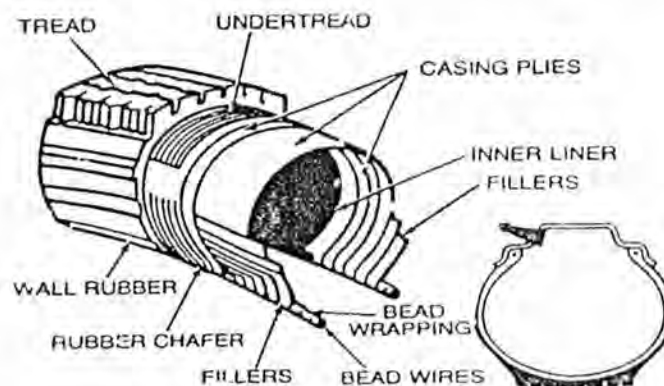


## CHAPTER II

### THEORETICAL BACKGROUND

Polymer blending is a widely practiced method of modifying the properties of polymers. Blends of various polymers, often intended for specific applications, are commercially available [7]. Among them are materials, which combine some of the properties of conventional elastomers and thermoplastics, ranging from so-called thermoplastic elastomer (TPE) [8] to semi-rigid materials such as elastomer-modified polypropylene (PP) [9]. Rubber-toughening process is one of the most successful methods developed for modifying polymer properties even when there is a small reduction in modulus and tensile strength.

Tires are composed of composite materials topped with rubber such as carcass, which is made with chemical cords e.g. polyester, rayon or aramid, and breakers, made of plated steel cords. Other components are made of rubber compounds of natural rubber (NR); styrene-butadiene rubber (SBR) or butadiene rubber (BR) reinforced with carbon black. Figure 2.1 shows the tire construction.



**Figure 2.1** Tire construction [10]

## **2.1 Reclaimed Tire-Rubber (RTR)**

### **2.1.1 Definitions**

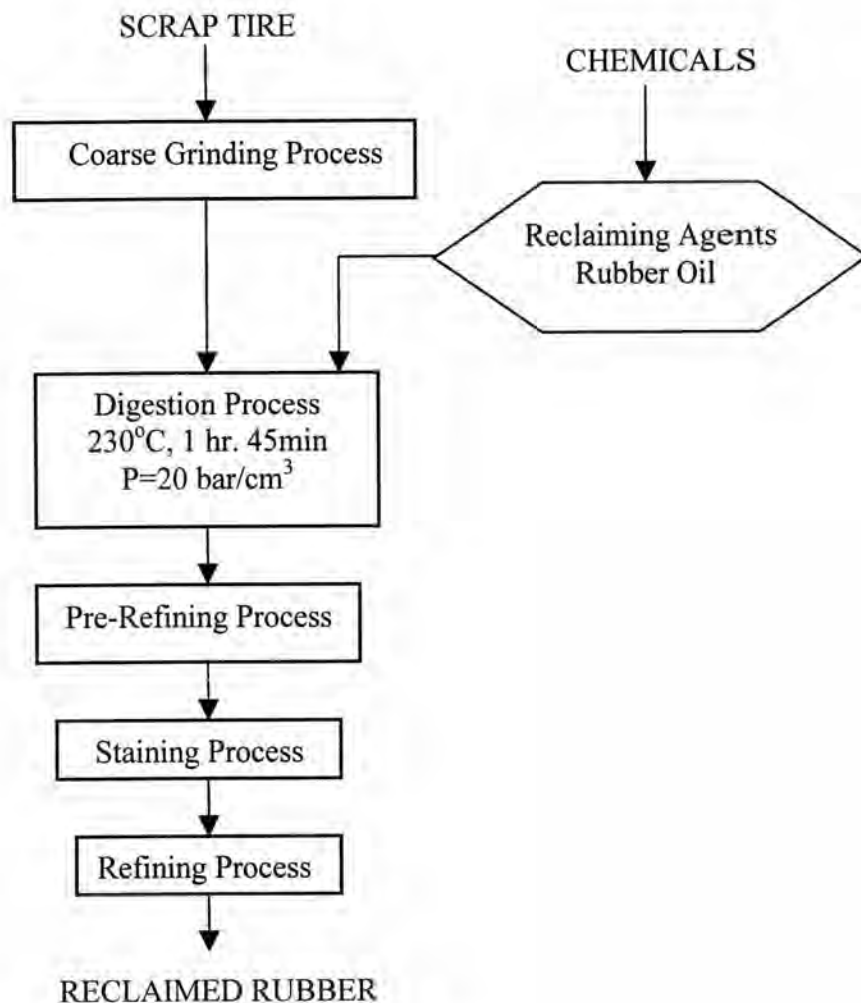
Reclaimed tire-rubber (RTR) is the product resulting when waste vulcanized scrap rubber tire is treated to produce a plastic material, which can be easily processed, compounded and vulcanized with or without the addition of either natural or synthetic rubbers. It is recognized that the vulcanization process is not truly reversible; however, an accepted definition for devulcanization is that it is a change in vulcanized rubber tire, which results in a decreased resistance to deformation at ordinary temperature [11].

