# 5 Polyethylene Terephthalate-Based Blends: Natural Rubber and Synthetic Rubber

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## OUTLINE



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## 5.1 Introduction

In recent years, the area of thermoplastics has been remarkably animated by the appearance of incipient polymer blends. Many publications, press releases, organization brochures, and patents granted over the past two decades, are a confirmation of the innovation and prosperous product advancement in the thermoplastics field, and significant advancement has been centered on polymer blends or poly blends. The mixing of two or more polymers together in order to produce blends or alloys is a well-established strategy for accomplishing specified and desirable physical properties, without the need to combine particular polymer networks [1]. Polymer blends have become a versatile and economically viable solution to the needs of the industry, in terms of improving the performance of engineering and specialty plastics. Consequently, the field of polymer blend has been developing rapidly, in terms of scientific and commercial utility. The blends normally come with the composition of a high thermoplastic–low rubber blend (e.g., a plastic/rubber ratio of 70:30). On the other hand, most of the thermoplastic and rubber pairs are immiscible due to the high interfacial tension and/or adhesion in the solid state, leading to gross phase separation, thereby giving rise to poor mechanical properties [2–7] and undesirable performance for target end uses. In spite of this inherent disadvantage, a wide range of new and useful materials with improved and unique properties have been obtained from such immiscible and incompatible polymer pairs, either by the addition of a third component, usually a graft or block copolymer, or by *in situ* formation of such copolymers during blending operations. These methods result in partial compatibilization of the otherwise incompatible polymers [8–11]. Hence, in this chapter, we discuss the preparation, properties, and applications of PET blended with either natural and/or synthetic rubber. The repeat units of some thermoplastic polymers are illustrated in Figure 5.1.

Among these thermoplastic polymers, polyethylene terephthalate (PET) is a very important engineering thermoplastic polyester because of its excellent chemical resistance, good mechanical and thermal properties, as well as excellent optical and barrier properties, which make PET an ideal candidate for use as beverage bottle applications, that are increasingly, replacing glass bottles. But, the same useful PET can also cause a huge pollution problem. Since it is highly nonresistant to atmospheric and biological agents, PET bottles are noxious materials and are a cause of concern regarding recent environmental protection issues. In 2011, over 7.5 million tonnes of PET bottles were collected worldwide and the trend has been growing, especially due to its superiority over glass for bottling beverage. In Europe alone, 1.6 million tonnes of PET waste bottles [12] were collected in 2011. As a consequence of this problem, in order to eliminate or reduce PET waste from the environment and reduce costs of manufacturing some products, a relatively new area of interest is the use of recycled polyethylene terephthalate (R-PET) bottling powder as a filler for rubber. However, PET is a very polar component having

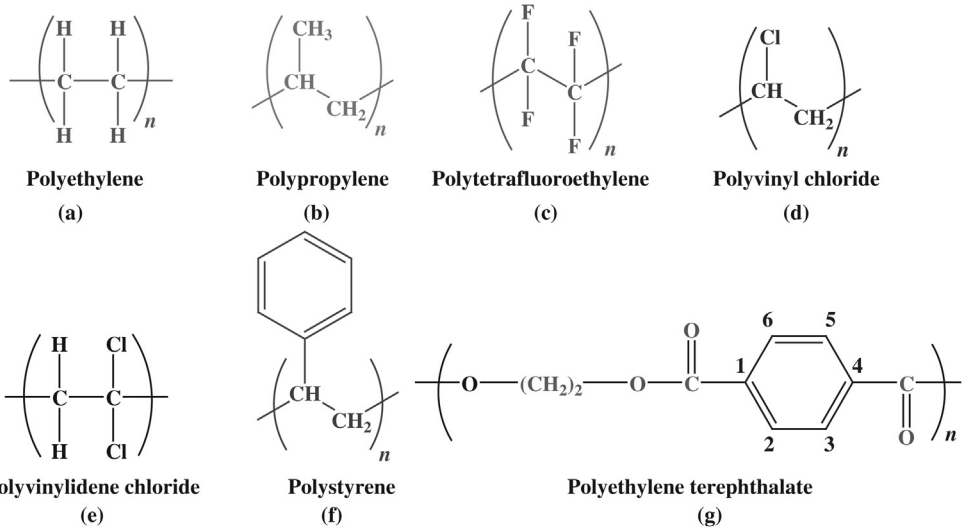


**Figure 5.1** Examples of thermoplastic polymers. (a–c) Additional polymers; (d–g) condensation polymers.

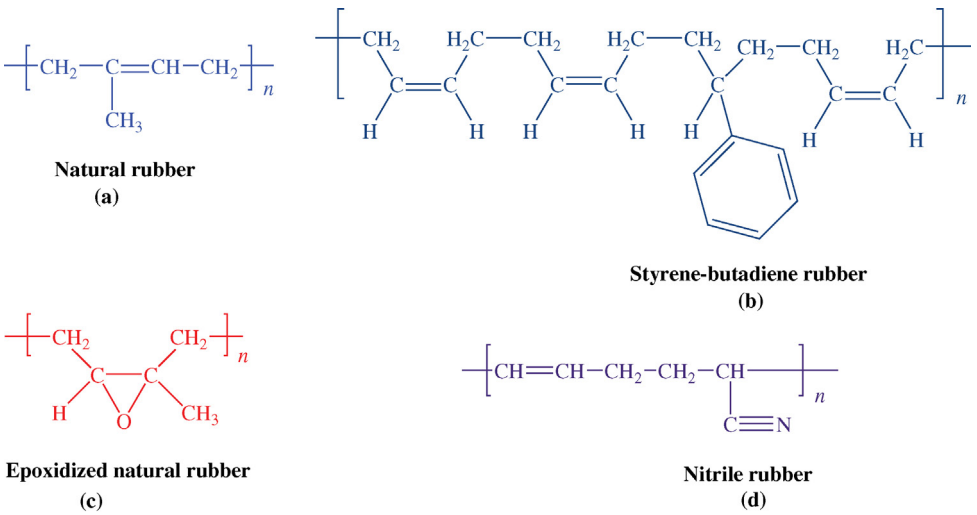


**Figure 5.2** Examples of rubbers. (a) Natural rubber; (b–d) synthetic rubbers.

two different functional end groups (i.e., hydroxyl and carboxyl groups), while rubbers, generally, are apolar due to a lack of functional groups. This gives rise to a high interfacial tension between the blend components.

The blending of thermoplastics and rubbers, generally, leads to immiscible systems with coarse phase morphology. The morphology is, furthermore, very unstable and will coarsen upon further processing on account of coalescence. An unstable morphology and poor interfacial adhesion will result in a material with poor mechanical properties [13]. In order to effectively develop thermoplastics/rubber blends with the desired fine phase morphology, the use of a reactive compatibilization strategy is necessary. Reactive compatibilization can be induced by using functionalized rubbers, thereby enabling a direct chemical reaction between the matrix polymer and the dispersed rubber. Another route consists of the addition of a third component that should, at least, be compatible with one of the two constituting components and have the possibility of reacting with the functional groups of the other component. The effect of compatibilization between rubber and PET matrix has been observed to play an important role in the resulting blend's behavior [3,6,14]. With different rubber types, it has been observed that maleic anhydride-grafted styrene-ethylene-butylene-styrene (MAH-*g*-SEBS) rubber can be effective in the toughening of PET [7,15]. Adding rubber is generally recognized to be a very effective method for the improvement of impact property in thermoplastics [14,16,17]. Rubbers appear to be the better toughening agents for PET. Their addition brings about enhanced toughness, if the rubber phase is finely dispersed in the PET matrix. This can be accomplished if the rubber is properly functionalized. The chemical structures of some rubbers are illustrated in Figure 5.2.

Based on the dispersion of small rubber particles in the PET matrix, rubber modification is generally recognized to be a very effective method for the improvement of notched impact behavior. From the theories involved in rubber toughening [13,18], it is known that the morphological characteristics of the blends, such as the average rubber particle size and the concentration of the dispersed phase, have a distinct influence on the final mechanical behavior. A finely dispersed rubber phase, at the submicron level, is often a prerequisite for obtaining the desired notched impact response. The rubber particles behave as stress concentrators, enhancing the fracture energy absorption of brittle polymers and ultimately resulting in a material with improved toughness. The effectiveness of rubber modification is found to be highly dependent on the following:

1. The rubber must act as a compatibilizer.
2. The rubber must be distributed as small domains in the PET matrix.
3. The rubber must have good interfacial adhesion to PET.
4. The glass transition temperature of the rubber must be at least 20°C lower than the temperature employed in the blending process.
5. The molecular weight of the rubber must not be too low.
6. The rubber must be thermally stable at the polymer processing temperatures [19].

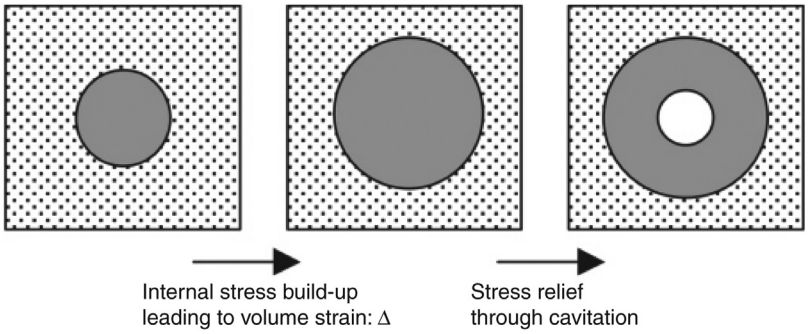


**Figure 5.3** Schematic representation of the steps involved in rubber cavitations [27].

Furthermore, rubber modification gives an effective method for enhancing the impact behavior of notch-sensitive PET [13,14,20]. The main role of the dispersed rubber particles is to induce a global deformation mechanism, rather than a localized type. When toughening notch-sensitive materials, the dispersed rubber particles are likely to cavitate and/or debond following the application of a load. The voiding of the rubber phase leads to a relief of the triaxial stress state ahead of the notch or crack, thus creating a stress state beneficial for the initiation of multiple matrix shear yielding [20–22]. In recent years, several models have been developed that quantitatively describe the cavitational process. The models developed by Dompas and Groeninckx [23] and by Lazzeri and Bucknall [24,25] are based on an analogous principle. Void formation occurs when the released internally stored stress build-up (volumetric strain energy) is greater than the energy required for the creation and expansion of the surface area of the void. The energy balance model of Lazzeri and Bucknall also stipulates that the energy released, additionally needs to cover the energy required for the stretching of the surrounding rubber, thereby adding an extra term to the equation. The volume strain energy present in the rubber particles can originate from two sources: mechanical loading and/or differential thermal contraction [26]. The basic mechanism of toughening is one of void formation and shear band formation (cavitation), when stress is applied. Figure 5.3 illustrates the different steps involved during the event of rubber cavitation.

