersion can be made possible by manipulating the mixing technique and controlling mixing parameters. The mixing process is optimised such that the breakage of the short fibres during mixing is minimal and the orientation of fibres is maximized.

1.2.5.5 Fibre concentration

The concentration of fibres in the matrix plays a crucial role in determining the mechanical properties of the fibre reinforced polymer composites. A lower concentration of fibres gives lower mechanical strength. This has been observed not only in rubbers [124] but also in thermoplastic elastomeric matrices [108, 125-127]. This behaviour has been attributed basically to two factors, (i) dilution of the matrix, which has a significant effect at low fibre loadings, and (ii) reinforcement of the matrix by the fibres which becomes increasingly important as fibre volume fraction increases. The matrix is not restrained by enough fibres at low fibre content and highly localized strains occur in the matrix at low strain levels causing the bond between fibres and the matrix to break, leaving the matrix diluted by non-reinforcing de-bonded fibres. However, at high fibre concentrations, the matrix is sufficiently restrained and stress is more evenly distributed thus the reinforcement effect outweighs the dilution effect [108]. As the concentration of fibres is further increased to a higher level, the tensile properties gradually improve to give strength higher than that of the matrix. The concentration of fibres beyond which the properties of the composite
improve above the original matrix strength is known as optimum fibre concentration. In order to achieve improvement in mechanical properties with short fibres, the matrix is loaded beyond this volume fraction of fibre. Quite often, at very high fibre concentrations, the strength again decreases, because there is insufficient matrix material to adhere the fibres together.

1.2.5.6 Fibre-matrix adhesion

Fibre-to-matrix adhesion plays a very prominent role in the reinforcement of short fibres in the polymer matrices. The fibre-matrix interfacial adhesion is important in determining the mechanical, dynamic mechanical and rheological characteristics of the composites since the stress transfer occurs at the interface from matrix to fibre. The polymer layer in contact with the fibre surface has different properties from the bulk matrix because of fibre/polymer interactions due to immobilization of the matrix chains, electrostatic forces or chemical bonds in presence of internal stresses, voids or microcracks in the interlayer [128]. The chemical structures of both the fibre and the matrix determine the extent of interfacial adhesion and, therefore, the strength of the composites. Though the mechanism of stress transfer is not clear, it has been postulated that it takes place through shearing at the fibre-matrix interface. In composites with low fibre-matrix adhesion, Derringer [129] observed that a region of yielding occurs extending over a large portion of the strain range which is accompanied by low tensile strength and high permanent set.

1.3 Fibre Reinforced Blends

It is well known that short fibres are extensively used as reinforcing materials for thermosetting as well as thermoplastic and elastomer matrices. Their use in thermoplastic-rubber blends is also increasing.
Chapter -1

Anuar et al. has reported the development of thermoplastic natural rubber (TPNR)/EPDM and PP/EPDM composites reinforced with kenaf fibre [73]. The mechanical properties and morphology of ternary composites based on PP/EPDM blends reinforced with natural flax fibres was analysed by Biagiotti et al. [70]. Gautam et al. [130] has investigated the mechanical, thermal and viscoelastic properties of ternary composites based on low density polyethylene (LDPE)/EPDM blend and high density polyethylene (HDPE)/EPDM blend reinforced with short jute fibres. The hybridization of TPNR based on carbon fibre and kenaf fibre was investigated for its mechanical and thermal properties by Anuar et al. [74]. Lopez-Manchado et al. [131,132] have explored the reinforcing effects of different synthetic fibres on the crystallization kinetics, rheology, dynamic mechanical analysis and mechanical properties of PP/EPDM blends. The results showed that the fibres act as an effective reinforcing agent to PP/EPDM blends, but the reinforcing effect was more pronounced at low EPDM content in the blend (25%). The effect of aramid fibre and maleic anhydride (MA)-g-PE compatibiliser on the mechanical and dynamic mechanical properties of TPNR composites was analysed by Ishak et al. [92]. The mechanical properties and morphology of TPNR/ Kenaf fibre composites along with MA-g-PP compatibiliser was investigated by Sameni et al. [75].