### **2.1.2 Reclaimed Rubber Production**

The first stage of any reclaiming process is size reduction of the scrap; this is most generally accomplished using corrugated two-roll cracker mills or rotating cutter. The tire bead wire is either cut from the carcass before grinding or manually removed after the first pass through the cracker. At many points in the system, the ground rubber is passed over magnetic separation equipment to remove remaining bead wire and steel belt wire. Classifier screens return the oversize rubber particles to the cracker for further size reduction. There may be more than one stage of grinding before the desired size of approximately 3/8 inch is obtained. The fiber from the coarse-ground tires is removed by some sort of fluidized-bed. The action of controlled streams of air moving through a bed of ground rubber on an inclined gyrating of special design causes the fiber to separate from the clean rubber. The size of the rubber particles may now be further reduced to perhaps 20 or 30 mesh by fine grinding. The coarse-ground rubber could be conveyed to the digester or processed further for one of the other devulcanization methods[11]. The flow diagram of manufacturing process for reclaimed tire-rubber shows in Figure 2.2.

### 2.1.2.1 Digester Process

A digester is essentially a steam-jacketed, agitator-equipped autoclave mounted either horizontally or vertically. This is a wet process in which the coarsely ground scrap is submerged in a solution of water and reclaiming agents. These agents may include many types of light and/or heavy oils, plasticizer, tackifier and chemical peptizers. Until the advent of synthetic rubber, the digesting solution also included caustic soda to remove free sulfur and to act as a defibering agent. In fact,



**Figure 2.2** Reclaimed rubber production diagram

the process was generally referred to as the *alkali digester method*. After World War II, it was found that scrap rubber containing SBR was totally incompatible with alkali cooks so the industry developed the *neutral process*, in which zinc or calcium chlorides are used as the defibering agents.

Weighed scrap, water, and reclaiming and defibering agents are dumped into the digester and the cook cycle is started. Steam, generally within a range of 150 to 250 psi, is injected into the jacket of the vessel for a digestion period that may be from 5 to 24 hours. During this time, the rubber becomes devulcanized and the fiber becomes hydrolyzed. After digestion, the charge is blown down and washed to remove the decomposed fiber and caustic soda or metallic chloride. The washed, devulcanized rubber particles are conveyed to a dewatering press and then to a dryer. The material is now ready for the final, refining stage of the reclaimed-rubber manufacturing process.

#### **2.1.2.2 Heater or Pan Process**

This is the simplest of all the reclaiming processes. A “heater” is a large, single-shell horizontal pressure vessel or autoclave. The ground rubber is mixed with reclaiming agents in an open ribbon mixer then placed into containers rolled into the vessel. The main consideration is to allow an even penetration of heat in the mass of rubber. To achieve this uniform steam penetration, shallow pans are used as the stock containers. Live steam at pressures of 100 to 250 psi with cycle times of 5 to 12 hours are typical.

This process yields fairly good results with some types of rubber scraps such as butyl inner tubes and marginal quality with other types such as fine-ground tires or low-specific-gravity natural-rubber scrap.

### **2.1.2.3 Reclaimator Process**

The Reclaimator process is the only commercially successful continuous technique for devulcanizing tire scrap; all the others are batch processes. Tires are ground, the metal and fiber are mechanically separated, and then the rubber is further ground to a fine particle size. This fine-ground rubber and the various reclaiming agents are all metered into a blending system and conveyed to the reclaimator.

The reclaimator is a special type of screw-extrusion machine. It is jacketed to provide for several zones of controlled temperature using either hot oil or cooling water; in addition, the clearances between the screw and the chamber wall are close and adjustable. The object is to subject the rubber to a controlled amount of high heat and pressure in a continuously moving environment. The residence time of the rubber in the machine is less than 5 minutes. During this period, the rubber undergoes devulcanization. After the softened rubber is discharged from the head of the machine, it is cooled and further processed in refining mills just as is done in other reclaiming methods.

### **2.1.2.4 Further Advantages of Reclaiming and Applications**

The intense mechanical work and chemical treatment given to the rubber in the reclaiming process results in further properties very beneficial to the end user. Reclaim can be expected to break down in mixing much more quickly than virgin polymers. The reduced mixing time equals more indirect savings in the form of greater productivity-more product using less labor and overhead cost per unit. In addition to the reduced mixing time when using reclaim, studies have shown that there is a sizable reduction in power consumption during mixing.

Reclaim can be used in great many different applications. Where cost is a primary consideration and tensile strength requirements are not particularly demanding, reclaim can be the sole source of polymer. Examples of such products are mats and semipneumatic tires. In other cases, reclaim is blended with virgin synthetic and natural rubber. The virgin polymer adds strength and the reclaim contributes to improved processing, cooler mixing, and less sensitive, less scorchy cure systems. Such applications include most of the constituent parts of both passenger and truck tires, bias and radial-ply.

Formulating with reclaim is not difficult, but the compounder must remember that reclaim, unlike most processing additives that do little to the cure except for dilution, enters into the cure system. The reclaim elastomers become part of the overall crosslinked system. However, it is unrealistic to expect that the optimum cure system used with synthetic and/or natural rubber polymers will remain the same when reclaim is added. The optimum cure system must be reestablished when reclaim is added, just as it should be whenever changes are made to the types or proportions of virgin rubber.

The material, mixing, manpower, and energy-consumption savings associated with reclaimed rubber are a part of the total benefit of its use. These savings are substantial and significant, but there are further positive aspects to the use of reclaim, which accrue to our society as a whole. They include the employment of hundreds of people in the reclaim industry and the alleviation of solid-waste-disposal problems. They also include the conservation of petrochemical raw materials, conservation of the energy required to convert the petrochemicals into synthetic rubber, and conservation of the foreign exchange needed to pay for imported oil, a large proportion of the petrochemicals' source[12].