## 5.2 Polyethylene Terephthalate-Based Natural Rubber Blends

PET is an important engineering thermoplastic polyester because of its good combination of properties, such as good thermal and mechanical properties as well as having excellent chemical resistance, and good optical and barrier properties. However, the notched impact strength of PET is very low, a property not desired in engineering thermoplastics, such as polyamides. Improvement in the notched impact behavior can be achieved by incorporating an elastomeric material, that is, natural rubber (NR) in PET. Unfortunately, NR and PET are immiscible and incompatible. Thus, the resultant blends do not attain optimal properties. This is due to the polar nature of PET and apolar character of NR, which requires that blends of the two be compatibilized in order to obtain a useful material that combines the strength of PET with the impact resistance of NR. Furthermore, the basis of the improvement depends on the fine dispersion of small rubber particles in the polymer matrix. Based on theories of rubber toughening [28], the blend morphologies and characteristics, such as, the average rubber particle size and the concentration of the dispersed phase, will have distinct influences on the final mechanical properties. Parameters influencing phase morphology development and the impact response of rubber-toughened polymers are: the type and content of the rubber, the type and content of the reactive compatibilizer, the viscosity ratio, and the mixing conditions [14,29]. A finely dispersed rubber phase, at the submicron level, is often a prerequisite for obtaining the desired notched impact response.

### 5.2.1 Preparation of PET/NR Blends

Unlike conventional rubbers, thermoplastics are processed on thermoplastic machinery. Preparation requires no separate vulcanization stage, as it is easily done by internal mixers or extruders, therefore productivity is high. The various methods of preparation of PET/NR are discussed below.

#### 5.2.1.1 Mixing

The mixing of NR and PET in order to prepare PET/NR blends is simplified as the number of additives necessary are considerably reduced. This saves time, energy, and capital costs of machinery. Varying the mixing temperatures near the melting points of PET will naturally yield NR materials exhibiting different physical properties. The mixing rate and duration of mixing also influence the properties of the PET/NR blend. Mixing is carried out using different machineries as described below.

##### 5.2.1.1.1 Brabender Plasti-Corder

One of the methods of preparing blends is by using an intensive internal batch mixer known as the Brabender Plasti-Corder. Torque and temperature are recorded online. The PET/NR blends are normally prepared in the laboratory via mixing in a Banbury mixer or Brabender Plasti-Corder attached to a mixer or a twin-screw compounder. The dried PET is first melted in the mixer and then masticated NR is added [30]. Additives, such as compatibilizers or stabilizers are added before the addition of the NR [31].

The temperature settings along the extruder barrel ranges between 280°C and 290°C, with the higher-temperature zone close to the extrusion die. The blended pellets are subsequently injection molded into end-gated rectangular plaques (150 × 80 × 3.2 mm). The plastic pellets are dried in an air-circulating oven at 80°C before melt processing. Tensile bars, single-edge-notch-bend and double edge-notch-tension specimens are machined from the plaques with the long dimension of the samples parallel to the long edge of the plaques [7]. After mixing in the internal mixer, the blends are taken out and sheeted through a two-roll mill. This is then compression molded in a hydraulic press.

##### 5.2.1.1.2 Two-Roll Mixing Mill

Prior to blending, PET is usually dried at 120°C for 10 h in an oven. Before blending with PET, the NR is milled for 1 min at 40°C on a two-roll mill, sheeted, and cut into small pieces. PET and rubber are tumble-mixed before feeding into a corotating twin-screw extruder (typically a prism, with a screw diameter of 25 mm, compression ratio of 3:1, die diameter of 16 mm, and L/D ratio 25/1) at different screw speeds and blend compositions. The temperature profile of the twin-screw extruder is set thus: 200, 220, 230, 240, 245°C for PET/rubber blends and the temperature profile of PET is set at: 210, 225, 235, 245, 250°C. The extrudate is cooled in a water bath before being cut with a granulator into pellets [32].

##### 5.2.1.1.3 Haake Rheocord

The Haake Rheocord is an alternate equipment that can be used to prepare PET-based NR blends. Prior to blending, all materials are normally dried overnight under vacuum. Before blending with PET, the basic NR and the compatibilizer are pre-blended at different ratios. Pre-blending the two dispersed phase components leads to small particle sizes. Pre-blending is performed on a batch mixer using a mixing chamber of 69 mL at 180°C and a screw speed of 50 rpm for 5 min. After pelletization, the preblends are mixed with PET, giving rise to ternary blends. The compounding of the blends is performed on the batch mixer using a mixing chamber of 300 mL at 280°C and a screw speed of 50 rpm for 10 min. After mixing, the blends are dried at 120°C before being compression molded into plaques. Therefore, the materials are first molten at 280°C and held under pressure for 90 s. The mold is then transferred directly into a second press held at a temperature of 180°C and kept under pressure for 5 min. Following removal from the press, the plaques are left to cool to room temperature. This procedure is to be carried out carefully in order to control the overall crystallization conditions resulting in an equal treatment for every material [4].

##### 5.2.1.1.4 Twin-Screw Extruder

Melt blending is also carried out using a twin-screw extruder. The screw speed is determined by the ease of processing and mechanical properties of the blends. The extrudate is quenched in a water bath at room temperature and then pelletized. The blends are dried in a vacuum oven and reextruded using the previous extrusion conditions. The blends are again dried in an oven and kept in desiccators at room temperature. Tanrattanakul et al. [33] performed melt blending of nylon 6 and epoxidized natural rubber using a twin-screw extruder.

#### 5.2.1.2 Solution Casting

Solution casting is a very convenient method when thin films of polymer blends are required. NR and PET are dissolved in a suitable common solvent

or a mixture of solvents and then cast on a glass plate. It has been proved that the nature of solvent used for casting in the preparation of the blend influences the compatibility and related properties. Other researchers reported [34] a case of polystyrene (PS)-poly(vinyl methyl ether) (PVME) mixtures. Clear blend films of PS–PVME mixtures were obtained on casting from solvents, such as benzene and toluene, while visually incompatible films result on casting from trichloroethylene and chloroform. Blends of polyvinyl chloride (PVC) and liquid natural rubber/epoxidized liquid natural rubber were prepared using a common solvent, 2-butanone [35]. Another research group prepared PVC/NR blends using tetrahydrofuron (THF) as the solvent [36].

## 5.2.2 Properties of PET/NR Blends

In the last decade, a number of polymer blends and alloys have been introduced into the market, especially engineering plastics. In general, blend properties depend on compatibility. For instance, for fully compatible blends, mechanical and thermal properties are expected to be close to the average of blend component. However, PET is a polar constituent, having two distinctive functional end groups, while NR, due to a lack of functional groups, generally is apolar in nature. This suggests that a high interfacial tension and lack of interfacial adhesion in the PET/NR blends lead to coarse phase morphology. The morphology is, furthermore, very unstable and will coarsen upon further processing on account of coalescence. An unstable morphology and poor interfacial adhesion will result in a blend with poor mechanical properties [13].

In order to viably develop a PET/NR blend with the desired fine phase morphology, the use of a reactive compatibilization strategy plays an important role, when two polymers are immiscible, such as PET/NR.

### 5.2.2.1 Influence of Compatibilizers

Most polymer pairs are immiscible due to high interfacial tension and lack of interfacial adhesion in the solid state, leading to gross phase separation and hence poor mechanical properties. Compatibilization techniques are important to achieve good performance in polymer blends. Generally, compatibility can be achieved, either by adding a third component (compatibilizer) capable of specific interfacial and/or chemical reactions with blend constituents or by blending suitable functionalized polymer(s) capable of enhanced specific interaction and/or chemical reaction [37]. Functionalized (reactive) rubbers, such as Lotader AX8900 (see Figure 5.4), are excellent toughening agents for PET as they improve interfacial adhesion and more, importantly, reduce interfacial tension, thus allowing the formation of smaller rubber particles (Figure 5.5). With regards to previous studies of PET/NR blends, most researchers focused on compatibilization methodologies, since PET and NR are incompatible due to the great difference in the solubility parameters between them. The incorporation of surface-active species, called compatibilizers, which concentrate at the interface, tends to improve the interfacial adhesion as well as refine and stabilize the blend morphology [38]. Therefore, compatibilization is necessary in order to obtain good interfacial adhesion and to reduce the

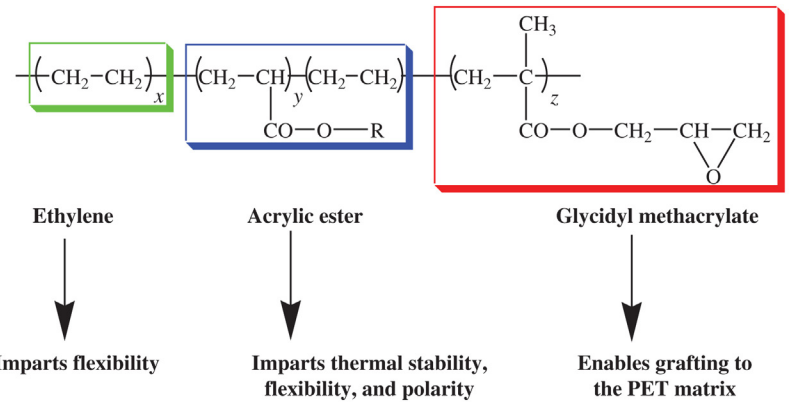


**Figure 5.4** Structure for random ethylene-acrylic ester-glycidyl methacrylate terpolymers that are effective rubber toughness for PET compounds. The ethylene-acrylic ester segments provide elastomeric properties, while the glycidyl methacrylate functionalities enable reactive grafting to the PET matrix via the hydroxyl and carboxyl chain ends of the latter [39].