1.3.1 Fibre reinforced rubber-toughened thermoplastics

Appropriate incorporation of rubber particles into a brittle plastic matrix is a well established means of improving fracture toughness [133]. Unfortunately, the addition of an elastomer to a rigid matrix invariably reduces strength and stiffness relative to the unmodified material. On the
contrary, incorporation of high aspect ratio rigid fillers such as high modulus fibres into a polymer matrix improves stiffness and strength [134].

In principle, combining fibre reinforcement with rubber toughening provides an approach to materials with high stiffness, strength, and toughness. While there is a large body of literature addressing each individual method, the idea of combining the two has received relatively little attention [135,136]. Increasing the fibre loading of rubber toughened blends has shown to increase stiffness and strength, as expected [137,138]. The extent of property enhancement, however, depends on several factors; these include fibre strength and modulus, aspect ratio (fibre length/diameter), effectiveness of coupling between fibre and matrix, fibre orientation, and concentration. So far most investigations on rubber toughened thermoplastic composite systems have been focused on polyamides. Gaymans [138] for instance reported that the incorporation of short glass fibres into polyamide-6/ethylene-propylene rubber (PA-6/EPR) blends has changed the mode of failure of the composites from a relatively clean pull-out for glass-fibre/polyamide composites to a sheathed pull-out for the blend with glass fibres. In the PA-6/EPR/glass fibre, the fibres are coated with a thick layer of matrix material and the thickness has been observed to be related to rubber concentration, temperature and deformation rate. A similar finding has also been reported by Bailey and Bader [139] for short glass fibre-reinforced polyamide 66 blends. More recently, Pacorini et al. [140] have reported the fracture behaviour of short glass fibre-reinforced polyamide-66/ethylene-propylene-diene terpolymer rubber (PA-66/EPDM) composites. They have noted that a balance of fracture strength and fracture toughness could be achieved via the combination of glass fibres and EPDM. The fracture behaviour of glass bead incorporated SBS-toughened polypropylene
composites was studied by Mouzakis et al. [141]. The effect of glass fibre surface chemistry on the mechanical properties of glass fibre reinforced, EPR-g-MA-toughened Nylon-6 were examined by Laura et al. [142]. Ishak et al. [143] investigated the fracture behaviour of short glass fibre reinforced rubber-toughened PBT composites. Laura et al. [144] studied the effect of glass fibres on the mechanical properties of maleated-EPR/Nylon-6 blend. The impact properties of short glass fibre/rubber/polypropylene composites were examined by Tam et al. [145]. The effects of rubber type and particle size on the mechanical properties of glass fibre reinforced blends of Nylon-6 and EPR/EPR-g-MA or SEBS/SEBS-g-MA were investigated by Laura et al. [146].

1.3.2 Studies on Rubber-toughening of polystyrene

Polystyrene is produced via the free-radical initiated chain polymerization of styrene. It is an odourless, tasteless, rigid thermoplastic. It has the following repeat unit in its molecular structure.

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{H}_2\text{C} \\
\text{C} & \\
\text{苯环} & 
\end{align*}
\]

The benzene ring reduces the ability of the polymer chain to bend and interferes substantially with other parts of the molecule. These characteristics prevent crystallization. Therefore, PS is essentially 100% amorphous [147].
Polystyrene is the fourth largest thermoplastic by production volume. It’s popularity is due to its transparency, low density, relatively high modulus, excellent electrical insulation properties, low water absorption, dimensional stability, ease of processing and low cost [148]. A major limitation of polystyrene in many applications is its brittleness. This limitation led to the development of rubber modified polystyrenes, the so-called high impact polystyrenes. Packaging and containers are by far the largest outlets. Other applications include housewares, toys, recreational products, housing for appliance parts, disposable food containers etc [149].

Several methods for incorporating rubber into PS matrix are known. Natural rubber (NR) latex was studied for its use as an impact modifier of several polymers [150-152]. Due to its broad particle size distribution, the existence of large size and high molecular weight [153], the NR latex particle might be suitable for the improvement of toughness of glassy polymers including PS. Tangboriboonrat et al. [154] reported an attractive method for the preparation of HIPS based on NR. The key steps involved the use of γ-radiation vulcanised natural rubber (RVNR) latex/phase transfer/bulk polymerisation. The phase transfer technique has been successfully used to transfer uncrosslinked, γ-radiation vulcanised and deproteinated NR latex particles from the aqueous phase in to the styrene monomer phase [155-157]. The toughened PS prepared exhibited the HIPS like morphology, and the impact energy was higher than that of the unmodified PS.