## 2.2 Blending Method

Polymer blends, in general, have been prepared commercially by melt mixing, solution blending or latex mixing. Elastomer-plastic blends of the type discussed here, containing rather large amounts of plastic, have generally been prepared by melt-mixing techniques. Melt mixing avoids problems of contamination, solvent or water removal, etc. In general, banbury mixers, mixing extruders and the newer twin-screw mixers are suitable for melt-mixing elastomer with plastics. However, for the purposes of this discussion, emphasis will be on laboratory melt-mixing techniques, which simulate what can be done in a factory.

## 2.3 Types of Dynamic Crosslinking in Thermoplastic Elastomer (TPE)

Thermoplastic elastomers (TPE) have many of properties of elastomers, but they are processable as thermoplastics. The best way to produce TPE comprising vulcanized elastomer particles in melt-processable plastic matrix is by the method called dynamic vulcanization. It is the process of vulcanizing the elastomer during its melt-mixing with molten plastic. Dynamic vulcanization is a route to new thermoplastic elastomers which have properties as good or even, in some cases, better than those of block copolymers.

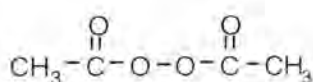
The properties of blend types of thermoplastic elastomers are considerably improved if the rubber is partially crosslinked during blending [13-15]. In certain circumstances, a higher degree of crosslinking may be permissible one series of EPDM/PP blends in which the rubber phase is fully cured can still be processed as a thermoplastic because the crosslinked rubber is dispersed as very small particles in a PP matrix [15]. The presence of crosslinks in the rubber phase enhances its modulus and strength while increasing its resilience. As crosslinking proceeds the viscosity of the rubber phase increases, causing the less viscous thermoplastic to form a continuous phase even at low volume fraction of plastic phase [16]. In the presence of a crosslinking agent, it is expected to improve adhesion between two phases which will lead to better physical properties.

### 2.3.1 Crosslinking with Peroxides [17,18]

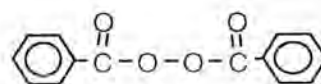
Crosslinking with peroxides has been known for a long time. In the meantime, one has also recognized their action in natural rubber (NR) and the classic diene types of rubber, styrene-butadiene rubber (SBR) and acrylonitrile-butadiene rubber (NBR). Based on the heat stability that can be obtained by peroxide vulcanization of diene rubbers, especially of NBR but also of ethylene-propylene-diene monomers polymer (EPDM), this type of vulcanization has achieved a great importance.

The temperature of decomposition (half-life) of the peroxides is the main determinant for scorch temperature and cure rate. For that reason, the composition of the peroxide determines its usefulness as a vulcanizing agent.

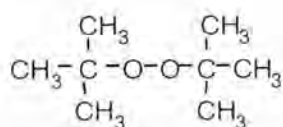
For the crosslinking of rubber, only peroxides can practically be used, which are stable and not dangerous during the usual handling, and that, on the other hand, decompose sufficiently fast at customary curing temperatures. For that purpose, peroxides with tertiary carbon atoms are suitable. Peroxides bonded to primary and secondary carbon atoms are less stable. One can distinguish two groups of organic peroxides that are stable enough for rubber processing.



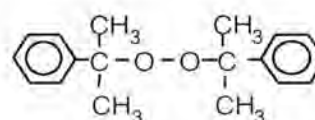
Diacetyl peroxide



Dibenzoyl peroxide



Di-tert butyl peroxide



Dicumyl peroxide

**Scheme 2.1** Types of peroxide with and without carboxy groups



The peroxides in the different classes have the following characteristics:

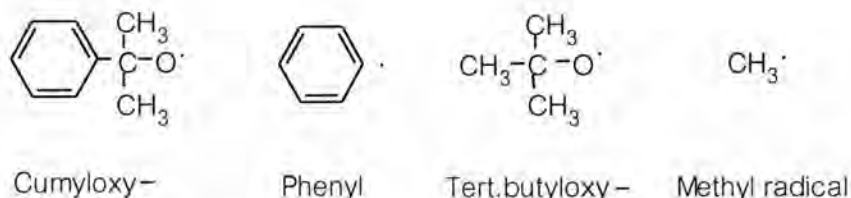
Carboxy group peroxides:

- Low sensitivity to acids
- Low temperature of decomposition
- High sensitivity to oxygen ; therefore, cure problems in the presence of carbon black.

Peroxides without carboxy groups :

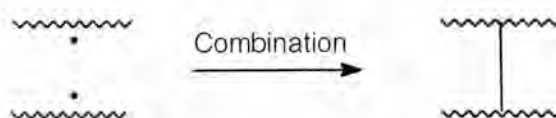
- Sensitivity to acids, aliphatic better than aromatics
- Higher temperature of decomposition.
- Lower sensitivity to oxygen than peroxides with carboxy groups.

For the curing of elastomers those peroxides are preferred that form the following radicals as shown in Scheme 2.2.