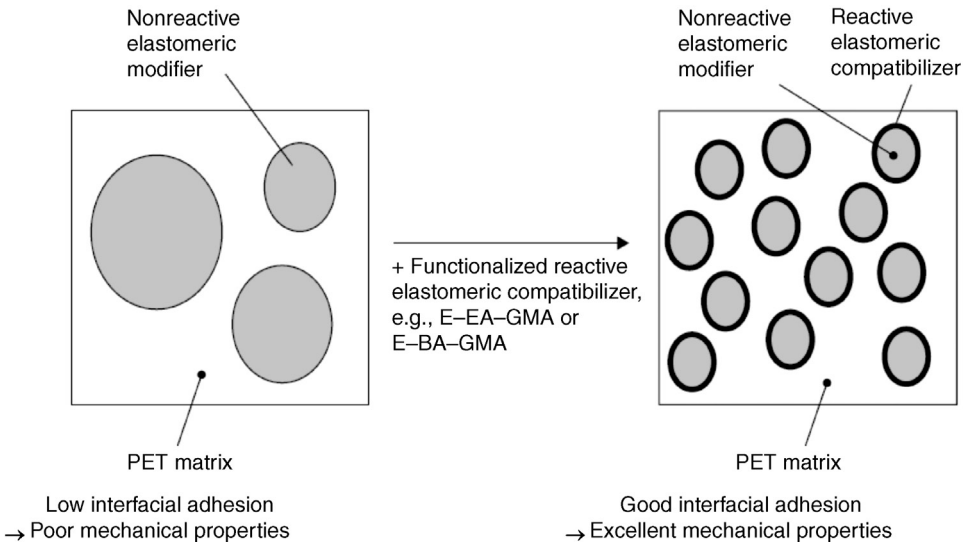


**Figure 5.5** Schematic diagrams highlighting the microstructure of rubber-toughened PET and performance improvements when nonreactive rubbers are blended with reactive rubbers [39].

interfacial tension between the components. Of all the compatibilizers used in PET/NR blends, reactive functional groups of maleic anhydride (MAH) and glycidyl methacrylate (GMA) are the most common. Furthermore, a grafting of the elastomer to the PET matrix occurs according to the following reaction:

$$\text{PET} - \text{COOH} + \text{Lotader AX8900} \rightarrow \text{Polyester-}g\text{-Lotader}$$

In recent years, GMA-containing copolymers are the most efficient species of compatibilizer for PET blends [40]. There are three main chemical reasons for their efficiency. Firstly, epoxy functionality of GMA is able to react with both hydroxyl and carbonyl end groups of PET, whereas MAH reacts only with the hydroxyl ends. Secondly, epoxy function of GMA has higher reactivity than MAH, towards hydroxyl groups of PET. Finally, the esterification reaction is reversible at high temperatures [40,41]. The overall expected reaction schemes are outlined in Figure 5.6. A successful compatibilization of immiscible polymer pairs would result in the compatibilizer locating at the interface between the discrete polymer phases, so that it can act as an emulsifier, which reduces the interfacial tension and improves adhesion between the phases, thus giving rise to improved mechanical properties and overall performance. Such compatibilization often results in a stabilized morphology with fine dispersion of the second (minor) phase in the matrix and subsequently would have a direct effect on the final properties of the blends [37,42].

#### 5.2.2.2 Influence of Blend Composition

Polymer blends are capable of providing materials with extended useful properties beyond the range that can be obtained from individual polymers. Blends of PET and NR were prepared by Phinyocheep et al. [32] in different ratios the twin-screw extruder technique. PET is dried in an air oven at 120°C for 10 h in order to avoid excessive moisture-induced degradation reactions, before processing in a corotating twin-screw extruder. The notch sensitivity of PET becomes quite apparent from the very low notched Izod impact strength (6.0 J/m) that was obtained by passing PET in the twin-screw extruder before injection molding into test specimens. It has already been demonstrated that the impact behavior of PET can be grately improved by rubber modification [2–4,14,29]. Phinyocheep et al. [32] reported that various amounts of NR were blended with PET in a twin-screw extruder using a screw speed of 100 rpm. According to Phinyocheep et al. [32], the Young's modulus and the notched Izod impact strength of PET/NR blends showed an inverse proportional relationship. When the NR content is increased, the impact property is enhanced while the Young's modulus decreased. This may be due to the elastomeric nature of NR. Similar results were also observed by [7] in the case of PET/styrene-ethylene-butylene-styrene (SEBS) blends. The explanation for the enhancement of notched impact strength of PET/NR blends may be the brittle transition of the modified blend by the presence of the NR diffusion phase. This phase can absorb and disperse in order to produce the crack energy that

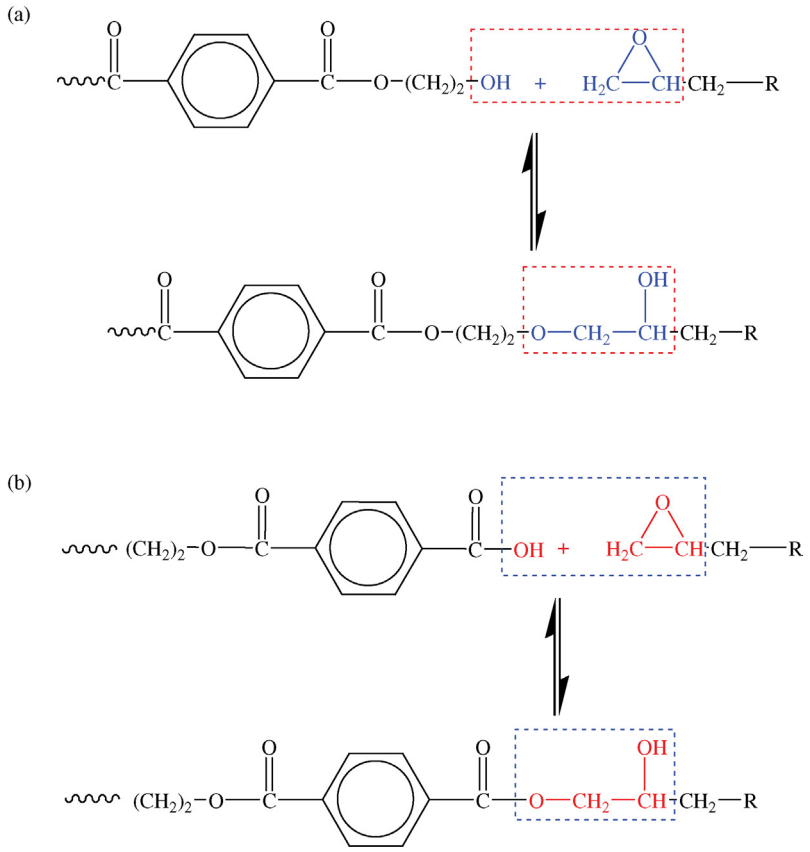


**Figure 5.6** Chemical reaction schemes. (a) Hydroxyl end group of PET and epoxy group of GMA; (b) carbonyl end group of PET and epoxy group of GMA [43].

prevents the unexpected breaking of the specimen. By increasing the rubber concentration, the acceptors of the dissipation energy are increased. This then induces a further enhancement of the impact strength [20]. The Young's modulus of the blends seems to have decreased following NR incorporation into the PET matrix. This may be due to two factors: the elastomeric nature of NR in the PET/NR blend and the extent of degradation of the PET matrix phase [44,45]. Fox et al. [46] reported a significant degradation of PET when it was part of a blend than when PET was alone. It happens that the degradation is catalyzed by some component, such as moisture in PET. Thorough drying, however, did not enhance the reduction of degradation in the blends. From their findings, it can be concluded that, when the amount of NR in the blend was increased, the Young's modulus decreased, but the Izod impact strength increased.

### 5.2.2.3 Influence of Extrusion Speed

Another important parameter in PET/NR blends is the extrusion speed. This plays an important role in the mechanical properties of blends. It is well known that the processing condition will be a significant factor in controlling the microstructure, the interparticle distance, and the particle diameter of the disperse phase, even without adding a third component or a compatibilizer into an immiscible blend. All these factors govern the performance, physical and mechanical properties of the blends. Various screw speeds, in the extrusion process, were reported by [32] in order to process the PET/NR blends of 80/20 wt% composition. From their studies, the effect of different extrusion screw speeds (60–150 rpm) influenced the mechanical properties of 80/20 wt% blends. It was reported that when the screw speed increased, the notched Izod impact strength and the Young's modulus did not change. This may be due to the control of these processing parameters of the injection process in the final step. This clearly suggests that the extrusion screw speed has less effect on the mechanical properties than does the NR content in the blend.

### 5.2.2.4 Morphology of PET/NR Blends

Scanning electron microscopy (SEM) analysis was employed [32] in order to identify the phase structure