Martinez et al. [158] has elucidated the connection between morphological structure and mechanical properties of PS/SBR blends using SBR with various structures. Sreenivasan et al. [159] has evaluated the
mechanical properties and morphology of nitrile rubber-toughened polystyrene. Some studies on impact modification of PS/EPDM blends by the addition of EPDM-g-styrene, EPDM-g-(styrene-co-methyl methacrylate) and EPDM-g-(styrene-co-maleic anhydride) as compatibilisers were reported [160-162] where improvement in impact strength was achieved because of the better compatibility and the interfacial adhesion of the copolymers with the PS matrix. Various styrene-butadiene copolymers were investigated as compatibilisers in polystyrene/butadiene blends [163]. Mathur et al. [164] has reported the effectiveness of PS-PB-PS triblock compatibilisers in improving the impact strength of PS/PB blends. Rubber toughening of syndiotactic polystyrene and poly(styrene/diphenylethylene) with hydrogenated styrene-butadiene-styrene (SBS) block copolymer increased the toughness in terms of notched impact strength and energy release rate [165].

Barbosa et al. [166, 167] and Soares et al. [168] studied the influence of a non-reactive compatibiliser, EVA-g-PS, on the mechanical and morphological properties of PS and the blends with EVA copolymers, whereas de Almeida et al. investigated the possibility of improving the miscibility of EVA in PS by introducing zinc sulphonate and sodium sulphonate groups on to PS. Tang et al. [169] has reported the rheological and mechanical properties of polystyrene/ethylene vinyl acetate blends compatibilised with polystyrene-block-polybutadiene. The mechanical properties were comparable to that of HIPS. PS was toughened with EPDM in the presence of styrene-butadiene-styrene (SBS) block copolymer and the incorporation of SBS into the PS/EPDM blends improved the impact properties [170].
The effects of dynamic vulcanisation using sulphur, peroxide, and mixed systems on the morphology and mechanical properties of thermoplastic elastomers based on natural rubber and polystyrene has been reported by Ashaletha et al. [171] Dynamic vulcanisation causes a decrease in the size of the dispersed particles and improvement in mechanical properties. The impact strength of blends consisting of PS and EPDM could be increased by adding poly(styrene-ethylene-propylene) (SEP) compatibiliser and an organic peroxide during reactive extrusion [172]. The increased impact strength could be related to an enhanced adhesion between the dispersed EPDM phase and the PS matrix, as a consequence of radical graftlink or co-crosslink reactions between the rubbery part (EP) of the compatibiliser and the dispersed EPDM rubber.

1.3.3 Composites of Rubber – Toughened Polystyrene

Braun et al. [173] has investigated that toughness could be improved by the addition of chalk to PS/BR blends with low BR concentrations. The addition of chemically treated rice husk powder (RHP) and maleic anhydride-polypropylene coupling agent improved the mechanical properties of PS/SBR blends [174] The effects of partial replacement of silica by RHP on the processing, mechanical properties, effect of thermo-oxidative aging, water absorption and morphology of PS/SBR blend were investigated by Zurina et al. [175].

However, no serious attempt has been made to evaluate the use of short Nylon-6 fibres as a reinforcing fibre for rubber-toughened PS. The main features of Nylon fibres are exceptional strength, high elastic recovery, abrasion resistance, luster, resistance to damage by oil and many chemicals, high resilience and outstanding durability. The reinforcement of
rubbers using Nylon fibres has been reported by various authors [176-178]. Sreeja et al. [179-181] studied the effect of short Nylon-6 fibres on the mechanical properties of NR, NBR and SBR composites. Physico-mechanical properties of EPDM/Nylon-6 short fibre composite was studied by Wazzan [182]. Cure characteristic and mechanical properties of short Nylon fibre reinforced composites based on NBR and CR containing epoxy based bonding agent was investigated by Seema et al. [183,184]. Mechanical properties of short Nylon fibre reinforced SBR/NR composites were studied in detail by Ma et al. [185]. Short Nylon fibre reinforced polypropylene composites [186] and recyclable high density polyethylene composites [187] was studied by Thomas et al.