**Scheme 2.2** Free-radicals of peroxides

Decomposition of peroxides can occur under the influence of the following factors: by heat, by light or high-energy radiation, or reactions with other materials. The saturated rubbers cannot be crosslinked by sulfur and accelerators. Organic peroxides are necessary for the vulcanization of these rubbers. When the peroxides decompose, free radicals are formed on the polymer chains, and these chains can then combine to form crosslinks, as shown below:



**Figure 2.3** Structural features of peroxide vulcanization

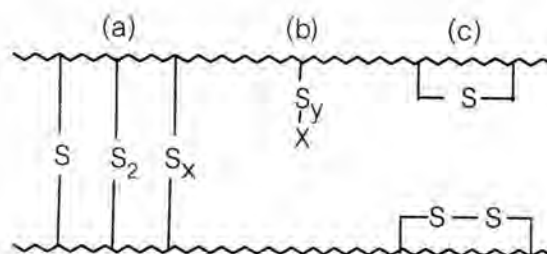
Crosslinks of this type only involve carbon – to – carbon bonds and are quite stable. Gamma radiation and X-ray radiation also form them. A disadvantage of peroxides when used in this manner is that they can initiate oxidation of the polymers. This is manifest as a deterioration of the surface of molded articles after exposure to sunlight and a reduction in their resistance to heat aging. These effects were found to persist in the presence of antioxidants, stabilizers and UV inhibitors.

### **2.3.2 Crosslinking with Sulfur [18,70]**

The most important vulcanization agent for rubber is the so-called vulcanization sulfur. For the preparation of soft rubber goods, dosages of about 0.25-5.0 phr are used. The sulfur quantity used for the preparation of soft rubber differs greatly with the amount of accelerators used and the demand on properties of the vulcanizate. For accelerator free NR compounds, hardly used in today's technology, relatively high sulfur levels are necessary (for example 5 phr). This type of vulcanization leads, aside from polysulfidic sulfur with intermolecular crosslinks, to many side reactions that do not lead to crosslinking (for example intramolecular cyclic structures with high efficiency parameter). In the presence of vulcanization accelerators, these side reactions are suppressed and, depending on activity and amount of accelerator used, the average number of sulfur atoms per crosslink is decreased. For that reason less sulfur is used with increasing amount of accelerator.

Because the high accelerator content leads to a more effective use of the sulfur and thus to shorter sulfur links as well as to a reduction of that amount of sulfur which is not used for crosslinking. When the amount of sulfur is reduced even further, the use of accelerators, which are at the same time sulfur donors (e.g. TMTD), is called for. For example, when 2.5-3.5 phr TMTD are used, vulcanization takes place with only very small amounts of sulfur (e.g. 0.2 phr) or even in the absence of all elemental sulfurs.

Sulfur is combined in the vulcanization network in a number of ways (Fig. 2.4), as enumerated by Porter (1969). As crosslinks, it may be present as monosulfide, disulfide, or polysulfide (Fig.2.4a), but it may also be present as pendent sulfides (Fig.2.4b), or cyclic monosulfide and disulfides (Fig.2.4c). An estimate of the number of sulfur atoms for each crosslink formed has been made :



**Figure 2.4** Structural features of vulcanizate network

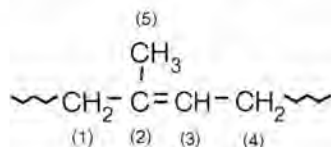
an unaccelerated rubber – sulfur vulcanizate may give a figure of 40-45, whilst in conventional accelerated sulfur vulcanizates this “inefficiency” figure may drop to 10-15. Special “efficient” vulcanizing systems can reduce it still further to 4 or 5, but for even lower values, so-called “non-sulfur” vulcanizing systems must be used (Section 2.3.3)

The initial step in vulcanization seems to be the reaction of sulfur with the zinc salt of the accelerator to give zinc perthio-salt  $\text{XS}_x\text{ZnS}_x\text{X}$ , where X is a group derived from the accelerator (e.g. thiocarbamate or benzthiazyl groups). These salts react with the rubber hydrocarbon RH to give a rubber bound intermediate



and perthio-accelerator groups, which, with further zinc oxide will form a zinc perthio-salt of, lower sulfur content; this may, nevertheless again be an active sulfurating agent, forming intermediates  $\text{XS}_{x-1}\text{R}$ . In this way each molecule of accelerator gives rise to a series of intermediates of varying degrees of polysulphidity. The hydrogen atom which is removed is likely to be attached to a

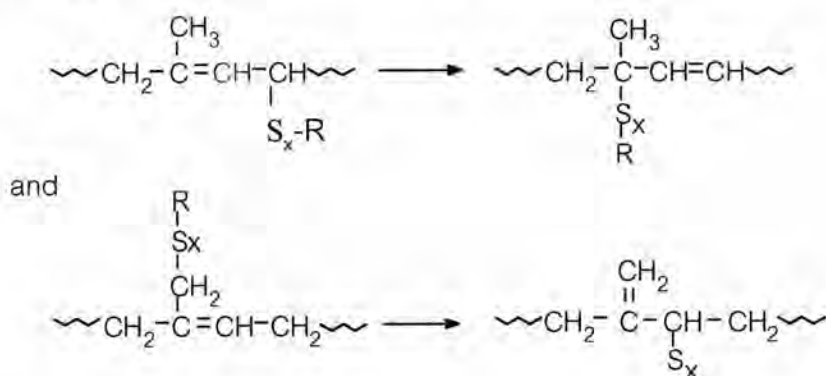
methylene group in the  $\alpha$ -position to the double bond, i.e. in natural rubber the hydrogen atoms at positions 4 and 5 are the most labile in this type of reaction.