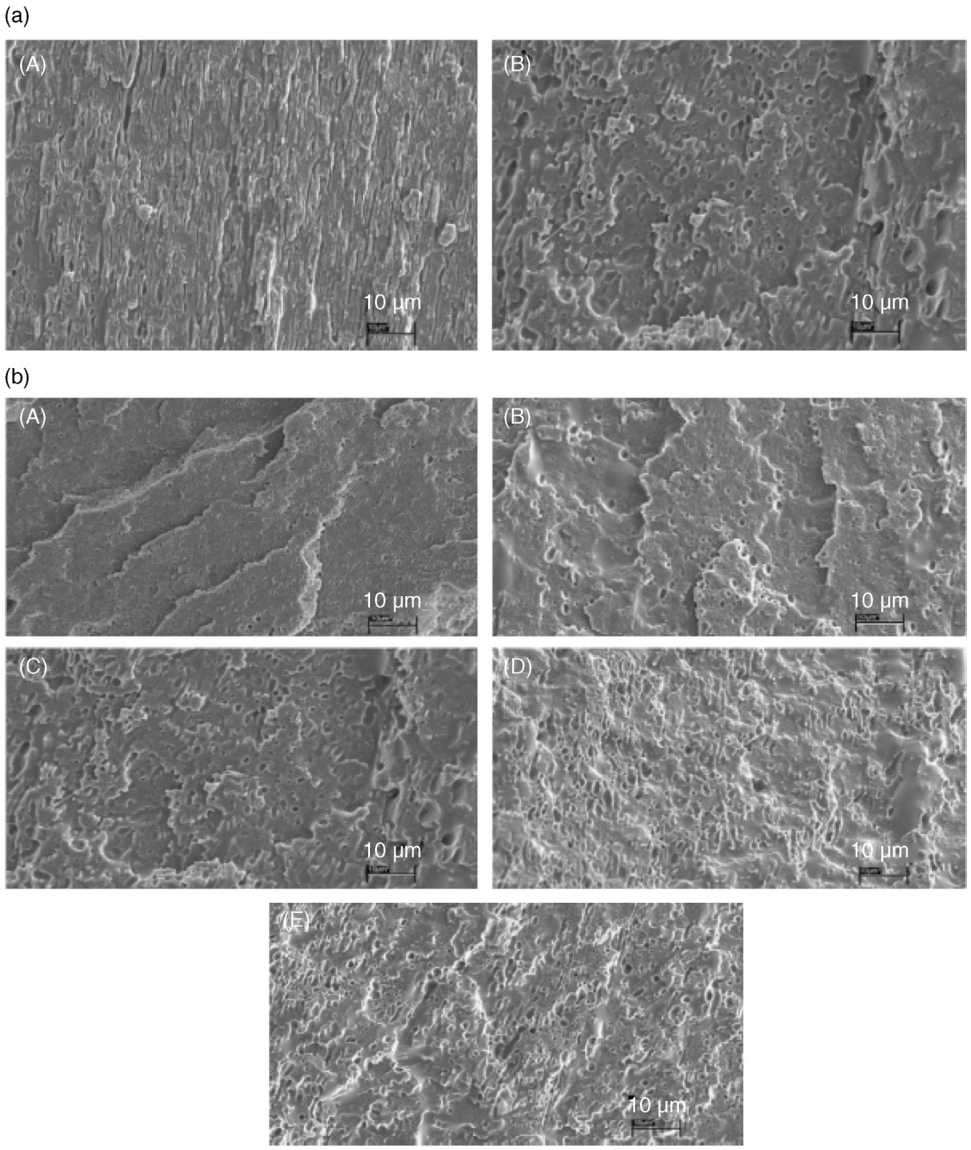


**Figure 5.7** (a) Cryofractured surfaces of the (A) outer and (B) inner zones of injection-molded impact specimens of PET/NR 80/20 wt%; (b) Cryofractured surfaces of the inner zone of the injection-molded impact specimens of PET/NR blends at: (A) 95/5; (B) 90/10; (C) 80/20; (D) 75/25 and (E) 70/30 wt% [32].

of the PET/NR blends. The micrographs of PET/NR blends of the outer and the inner zone of an injection-molded specimen of the 80/20 wt% PET/NR blend that was cryogenically fractured in the transverse direction are shown in Figure 5.7. These results suggest the fact that the PET/NR blends exhibited a skin-core morphology, similar to those seen in other rubber-modified PET systems, such as PET/SEBS [7,47], polybutylene terephthalate-phenoxy/maleinized polyethylene-octene (PBT-Ph/mPEO) [48], or PBT/PEO [49]. The holes near the edge of the sample containing the NR domains are elongated NR that is predominantly rod shaped, as shown in Figure 5.7a(A). A few holes were oval, suggesting that some of the elongated NR domains were slightly flattened just as was observed in the PET/SEBS-*g*-MAH blend [7,47] and PBT/PEO blend [50]. However, the thinness influence on the mechanical properties of PET/NR as determined by Phinyocheep et al. [32] is negligible, therefore the morphology of the core, seen in Figure 5.7a(B), is omitted. Only the morphological data of the inner part of the specimens are considered in their report. Figure 5.7b shows the SEM micrographs of the various blends ratio of PET/NR. According to Ref. [32] the average particle size did not increase linearly with the amount of NR added. An average particle diameter

of about 1.4 mm was obtained when 5% of NR was added. This value was relatively constant up to 20% of NR content. The average particle size increased again when the amount of NR was increased to 25%. It remained constant as the amount of NR was increased to 30%. The binary PET/NR blends displayed very coarse phase morphology with large average particle sizes of about 2.8 mm. This is due to the coalescence of NR at high rubber content. From these results, large particle sizes are expected because of the high viscosity ratio ($\eta_{NR}/\eta_{PET}$) and the high interfacial tension ($\sigma$) between the two phases. The SEM micrographs of the cryogenically fractured surfaces of the PET/NR blends, at various screw speeds, were also reported by Phinyocheep et al. [32]. The authors also explained the average particle diameters versus the impact strength of the blends at various screw speeds in the extrusion process. From their study, the smallest particle size of the rubber particle (1.46 mm) dispersed in PET resulted in the highest impact strength of the blend (43 J/m). It can also be stated that the PET/NR, blend processed at 150 rpm, had a relatively high impact strength even though the rubber particle size was 2.2 mm. Therefore, in the PET/NR blends, the size of rubber dispersed is not too critical for the control of the mechanical properties of the blends.

### 5.2.2.5 Molecular Characteristics of PET/NR Blends

The PET/NR blend was a solid material and it responds to organic solvent at room temperature. The analysis of the molecular characteristics in the solid form can be done by solid-state carbon-13 nuclear magnetic resonance ($^{13}$C NMR) spectroscopy. The molecular characteristics of the PET/NR blend were investigated by [32] using solid-state $^{13}$C NMR spectroscopy with MAS and CP/MAS (cross-polarization and magic angle spinning) instruments. The impact strength of the PET/NR blend was higher when compared to the pure PET. The authors [32] proposed that the NR has some physical or chemical bonding with PET. From the solid-state $^{13}$C NMR spectra, the PET/NR blend at 80/20 wt% exhibited two peaks; the sharp peak belongs to NR, while the broad peak is assigned to PET. In the case of NR segment, there were three peaks at 23, 26, and 32 ppm, which can be assigned to the methyl carbon and two methylene carbons of NR, respectively. Two more peaks at 125 and 134 ppm were observed and assigned to olefinic carbons of NR, while the PET segment has a singlet at 61 ppm, a doublet at 129 and 133, and a singlet at 164 ppm. These were assigned to methylene, aromatic, and carbonyl carbon, respectively. They further analyzed the molecular characteristic of the PET/NR blend by varying the contact time. The stack plots of solid-state $^{13}$C NMR spectra of PET/NR 80/20 wt% with the contact time ranging between 0.01 ms and 20 ms were reported [32]. It can be found that at the lowest contact time (0.01 ms), two significant peaks were observed at 61 and 129 ppm. These are assigned to the resonance of the methylene and aromatic carbons, corresponding to large dipolar $^{1}$H–$^{13}$C interactions. They reported the fact that the carbon resonance of carbonyl (164 ppm) and aromatic groups (133 ppm) appeared at longer contact times and their intensities progressively increased with longer contact times.

A comparative study [32] of PET in a PET/NR blend was done and it was found that the relaxation time ($T_{1\rho}^{H}$) is smaller for the carbonyl group at 164 ppm (8.3 ms) and the methylene carbon at 61 ppm (8.7 ms). Owing to the experimental errors, no positive conclusion could be drawn for the aromatic carbon at 133 and 129 ppm. Phinyocheep et al. concluded that, the smaller $T_{1\rho}^{H}$ values indicate a faster proton relaxation in the rotating frame. This is identified with the conceivable interaction between the PET and NR chains near the carbonyl or the methylene positions, which slightly influenced the molecular mobility of PET in the kilohertz (KHz) range. It has been reported [32,51] that the molecular chain of NR contains some abnormal groups, such as epoxide, amine, and hydroxyl. The epoxide concentration was reported [51] to be about 0.53 mol% and the amount of amine (or hydroxyl) was found to be half of the epoxide content. It was reported by other researchers [52], in the case of thermoplastic polyurethane elastomer and polyethylene blend, that its properties could be improved when the polyethylene was grafted with 0.5 wt% MAH. Therefore, it can be concluded that the presence of a small amount of hydroxyl groups in NR may interact with the carbonyl group of PET, via hydrogen bonding, as shown in Figure 5.8. Furthermore, the spin diffusion time ($T_D$) of the carbonyl group is larger in the PET/NR blend (3.9 ms) than that in PET (2.8 ms). This will correlate with a slower spin diffusion rate. This clearly indicates that cross-polarization at the carbonyl group in the PET/NR blend is less efficient than that in PET, which will result in more mobile remote protons. Within the error range, the other relaxation times are unaffected. This further confirms that interactions can occur between the carbonyl group of PET and abnormal groups, such as the hydroxyl functional group of NR.

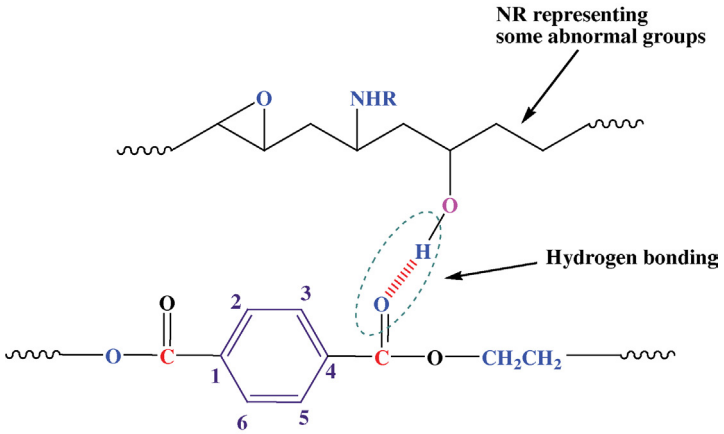


**Figure 5.8** Proposed interaction via hydrogen bonding between the carbonyl group of PET with abnormal groups, such as the hydroxyl functional group in NR. *Redrawn structure from Ref. [32].*

### 5.2.2.6 Thermal Properties of PET/NR Blends

Since PET is a semicrystalline polymer, the incorporation of NR in the PET matrix can affect the crystallinity of PET. This will influence the mechanical properties of the PET/NR blend. Differential scanning calorimetry (DSC) heating thermograms normally provide vital information corresponding to the phase structures of PET and PET/NR blends, that is, melting temperature ($T_m$), cold crystallization temperature ($T_{cc}$), and crystallization temperature ($T_c$). According to Phinyocheep et al. [32], the heating thermograms of NR, PET, and PET/NR blended at 80/20 wt% samples were almost amorphous as indicated by well-defined glass transition temperature and large cold crystallization exotherm. The transition temperatures at −67 and 84°C that were observed, related to the glass transition temperature of NR and PET, respectively. The endotherm peak at 248.5°C is due to the melting of PET ($T_m$). The exothermic peak at 171.2°C is the result of the cold crystallization of PET ($T_{cc}$). However, $T_m$ of PET in PET/NR blends at 80/20 wt% occurred at a similar position to that of pure PET. This temperature indicated that PET/NR is not compatible. This is further supported by the scanning electron micrographs. The percentage crystallinity of PET in the PET/NR blend ($\%\chi_C$) was determined by using Equation (5.1).