1.4 Scope and objectives of the work

Polystyrene is a versatile material with very interesting characteristics which makes it a high consumption polymer. However, its major limitation is its poor impact behaviour. In order to improve this deficiency, different elastomers has been used to produce toughened polystyrene. Unfortunately this results in the loss of stiffness and strength, because most rubbers are immiscible with polystyrene. Compatibilisation of the blend may alleviate this problem. The goal of compatibilisation is to obtain a stable dispersion that will lead to the desired morphology and properties. Successful compatibilisation will be able to 1) reduce interfacial energy, (2) permit finer dispersion during mixing, (3) enhance the stability of dispersion against agglomeration or phase separation throughout the processing/conversion to the final product, and (4) improve the interfacial adhesion. One method of compatibilisation is the dynamic vulcanisation of the elastomeric phase of the blend.
To improve the stiffness-toughness balance of rubber-toughened polystyrene, short fibres may be incorporated in blends. The studies so far reported proved that utilisation of short fibres as reinforcements in single polymer composites offer economical, environmental and qualitative advantages. The use of short Nylon-6 fibres as reinforcing agents opens a new avenue for the utilisation of waste fibres, available in plenty from fibre and textile industries. The properties of short-fibre containing composites depend critically on fibre content, orientation and fibre – matrix interface bond strength. A detailed study of the effect of these parameters on the composite properties will be highly informative. A strong interfacial bond can effectively transfer load from the matrix to the fibre and hence can improve the overall performance of the composite.

The main objectives of the present work are:

- To investigate the effect of blend ratio for toughening polystyrene.

  One of the principal weaknesses of polystyrene in many applications is its low impact resistance. To counteract this problem, it is necessary to toughen it with rubbers. The shape, size and distribution of the dispersed phase along with the interfacial characteristics decide the mechanical properties of the blend. The effect of blend ratios of PS/NR, PS/SBR and PS/WTR (whole tyre reclaim) on the mechanical and dynamic mechanical properties has been investigated.

- Evaluation of the effect of dynamic vulcanisation.

  The PS/rubber blend systems are incompatible resulting in inferior mechanical properties. Hence it is necessary to
compatibilise it for satisfactory product performance. Dynamic vulcanisation was adopted as a compatibilisation technique. Dicumyl peroxide (DCP) was used as the crosslinking system. The effect of DCP content on the mechanical properties, morphology and dynamic mechanical properties of PS/NR and PS/SBR blends were investigated.

- To study the effect of short Nylon-6 fibres on the blend.
  The incorporation of rubber into PS improves the toughness of PS but reduces its strength and elastic modulus. To improve the mechanical properties, an attempt was made to determine the suitability of short Nylon-6 fibres in PS/NR, PS/SBR and PS/WTR blends. The effect of fibre loading on the mechanical and dynamical mechanical properties of the blend were investigated.

- To investigate the effect of RFL-coated Nylon-6 fibre on the blend.
  For further improvement of the mechanical properties of the rubber-toughened blends, RFL-coated Nylon fibres were used. The effect of fibre loading on the mechanical and dynamic mechanical properties of PS/NR, PS/SBR and PS/WTR blends were studied.

- To evaluate the influence of surface modification of Nylon fibres and use of compatibiliser on the blends - PS/NR, PS/SBR and PS/WTR.
  The interaction between the polar fibre and non-polar blend is poor. Modification of interfacial interaction is carried out by surface hydrolysis of the Nylon fibre and the use of a reactive compatibiliser, maleic anhydride-grafted-polystyrene (MA-g-
Introduction

PS). The effect of untreated and surface hydrolysed Nylon fibre in conjunction with the compatibiliser on the mechanical and dynamical mechanical properties of PS/NR, PS/SBR and PS/WTR blends were investigated.

- Evaluation of thermal degradation behaviour of the blend and the composites.
Since most of the polymeric materials are manufactured by melt processing, it is essential to study the thermal stability of these materials. One of the most accepted methods for studying the thermal properties of polymeric materials is the thermogravimetry. The thermogravimetric curve and its derivative (DTG) provides information about the nature and extent of degradation of polymeric materials. The effect of blend, dynamic vulcanisation, short Nylon-6 fibres and surface hydrolysed fibres in conjunction with compatibiliser on the thermal stability were evaluated.

1.5 References


Chapter -1


Introduction

Chapter -1


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Introduction

Chapter -1


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Chapter -1


Introduction


Chapter -1


50
Introduction


Chapter 1


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