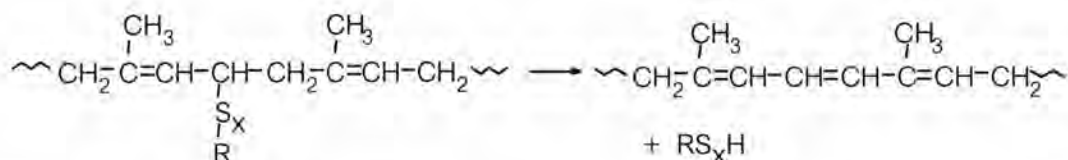
The intermediate  $\text{XS}_x\text{R}$  then reacts with a molecule of rubber hydrocarbon  $\text{RH}$  to give a crosslink and more accelerators is regenerated:



Even this is not the whole story, for, on further heating, the degree of polysulphidity of the crosslinks declines. This process is catalysed by  $\text{XS}_x\text{ZnS}_x\text{X}$  and can result in additional crosslinks. It is also evident that the crosslinks, which were initially at positions 4 and 5, undergo an allylic shift, with the result that new configurations appear:



At the same time, disappearance of crosslinks of the disulfide and polysulfide type occurs, with formation of conjugated trienes:

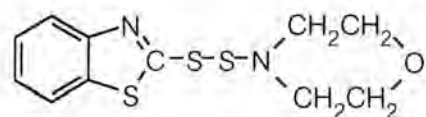


This destruction of crosslinks is apparently associated with the formation of the cyclic sulfides (Fig.2.4c), but this has not been investigated in detail.

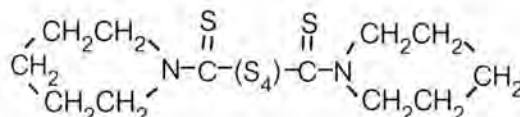
### 2.3.3 Crosslinking with Sulfur Donors [18]

Sulfur donors are the compound that contain sulfur can also be liberated sulfur at the vulcanization temperature; subdivided into those that exhibit an accelerator activity and can be substituted directly for sulfur, without drastic change of the vulcanization characteristics, and those that are simultaneously vulcanization accelerators.

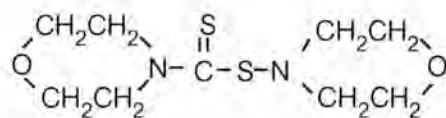
For sulfur donors that are at the same time vulcanization accelerators, the vulcanization system has to be properly modified, thus, for example, 2-morpholino-dithio-benzothiazole (MBSS), dipentamethylene thiuramtetrasulfide (DPTT), N-oxydiethylene dithiocarbamyl-N-oxydiethylene sulfenamide (OTOS) as well as tetramethyl thiuramdisulfide (TMTD), whose main function is the of an accelerator.



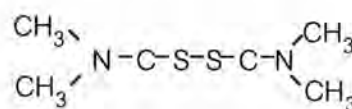
MBSS, MW:284, active sulfur 11.3mol%\*



DPTT, MW:384, active sulfur 16.6%\*\*



OTOS, MW:248, active sulfur 12.9%\*



TMTD, MW240, active sulfur 13.3%\*

\* Refers to one available sulfur atom (monosulfidic structure)

\*\* Refers to two available sulfur atom (disulfide structure)

**Scheme 2.3** Types of vulcanization accelerators

MBSS and TMTD have only two sulfur atoms that can be activated for crosslinking and can lead to mono- or disulfidic bonds. In comparison, OTOS contains only one sulfur atom, that can be activated and therefore its use in EV-systems leads strictly to monosulfidic crosslinks.

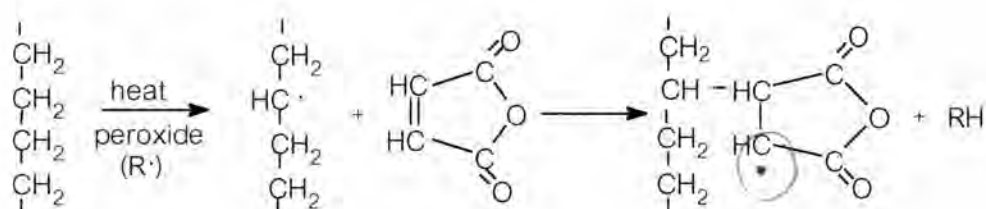
In such low sulfur systems the application of sulfur donors is essential, where TMTD plays the most important role as accelerator and sulfur donor. A sulfur substitution by using TMTD or other accelerators with sulfur donating capacities cannot be accomplished without a complete change of the vulcanization characteristics. Practically, this means that completely different vulcanization systems are required as the sulfur content is lowered. The amount of sulfur donors required to replace the elemental sulfur is in relation to the existing sulfur/accelerator ratios.

TMTD was used as the sulfur donor and the system was made suitable for dynamic crosslinking by including zinc oxide, stearic acid and 3-mercapto-benzothiazole (MBT), the latter to prevent premature reaction. It has to be decomposed into the corresponding dithiocarbamates to begin their own activity. Therefore, the onset of vulcanization is slower than with the corresponding dithiocarbamates.

The TMTD reacts with the zinc oxide to give some tetramethyl thiuram polysulfide, which reacts with the rubber, and more zinc oxide to give a rubber – bound intermediate compound containing a polysulfide group. This then reacts with more rubber and zinc oxide to form a vulcanized rubber with polysulfide crosslinks, which, as cure proceeds, give mainly monosulfide crosslinks. The remainders of the intermediate compound forms zinc diethyl dithiocarbamate, which is always found in the vulcanisate, although never in more than about 65% of the theoretical yield:



the unsaturation in the base polymer for reaction sites and does not require an initiator. Accordingly, some remaining unsaturation may be desirable in the hydrogenated butadiene based polymers to obtain MA attachment by this reaction to the polymer. Whereas, saturated hydrocarbon polymers can also be functionalized with MA by exposing the polymer to sufficiently high temperatures or the use of organic peroxides to form polymeric free radicals which will result in the addition of MA to the polymer chain by the scheme shown in Scheme 2.5.