$$\%\chi_c = \frac{\left[\dfrac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0}\right]}{\Phi_{PET}} \times 100 \tag{5.1}$$

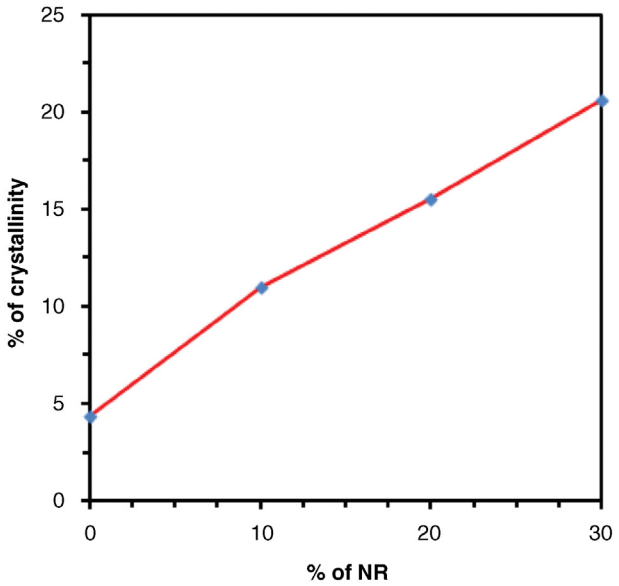


**Figure 5.9** Percentage of crystallinity as a function of percentage NR. *Data taken from Ref. [32].*

From Figure 5.9, the authors [32] concluded that the crystallinity of the PET/NR blend significantly changed from that of pure PET. By increasing the NR percentage in the PET/NR blend, the percent crystallinity of PET in the blend increased almost linearly. This may be due to the fact that rubber acted as a nucleating agent in the PET matrix, causing an approximately 40°C lowering of the $T_{cc}$ of PET. The decrease of the $T_{cc}$ of PET has also been reported [7] in PET/SEBS-*g*-MAH. The thermal behavior of the PET/NR 80/20 wt% blends at various extrusion screw speeds were investigated using the DSC technique. It was concluded that increasing the screw speed does

not affect the $T_m$ and $T_c$ of PET in the blend. The 80/20 wt% PET/NR blend processed at various speeds had similar percent crystallinity. This indicated that the crystallization of the PET/NR blend is not controlled by the screw speed in the extrusion process.

### 5.2.3 Applications

PET/NR blends possess excellent properties, such as: reduced permanent set, improved mechanical properties, greater resistance to attack by fluids, improved high-temperature utility, etc. [53] and therefore provide very useful and attractive applications in different fields, such as: automotive parts, building materials and construction equipment, wire and cable insulation, etc. [54]. PET/NR blends are generally used for making automobile parts where operations, such as abrasion, flexing, and tear are prominent factors leading to the fracture of the products [55]. PET/NR blends currently attract markets in many applications where vulcanized rubbers have traditionally been used. PET/NR blends are ideal candidates for use in beverage bottle applications, that are increasingly replacing glass bottles. They are also used in products that require better performance than can be obtained with general-purpose thermoplastics, such as PVC and polyethylene. PET/NR-type blends have potential uses in flexible automotive components. Moreover, they provide immense potential for scrap and reject recycling and blends have the ease of property manipulation through composition change.

## 5.3 Polyethylene Terephthalate/ Synthetic Rubber Blends

Rubber materials have remarkable and versatile properties, which are widely used in different mechanical applications, especially under dynamic conditions. However, the primary disadvantage of rubber is that it is not used for reprocessing and recycling because of its thermosetting nature. One possibility is to reuse or recycle rubber materials in order to reclaim rubber, which requires a few processing steps. First and foremost, scrap rubber (natural or synthetic) is pulverized into small pieces, then the fragmented scrap is processed in hot caustic soda solution, and finally recovering agents are included. It is well established that reclaimed rubber does not hold all the rubber properties of the virgin rubber. Hence, it is typically used in blends with virgin rubber, or by itself in low-grade rubber products. On the other hand, thermoplastic polymers (see in Figure 5.1) can be recycled without loss of their inherent and unique properties. In comparison to rubber, thermoplastic polymers have limited upper service temperatures and poor elastic properties. Therefore, blending rubber with thermoplastic polymers provides an important route to obtain new materials that combine both the rubbery and thermoplastic properties. Thermoplastic elastomers (TPEs) are polymer blends obtained by blending rubber with thermoplastic, with good control of the blend morphology. The development of TPEs by blending a thermoplastic and an elastomer is currently pursued very actively. These materials are economically significant and also a fundamentally fascinating class of polymeric materials. TPEs consolidate properties of irreversibly cross-linked elastomers, for example, impact resistance and low temperature flexibility, with the characteristics of thermoplastic materials, particularly the ease of processing and recyclability [56]. Since it is a renewable resource, natural rubber is the most frequently used elastomeric component in TPEs. TPEs are generally prepared by blending NR or its derivatives with various types of thermoplastics [57–61].

PET is an engineering plastic and is widely used as an engineering thermoplastic: often in packaging, electronics, and other applications [62]. One drawback of this plastic is its sensitivity to notch formation, which causes brittle failure at room temperature. One of the methods for overcoming this problem is blending this plastic with an elastomer [4,13,63,64]. However, this plastic is incompatible with most rubbers [65,66]. Therefore, a simple blend of PET with synthetic rubber (SR) will result in low mechanical properties. This is due to the phase separation of the two polymers, which is the result of their incompatibility. Therefore, an increase in the compatibility of the two polymers, by adding the third component (grafting agent), is practicable, which will result in better mechanical properties. Usually, the method in use involves the grafting of rubber with MAH in order to build chemical links between the rubber and PET. The synthetic rubbers available in the literature include styrene-butadiene rubber (SBR) and acrylonitrile-butadiene-styrene (ABS).

### 5.3.1 Preparation of PET/SR Blends

PET/SR blends are technologically very important because they can be processed as thermoplastics; this is their main advantage when compared with cross-linked

elastomers. They can be remelted or devitrified and reshaped. Hence, they are generally prepared by extrusion and injection molding, which are the most common processing methods used in thermoplastics. Several factors including viscosity or rheology of the two-phase polymer, temperature at which the hard phase can be processed, thermal stability since the complex structures will, potentially, have several weak chemical links, thermal conductivity since the hard phase is surrounded by a soft phase, crystallinity in the hard phase that must be melted with excess enthalpy, and moisture that may cause hydrolysis at the processing temperatures, must be taken into account during the processing of TPEs.

#### 5.3.1.1 Preparation of PET/Styrene-Butadiene Rubber (SBR) Blend

*Grafting of SBR*: Usually, SBR is dried at 80°C for 6 h and then fed into an internal mixer at 160°C. After 4 min, MAH is added and after 1 min, benzyl peroxide (BPO) is added to the mixture. The roller speed can be set at 50 rpm with a total mixing time of about 10 min. Different formulations at different rubber concentrations, PET-SBR*g* and PET-SBR, can be made. The extent of the MAH-SBR reaction can be determined by a titration method. This can be done through the dissolution of 1 g of grafted rubber in 100 mL of toluene and refluxing at 65°C for 3 h. Subsequently, 50 mL of water is added and three different phases: (1) an organic phase containing SBR grafted with MAH, (2) an aqueous phase containing unreacted MAH, and (3) a gel consisting of cross-linked rubber can be formed. The organic phase is separated and titrated with KOH solution in ethanol with 0.1 N thymol blue as an indicator. An excess of 0.5 mL of KOH is added to the solution (the color changes from yellow to blue) and it will be re-titrated with HCl (until the color changes to yellow). The acid number and the percentage of MAH that reacted are calculated according to the following relations:

$$\text{Acid number (mg of KOH/g of rubber)} = \frac{\text{mL of KOH} \times \text{NKOH} \times 56.1}{1\,\text{g of rubber}}$$

$$\text{Reacted MAH}(\%) = \frac{(\text{Acid number}) \times 98\,\text{g of rubber}}{2 \times 561\,\text{g of MAH}}$$

where rubber is the SBR used in the sample formulation. The measurements of MAH grafting reaction efficiency through titration are well known [67–69]. Some of the extracted organic phases before titration are placed in a watch glass and then transferred to an oven for 10 min at 100°C where thin films are formed [70].

*Blending procedure*: According to Jazani and Azar [70], a PET bottle was collected, ground, washed, and then dried for 12 h at 110°C. Depending on the formulations chosen, blends can be prepared with an internal mixer at a speed of 50 rpm at 260°C. The component addition sequence is as follows: PET with Irganox is added and then after 4 min, styrene-butadiene rubber-grafted-maleic anhydride (SBR-*g*-MAH) is added to the system. After 7 min, mixing can be stopped. After the mixing, the ground samples are kept in an oven for 4 h at 120°C. The specimens for tensile and impact tests are injection molded with a mold temperature of 7°C and a feed stage temperature of 260°C.

#### 5.3.1.2 Preparation of PET/Acrylonitrile-Butadiene-Styrene (ABS) Blends

*Grafting of ABS*: According to Nikos et al. [71], ABS (25 g) is dissolved in 100 mL toluene, then degassed and blanketed with an inert gas. To the thermos-stated solution at 90°C, 2.5 g MAH, followed by 0.31 g BPO, were added with continuous stirring. The solution was stirred vigorously for 1.5 h in order to complete the reaction and the product precipitated with constant stirring in excess methanol, washed and finally extracted with methanol in order to remove the unreacted MAH. The product can be dried overnight at 50°C in a vacuum oven. The amount of MAH grafted was determined [72] by titrating a THF solution of ABS-*g*-MAH with a 0.1 N KOH solution with phenolphthalein as an indicator. Analysis gives 3.5 wt% MAH grafted for a 1.5 h reaction time and 4.6 wt% for a 4 h period [71].