**Scheme 2.5** Maleic anhydride reaction with saturated hydrocarbon polymers.

The amount of MA modified polymer can be determined by oxygen analysis [19], IR spectroscopy [20,21] or a titration method [20,21]. And MA modified polymers have been used as an impact modifier or compatibiliser in several types of immiscible blend.

## 2.5 Rubber Toughening Mechanisms

Toughening is a very important property for many applications of materials. There are two categories of toughening mechanisms in dispersed systems: the energy is absorbed mainly by formation of craze at the rubber particles or the energy is absorbed through shear yielding between the modifier particles. Therefore mechanism of deformation can be classified to be due to the following effects, energy absorption



by rubber particles, matrix crazing, shear yielding or a combination of shear yielding and crazing.

### **2.5.1 Energy Absorption by Rubber Particles [22]**

Merz, Claver and Baer [23] proposed the idea of rubber particles absorbing energy for the toughening mechanism of toughened polymers. They observed that in high-impact polystyrene (HIPS) an increase in volume and stress whitening accompanied elongation of the material and concluded that these phenomena were associated with the formation of many microcracks. It was suggested that the fibrils of styrene-butadiene copolymer bridged across the fracture surface of a developing crack and in so doing prevented the crack growing to a catastrophic size. This resulted in more energy being absorbed than an equivalent volume of the polystyrene matrix. The amount of energy absorbed in impact was attributed to the sum of the energy to fracture the glassy matrix and the work to break the rubber particles. More recently Kunz-Douglass, Beaumont and Ashby [24,25] have proposed a similar mechanism for rubber modified epoxies in which the elastic energy stored in the rubber particles during stretching is dissipated irreversibly when the particles rupture.

However, the main disadvantage of these proposed theories is that then is concerned primarily with the rubber rather than with the matrix. It has been calculated [26] that the total amount of energy associated with the deformation of the rubbery phase accounts for no more than a small fraction of the observed enhanced impact energies. Consequently, this mechanism plays only a minor role in the toughening of multiphase polymers. Further toughening theories concentrated on the deformation mechanism associated with the matrix, which are enhanced by the presence of the rubber phase.

### 2.5.2 Matrix Crazing

Crazing is a more localised form of yielding and occurs in planes normal to the tensile stress. Crazes grow by macroscopic internal drawing of materials from the craze walls to increase the fibril length. A craze consists of polymer microfibrils (0.6 to 30 nm in diameter) stretched in the direction of tensile deformation. The microfibrils are surrounded by void space, which can represent as much as 90% of the total volume of the craze. Figure 2.5 reveals the cross section of a craze showing its discontinuous structure and expanded volume. The craze consists of highly drawn treads of polymer associated with empty space. This means that the craze occupies roughly double the volume of the undrawn polymer and it achieves this by doubling only one dimension. When plastic materials fail principally by crazing, the impact modifier must initiate a large amount of crazing, the same modifier must then also terminate the crazes.



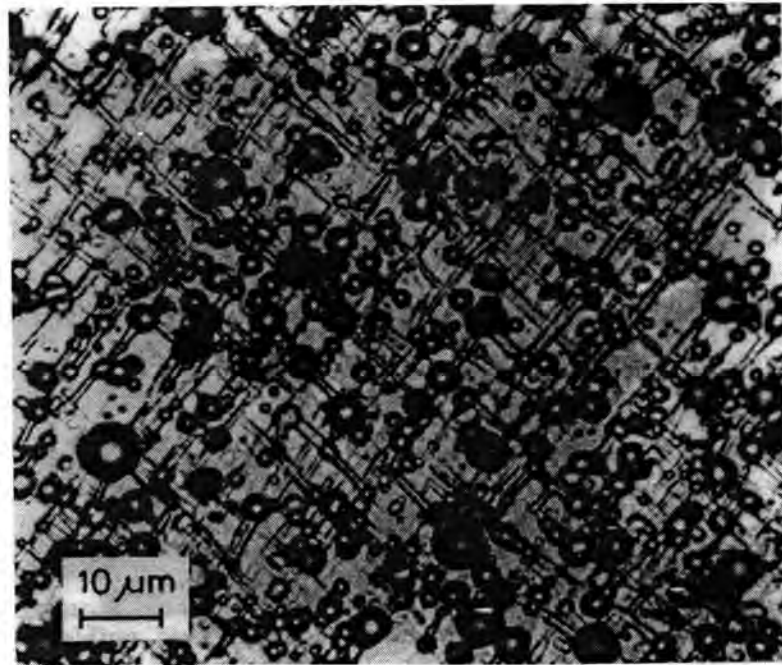
**Figure 2.5** An example of craze fibrils [27]

If it does not terminate the crazes a critically large void could form that would lead to formation of a crack and hence failure. The ability of an impact modifier to initiate and terminate crazes is related to the size of its particles where they are distributed in polymer matrix. Colyer A.A. [22] has reported that particles larger than 1  $\mu\text{m}$  are capable of controlling craze growth as a result of their ability to initiate and terminate crazes while smaller particles are not only poor craze terminators but also poor initiators in which system of HIPS.

### 2.5.3 Shear Yielding

Shear yielding in the matrix phase also plays a major role in the mechanism of rubber toughening in polymer blends; shear yielding involves macroscopic drawing of material without a change in volume. The polymer will form regions of localised shear deformation, shear bands, which develop at angle of  $45^\circ$  to the stretch direction. In general, shear band formation is a dominant mode of deformation during tensile yielding of ductile polymers. An example of shear banding is shown in Figure 2.6, a host of shear bands developed in conjunction with rubber particles. As before, the rubber particles provide stress field perturbations, but the rubber by itself adds an extra feature, compression of the matrix. Shear yielding usually occurs in addition to elastic deformation. Not only does this phenomena act as an energy absorbing process but the shear bands also present a barrier to the propagation of crazes and hence crack growth, therefore delaying failure of the material.

Although cavitation of the rubber particles does involve energy absorption, the enhanced shear yielding of the matrix is the major energy absorbing mechanism. However, cavitation of the rubber particles is a prerequisite for enhanced toughness where shear yielding is the principal mechanism.



**Figure 2.6** An example of shear banding [74]

#### **2.5.4 Crazeing and Shear Yielding**

Crazeing and Shear Yielding may occur simultaneously in many rubber toughened plastic. The dominant mechanism is the one by which the unmodified matrix would typically fail. However, the contribution of each mechanism to the toughening of the system depends on a number of variables such as the rubber particle size and dispersion, the concentration of the rubber particles and the rate and temperature of the test. The contribution of each mechanism to the toughening process can be assessed to some extent by using tensile dilatometry. It is assumed that deformations such as voiding and crazeing are dilatational processes, which manifest themselves by an increase in volume strain. Unfortunately, if both voiding and crazeing occur simultaneously, it is impossible to separate their contributions to

volume strain. However, when shear yielding occurs, a decrease in the volume strain rate occurs since shear yielding is a non-dilational or constant volume process.

## **2.6 Parameters Affecting the Toughening**

The rubber particles act as stress concentrators in rubber toughened plastics. Therefore the impact properties and tensile properties are significantly dependent on the parameters of the rubber.

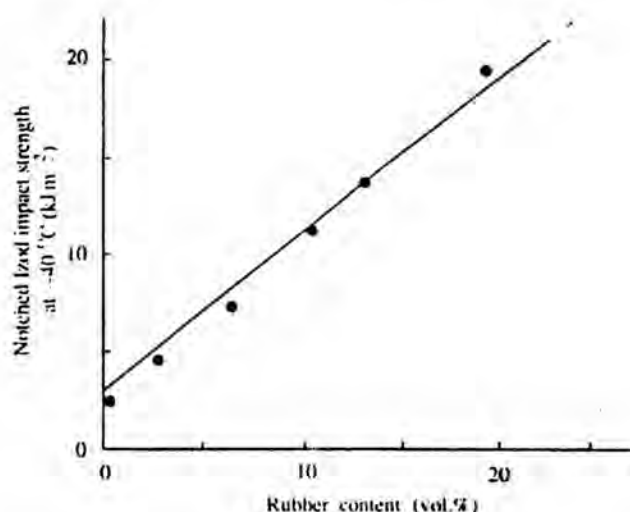
### **2.6.1 Rubber Type**

The effect of the rubber is difficult to evaluate as it depends on the mechanism by which toughening is believed to occur, be it as a stress concentrator to initiate crazes or shear bands or to alleviate local hydrostatic stresses by cavitation. When the modulus difference between the rubber and matrix,  $G_R/G_M > 0.1$  where  $G_R$  and  $G_M$  are the shear moduli of the rubber and matrix respectively, the stress concentration at the particle-matrix interface occurred, there will be improvement in toughening [28]. The modulus difference will cause the concentration of stress around the particles, leading to a nucleation of crazes or shear bands [29].

### **2.6.2 Loading of Rubber**

The percent loading of the rubber was the main factor that affected mechanical properties of the blends. Increasing the loading of the rubber phase decreases the blend modulus and tensile strength irrespective of whether the matrix is brittle or pseudo-ductile. The main findings are that up to 30% rubber the  $T_g$  values of the two phases are unaffected by rubber concentration in PA6-EPDM

blends, but the brittle-bough transition temperature  $T_{BT}$  is reduced as the loading of rubber is increased [30]. The variation of notched Izod impact strength with rubber content as shows in Figure 2.7. The relationship is linear up to 30% EPDM in PA6, but higher rubber loading show a marked decrease in impact strength [31].

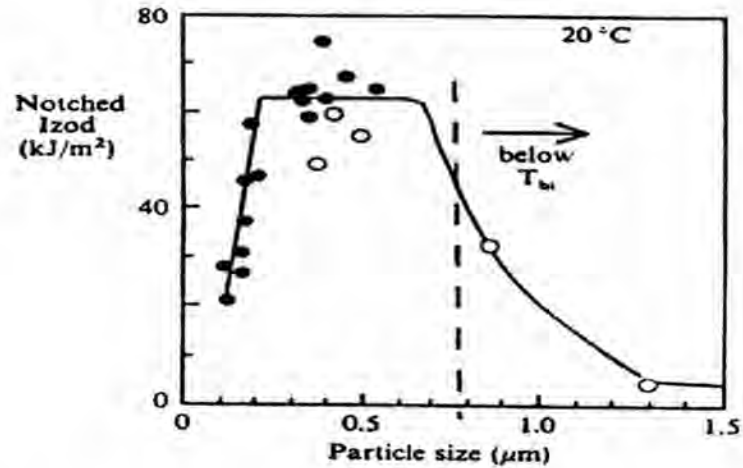


**Figure 2.7** Notch-Izod impact strength at  $-40^{\circ}\text{C}$  vs volume fraction of EPDM in PA6. Particle size and interfacial adhesion are constant.