*Blending procedure*: Usually, PET was dried in a vacuum oven at 150°C for 12 h, ABS at 60°C for 10 h. Two series of blends were prepared by [71]: PET melt blended with unmodified ABS at 280°C, using a CSI Max Mixing Extruder, Model CS-194 AV at 45 rpm. Compositions are: 95/5, 90/10, 87.5/12.5, 85/15, and 75/25, the first number denoting PET. The other series of blends contained ABS-*g*-MAH with compositions: 95/5, 90/10, 85/15, and 80/20, with an MAH content of 3.5 wt%. The authors studied the types of blends before and after storage for a period of 7 days at ambient temperatures. In order to determine the influence of acrylonitrile (AN) content in ABS, poly(styrene-*co*-acrylonitride) (SAN) having

30 wt% AN was melt-mixed with ABS so that it can increase its AN content to 25 wt%. In order to provide adequate reaction time, blends with ABS-*g*-MAH were prepared in a small glass reactor at 280°C under inert gas with mechanical stirring. Mixing time was 12 min. The authors [71] prepared films for testing by compression molding between Teflon sheets at 275°C and 50 kg/cm$^{-2}$ pressure, followed by pressure release and quenching to 0°C.

## 5.3.2 Properties of PET/SR Blends

The blending of polymers is a topic that is broadly investigated because of the low cost, excellent properties, and benefits that may be obtained in blends. Unfortunately, most polymers are thermodynamically incompatible. When they are mixed, the free energy, $\Delta G_m$, of the system is positive, which leads to a phase separation manifested as a reduction of the blend properties when compared to those of the polymers alone. The type of synthetic rubbers available in the literature include SBR and ABS and are described in detail. These rubbers are incompatible with PET and consequently the blends of those polymers possess low mechanical properties. The enhancement of mechanical and impact properties requires high miscibility among the different phases. The properties followed here, by the authors [66,73,74], involve materials resulting from the grafting of the SR with MAH in order to build chemical links between SR and PET.

### 5.3.2.1 Influence of Rubber (without Grafting) on PET/SBR Blends

Figure 5.10a and b shows the results of the viscosity variation with the shear rate for PET/SBR blends without grafting with MAH and for several rubber

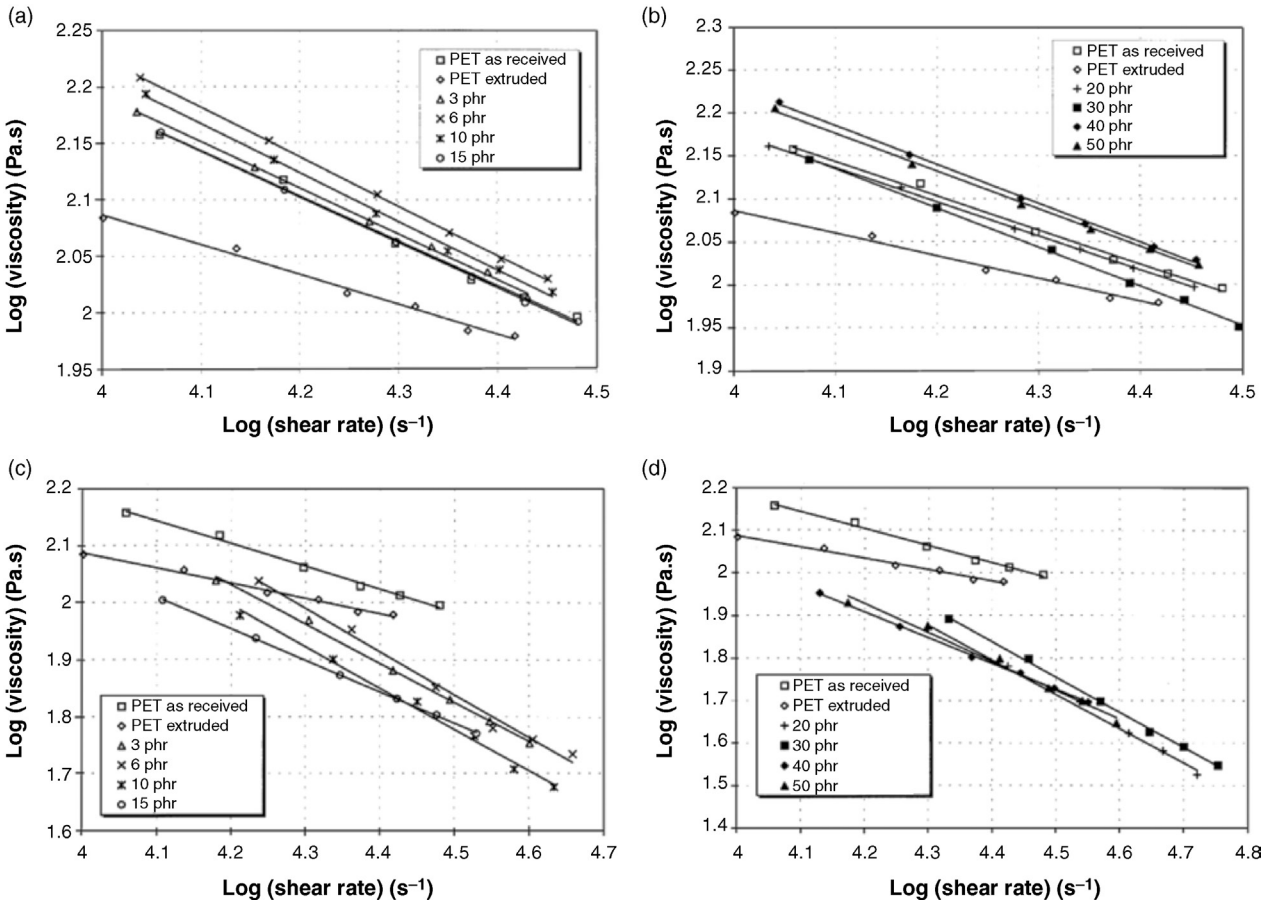


**Figure 5.10** (a) PET–SBR viscosity as a function of shear rate for various SBR contents in the blend (3–15 phr). Blends were prepared at 50 rpm screw rotational speed; (b) same as (a) with SBR contents of 20–50 phr; (c) PET-SBR*g* viscosity as a function of shear rate for various SBR*g* contents in the blend (3–15 phr). Blends were prepared at 50 rpm screw rotational speed with an MAH content of 2 phr and (d) same as (a) with SBR*g* contents of between 20 phr and 50 phr [66].

concentrations. In Figure 5.10a, rubber contents lie in the range 3–15 phr, whereas in Figure 5.10b, rubber concentration varies from 20 phr to 50 phr. The viscosity of PET alone was determined, either by using the polymer as received or in samples already extruded just once. As observed, the PET online viscosity presents a substantial decrease, due to the thermomechanical degradation at the processing conditions [75]. It is important to note that the viscosity variation with shear rate, in the physical blends, is such that the viscosity curves lie above the PET curve. The rubber particles infused an increasing resistance to flow, as observed in polymer-filler systems [76]. From these results, the authors observed a low degree of dispersion of the rubber particles in the matrix, with presumably, high coalescence that formed agglomerates.

#### 5.3.2.2 Influence of Grafting Rubber on PET/SBR Blends

The blend of PET and SBR grafted with MAH groups (PET-*g*-SBR) possesses lower viscosity than the physically blended PET/SBR, as shown in Figure 5.10c and d, for low and high rubber contents, respectively. Blends were prepared at an extrusion speed of 50 rpm with an MAH content of 2 phr. As the rubber amount increases (from 3 phr to 20 phr) the viscosity diminishes gradually, down to the highest concentrations (30–50 phr), where it levels off. MAH grafting provides polar groups, which are also reactive groups that may induce an alcoholysis reaction with the terminal hydroxyl groups of PET, producing the corresponding copolyester PET-*g*-SBR. MAH grafting may produce a better interfacial adhesion of the rubber to the PET matrix and simultaneously inhibits coalescence, resulting in an improved dispersion. The effect of reduced coalescence is combined with the breakage of agglomerates due to high-shear stresses, which leads to an overall decrease in the blend viscosity, similar to the effect of processing aids [77].

#### 5.3.2.3 Influence of MAH Concentration on the Rheological Properties

In Figure 5.10c and d, the results of the viscosity are presented, considering a fixed MAH concentration of 2 phr. However, it is important to analyze the effect of the amount of grafting on the overall blend viscosity. It may be such that increasing the amount of graft will provide better particle dispersion and coalescence inhibition. The effect of varying the MAH concentration used in the SBR grafting process, for a fixed rubber concentration (10 phr), is shown in Figure 5.11a and b. The interfacial effect of the grafted groups is clearly shown, as the viscosity is plotted as a function of the shear rate (Figure 5.11a) and as a function of the MAH content (Figure 5.11b). In Figure 5.11a, the first group of curves, corresponding to 0.5, 1.0, and 1.5 phr MAH concentrations, lies above the PET viscosity curve, while the second group has larger MAH concentrations (2–3.5 phr) and lower viscosity than that of PET. In order to illustrate the variation of viscosity with MAH concentration for a given shear rate, data from Figure 5.11a are plotted in a different form in Figure 5.11b, where some points have been interpolated and extrapolated, without changing the qualitative trends of the results. A steep drop in viscosity is observed between 1 phr and 2 phr of MAH, becoming lower than the viscosity of PET alone, for most of the shear rates. The MAH concentration used in the grafting reaction is proportional to the percentage of MAH grafted in the unsaturated butadiene chain. According to Sánchez-Solís et al. [66], the lower viscosity may be the result of better dispersion with inhibited coalescence, induced by the effect of the grafted groups on SBR, which begins at a critical concentration of MAH; this is for concentrations larger than 2%. It is precisely at this concentration that the impact strength attains a maximum.

To illustrate quantitatively the effect of the grafted groups on the viscosity of the blends, Figure 5.11c shows the viscosity plot against the number of MAH molecules grafted per SBR molecule, calculated from the knowledge of the rubber molecular weight, rubber proportion in SBR, and percentage of grafting. From their finding [66], it can be summarized that a small number of grafted molecules of MAH in the polybutadiene chain, produces a large effect on the rheological properties of the resulting PET/SBR blend.

#### 5.3.2.4 Morphology of PET/SBR Blends

The synthesis and characterization of micro- and nanomaterials have received great attention and have become a leading edge in materials science and technology. Functional micro- and nanomaterials endow us with the possibility to develop devices with distinguished performance in electronics, magnetics, optics, and photonics. In addition to the composition, the size and shape are two other important factors that determine the properties of functional materials. Some important functional materials are characterized by

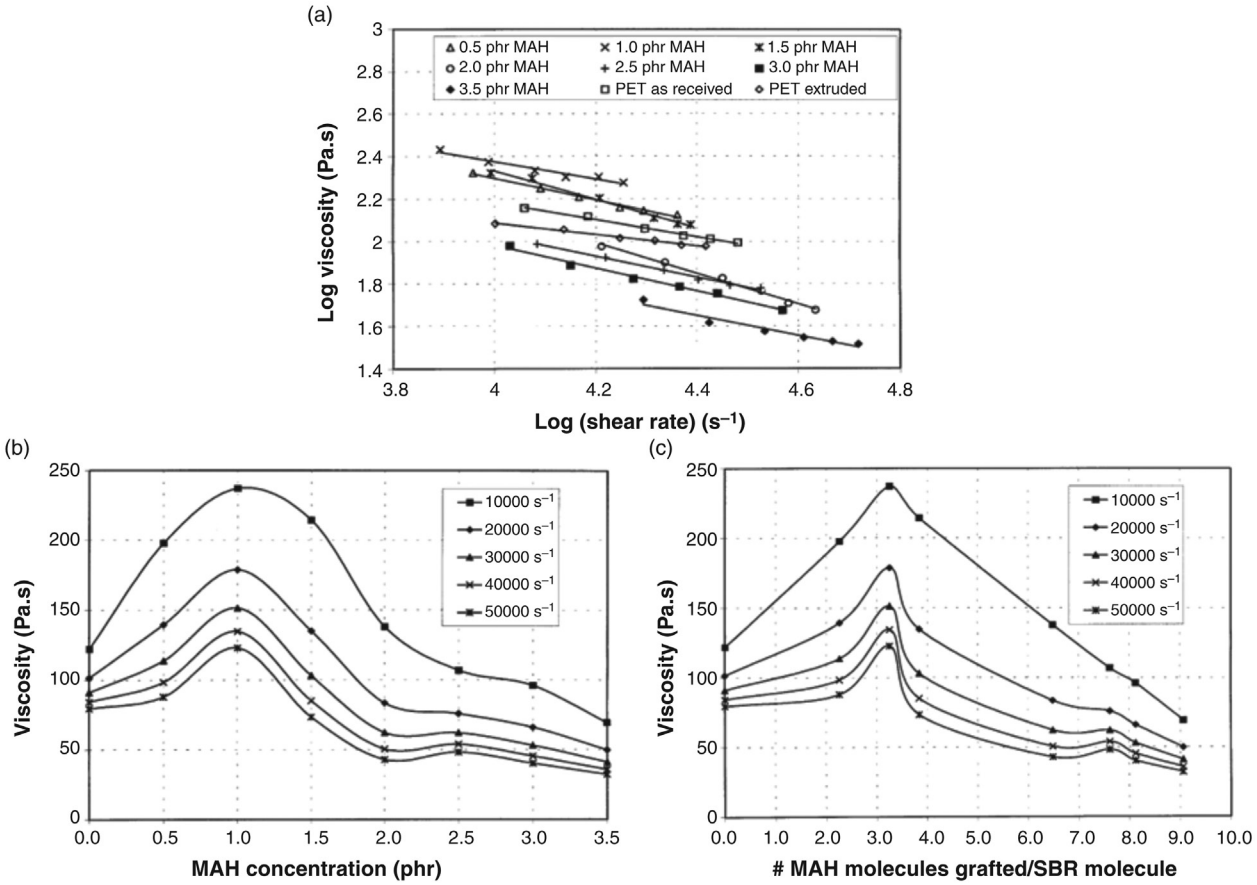


**Figure 5.11** (a) Viscosity of PET–SBR*g* blends as a function of shear rate. Concentration of SBR*g* is 10 phr. Blends were prepared considering several MAH contents at 50 rpm extruder screw speed; (b) viscosity of PET–SBR*g* blends as a function of the amount of MAH used in the preparation of the blends, for various shear rates. Concentration of SBR*g* is 10 phr. Screw rotational speed is 50 rpm and (c) viscosity of PET–SBR*g* blends as a function of the amount of MAH molecules grafted per SBR molecule [66].

SEM. The SEM images of the various PET/ABS blends are shown in Figure 5.12 and depending on the formulations chosen, blends are shown in Table 5.1.

Figure 5.12 shows the micrographs for formulations (K2–K5). According to the authors [73], SBR droplets appear as large holes, which is common in uncompatibilized polymer blends. Therefore, SBR has been maleated (modified with MAH as compatibilizer) in order to achieve a high level of interface, which leads to higher impact resistance. In formulation K3, although the droplets are stretched and some are big, the effect of compatibilization of PET and SBR was more obvious than for formulation K2. Subsequently, in formulation K4, the authors recorded a good dispersion of SBR droplets. The results in formulation K5 were the same as the former (K4), but the droplets were slightly larger. The results show the role of compatibilizer in increasing the interfacial adhesion [73].

### 5.3.2.5 Morphology of PET/ABS Blends

ABS is a tough, nonpolar, thermoplastic styrenic polymer with good mechanical properties; however, it lacks oil resistance and high heat deflection temperature, which a polar, semicrystalline polyester, PET, has. A blend of ABS/PET can not only offer a range of very useful properties, but also presents a scientific challenge associated with the potential coexistence of four discrete phases in the solid state arising from the potential of combination of chemical polarity, crystallinity, and toughening process. However, after the development of the blends, morphology is a key factor that affects the total physical-mechanical properties of the blends. Figure 5.13 illustrates the SEM micrographs of the different blends, having different amounts of ABS (or ABS-*g*-MAH). According to the composition, the dispersed domains are related to the ABS particles, etched with THF. As expected, with ABS content increasing from 5 phr to

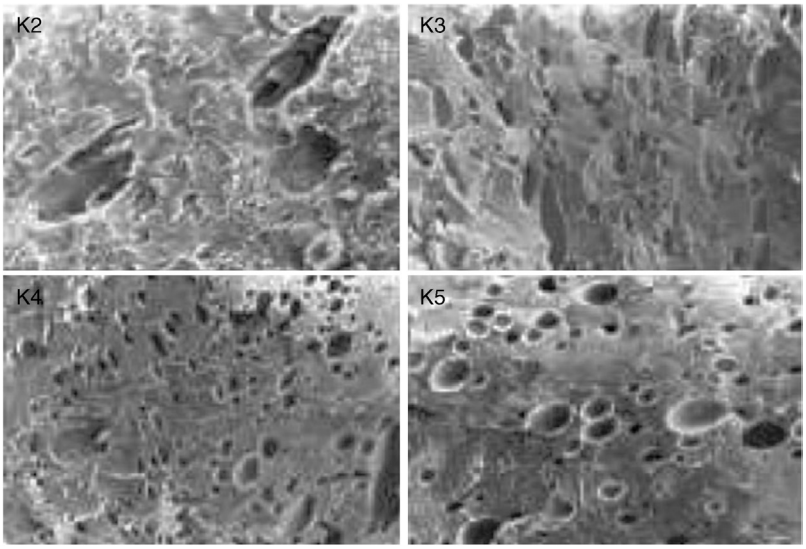


**Figure 5.12** SEM illustration for K2, K3, K4, and K5 formulation [73].

**Table 5.1** Formulations Used in Blending [73]

| Code | Formulation | PET (phr) | SBR-*g*-MAH (phr) | Irganox (phr) |
|---|---|---|---|---|
| K1 | PETW50 | 100 | 0 | 0.1 |
| K2 | PETWSBRP | 100 | 15 | 0.1 |
| K3 | PETWSBRd2 | 100 | 15 (1.5 phr MAH) | 0.1 |
| K4 | PETWSBRd3 | 100 | 15 (2 phr MAH) | 0.1 |
| K5 | PETWSBRd4 | 100 | 15 (2.5 phr MAH) | 0.1 |

30 phr, the number of domains clearly increases. In both compositions, introducing ABS-*g*-MAH into the blend causes a decrease in the dispersed particle size. As depicted in Figure 5.13, the average particle size decreases from 7.2 μm to 1.7, μm when using grafted ABS and from 8.3 μm to 3.5 μm for ABS contents of 30 and 5 phr, respectively. This may be due to the strong interaction between the two phases, caused by the successful compatibilization process; the same effect was also observed by other researchers [70,78,79] in the presence of compatibilizer. In compatibilized PET/ABS-*g*-MAH blends, reduction of interfacial tension may occur through the formation of a graft copolymer in a reaction between the carboxyl groups of MAH and the hydroxyl groups of PET [71,80]. From the SEM micrographs, the effect of grafting is more evident in the blend with higher ABS content. This result may be due to the greater possibility of copolymer formation in the presence of large amounts of ABS-*g*-MAH. Lashgari et al. [74] also reported on the particle size distribution. As mentioned earlier, incorporating MAH causes the particle size to reduce dramatically from 7.2 μm to 1.7 μm. On the other hand, the compatibilized PET/ABS-*g*-MAH blend has a better uniform particle size distribution (<4 μm) than the uncompatibilized blend (2–20 μm). Therefore, it can be concluded that using ABS-*g*-MAH is an effective method of producing compatibilized PET/ABS blends.

### 5.3.2.6 Influence of Fracture Behavior on Mechanical Properties of PET/ABS Blends

Figure 5.14 depicts the stress/strain behavior of ABS2/PET blends. In all cases, ductile behavior is observed and as the wt% PET is increased, the yield stress, modulus, and breaking strain increased. However, Cook et al. [81] further reported on the relationship between the flexural yield stress and modulus, as functions of composition with variation of ABS concentrations. The modulus of the PET/ABS blends depends on the amount of ABS concentrations. When

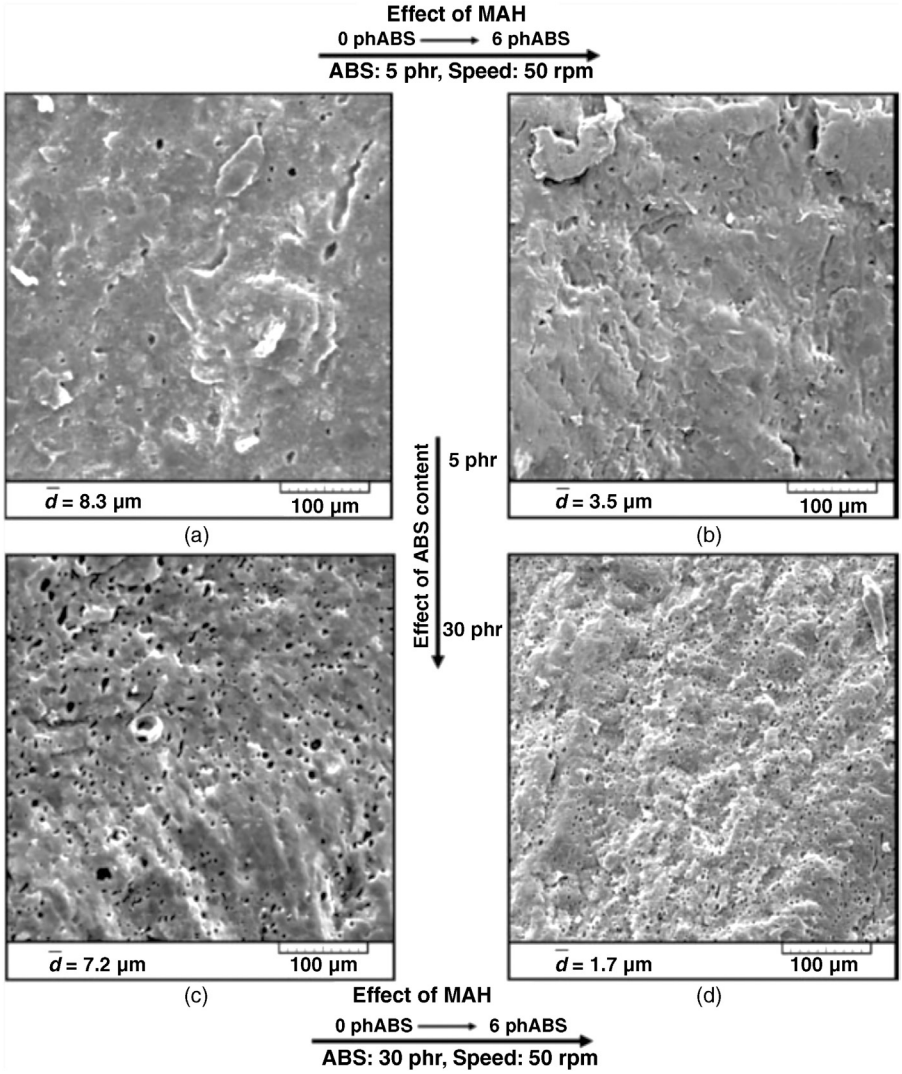


**Figure 5.13** SEM micrographs of PET/ABS blends: (a) PET/ABS (95:5 phr); (b) PET/ABS*g* (95:5 phr); (c) PET/ABS (70:30 phr) and (d) PET/ABS*g* (70:30 phr) [74].

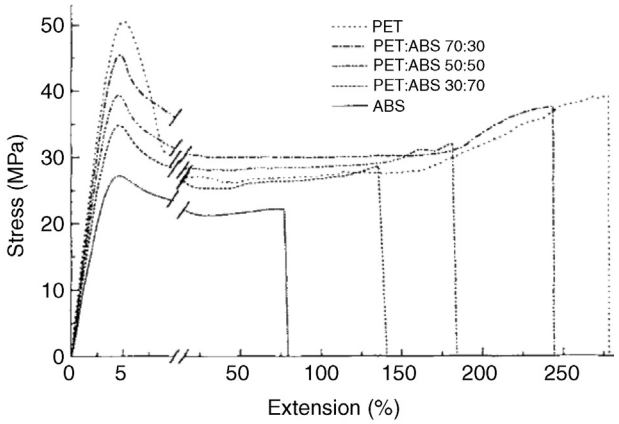


**Figure 5.14** Tensile stress (nominal) versus percentage elongation for: 0/100, 30/70, 50/50, 70/30, and 100/0 wt% blends of ABS2/PET [81].

the ABS content increased, there was an increase in the PET/ABS blends' modulus, which enhances the flexibility of the ABS component. The higher concentration of rubbery particles in ABS also appears to enhance yielding by reducing the triaxiality of the stress state in the matrix that surrounds the rubber particles. The tensile yield stress was approximately 63% of the flexural yield stress [81], which is close to the theoretical factor of 2/3. The yield stress and modulus are almost linear functions of the composition, as reported by Lombardo et a1. [82], Suarez et al. [83], and Wu et al. [84] for ABS/PC blends. According to Kolarik [85], immiscible polymer blends with high interfacial strength exhibit simple additivity of the yield stress, suggesting that the ABS/PET system exhibits some miscibility at the interface.

#### 5.3.2.7 Influence of ABS Content on Mechanical Properties of PET/ABS Blends

Lashgari et al. [74] reported that the PET/ABS blends with high ABS content have higher impact resistance, thus attesting to the good impact property of ABS. On the other hand, the impact strength of the blends increases with MAH content, a finding that suggests that using grafted ABS, instead of neat ABS, enhances the impact strength through the compatibilizing process, because of the bond formation between functional groups of PET and ABS-*g*-MAH. Furthermore, the average size of the dispersed particles reduces when the MAH content increases, hence their performance as stress dispersant can be more effective. On the other hand, the strong interfacial adhesion that formed easily, transfers the stress field from the PET matrix to the dispersed phase. Therefore, the impact strength rises as the MAH concentration increases [79,86].

According to [74], increasing the rotor speed results in the improvement of impact strength of the blend. This observation can be explained in terms of the Wu equation [80], which estimates the size of the dispersed phase in the blend. As mentioned earlier, ABS has a shear thinning nature, while PET shows a Newtonian behavior. With increasing rotor speed, the viscosity of ABS falls down rapidly, whereas the viscosity of PET remains relatively constant.

#### 5.3.2.8 Thermal Properties of PET/ABS Blends

DSC analysis of ABS, PET, ABS/PET (70/30), and ABS/PET/SMA (styrene maleic anhydride) (64/30/6) blends was reported by [87]. According to their studies, the melting curves of the ABS/PET and ABS/PET/SMA blends show the characteristics of PET, such as the glass transition temperature ($T_g$) and melting point ($T_m$) that are still retained. They reported the fact that there was not a clear shift of the $T_g$ near 80°C of the amorphous PET phase, but in the ABS/PET and ABS/PET/SMA blends there was an exotherm near 112°C, which indicated the $T_g$ near 105°C of ABS was overlapped with a PET recrystallization exotherm [81] near 130°C. They concluded that when SMA was added, the melting peak area of PET in the ABS/PET/SMA blend was lower than that of the ABS/PET blend. This means that the crystallinity of PET in the ABS/PET/SMA system decreased. It is believed that SMA inevitably interfered with the crystallization process because the PET-*g*-SMA copolymer hindered the process of crystallization and crystal growth. Another interesting phenomenon highlighted is that there was no crystallization peak of PET in the crystallization curves of the ABS/PET and ABS/PET/SMA blends, which meant that not only SMA but also ABS had an effect on the crystallization behavior of PET. This was mainly because both of them hindered the movement of the macromolecular chains of PET with a decrease in the crystallization rate. Such effect has been reported by Hage et al. for PBT/ABS blends [88].

### 5.3.3 Applications

Application possibilities of PET/SR blends are broad and varied. It has been shown that epoxy-containing polymers are probably the best candidates as reactive compatibilizers for PET-related blends due to the fast reactions between epoxy and carboxylic acid or hydroxyl groups. However, noting the significant morphological and mechanical differences, rubbers are used as toughening agents for PET. In particular, good results can be obtained by using an ethylene–ethyl acrylate–glycidyl methacrylate copolymer. The resulting blend can display good particle distribution and the latter can be related to the chemical interactions between the rubber epoxy groups and PET terminal groups, including the effect of low molecular weight and polymeric amine catalysts, to the extrusion conditions. Furthermore, blends of PET and ABS terpolymer are not uncommon with the latter being used as an impact modifier for thermoplastic, such as polyvinylchloride, polycarbonate, and polyamide 6. Optimizing the chemical polarity, crystallinity, and toughness of these materials during blendings, poses a major scientific challenge. PET/ABS has substantial commercial significance and can replace the expensive polymer blends commonly used in industrial applications. Although improvements of PET toughness under quasistatic and impact loading rates can be achieved by blending with rubber, however, one of the major drawbacks is the loss in tensile strength and stiffness. Like most polymers, the incorporation of short glass fibers into the PET matrix can provide improvements in tensile strength and tensile modulus. It will therefore be of interest to develop short glass fiber-reinforced and rubber-toughened PET blends.

## 5.4 Conclusions

PET-based blends with natural and synthetic rubbers are a very important class of polymer blends with great commercial importance. The selection of rubber type plays an important role in influencing the morphology and the related mechanical properties in rubber blends composed of PET (50 wt%), compatibilizer (30 wt%), and rubber (20 wt%). It has been observed that the incorporation of suitable compatibilizing agents is essential in order to establish an optimal level of interaction between PET and the elastomeric components. The compatibilizing effect of ethylene-glycidyl(meth)acrylate was slightly better than a home-made GMA-grafted ethylene propylene rubber at comparable GMA functionality. The best mechanical performance was established for those thermoplastic elastomers that contained nitrile butadiene rubber of high acrylonitrile content instead of polyolefin rubbers. Toughened PET can be obtained by the addition of NR using a twin-screw extruder. By blending PET with rubber in a suitable manner, materials with high toughness can be produced. The compatibility between rubber and the PET matrix have been observed to play an important role in the resulting blends' behavior. With different rubber types, it has been observed that MAH-grafted MAH-*g*-SEBS rubber is effective in the toughening of PET

This chapter has clearly revealed that the mechanical, thermal, and morphological properties of the PET/rubber blends are influenced by the amount of rubber and processing conditions. High-impact strength values can be obtained without prior chemical modification of the rubber. Solid-state CP/MAS $^{13}C$ NMR spectroscopy revealed that the interaction between PET and rubber occurred though the observation of an increase in cross-polarization time ($T_D$) of the carbonyl carbon and a decrease of $T_{1\rho}^{H}$ relaxation of the carbonyl group in the PET/rubber blend. This comes from the interaction between the carbonyl group of PET with the abnormal groups, such as hydroxyl function in NR, resulting in an improvement of the compatibility of the studied blends, hence increasing the toughness.

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