### 2.6.3 Particle Size and Distribution of Rubber

The particle size and distribution of the dispersed phase significantly influences the deformation and failure properties of heterogeneous blends. The rubbery phase can act as an effective stress concentration and enhances both crazing and shear yielding in the matrix when highly dispersed. Ultimately the optimization of the size distribution of the dispersed phase depends on identifying the preferred deformation mechanism of the matrix polymer. A crazing mechanism is better suited to a higher particle size than a shear yielding mechanism. Generally, for the rubber to be effective the particle size has to be small ( $0.1\text{-}2\ \mu\text{m}$ ). Very small particle sizes

are not effective. The impact strength as function of particle size are shown in Figure 2.8



**Figure 2.8** Impact strength of PA6-EP blends as a function of particle size (26 vol.% EP rubber; 20°C) the different symbols refer to different manufacturing methods [32]

There is a lower limit at about 0.1 μm and upper limit at about 1 μm. The reason for this might be that the material with very fine particles mainly consists of an interphase layer and no neat nylon or rubber is present any longer.

#### 2.6.4 Rubber-Matrix Adhesion

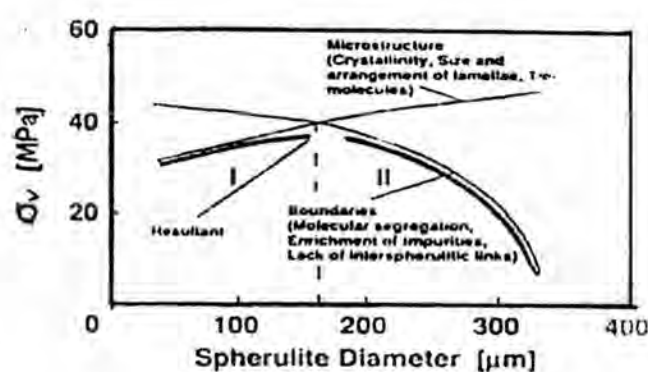
When the bond between the rubber and the matrix is weak to make the craze termination mechanism also fails. Instead of stabilizing the craze, a weakly bonded rubber particle is pulled away from the matrix, leaving a hole from which the craze can propagate further, and from which breakdown of the craze to form a crack is probable. When there is good adhesion between the rubber and the surrounding matrix, fracture surfaces reveal rubber particles that have fractured into halves along the equatorial plane.

### 2.6.5 Matrix Types

If the molecular weight of the matrix is higher the melt viscosity increases and a fine dispersion is obtained more easily. The high molecular weight has also the advantage that the number of entanglements per chain is higher. In this way the material is more resistant to craze formation and a somewhat higher impact strength can be expected.

## 2.7 Crystallization Behavior

It is generally accepted that crystalline polymers have superior impact properties to amorphous ones, This is due to the crystallisation behavior of the polymers. Nevertheless, in the literature one can find lots of papers claiming a toughness deterioration with increasing crystallinity [33]. On the other hand, Karger-Kocsis J. [34] assumed that the toughness of semicrystalline polymer goes through a maximum in function of crystallinity as depicted in Figure 2.9.



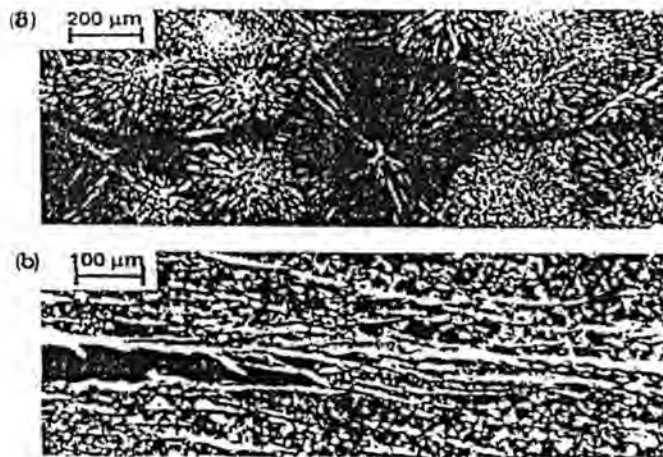
**Figure 2.9** Effect of microstructure and boundaries of crystalline polymers as function of spherulite diameter [34]



### 2.7.1 Crystallisation of Polypropylene

Polypropylene is a semi-crystalline polymer. Its properties are determined by its crystalline structure and the relative amount of amorphous and crystalline phases, crystal modification, size and perfection of crystallites, dimensions of spherulites and the number of tie molecule [34]. The crystalline phase of polymers consists of thin plates or ribbons with the chains oriented along the thin dimension. The amorphous region consists of chain-end cilia, totally occluded chains, and chains which are incorporated into two or more crystals (tie chains). The tie chains determine the mechanical continuity of the system and thereby control the elastic modulus as well as yield strength.

The higher crystallinity of the PP with coarse spherulitic structure leads to a larger volume contraction and thus to formation of voids and microcracks. Consequently, the crack path tends to follow the weak spherulite boundaries, resulting in a very low fracture toughness value as shown in Figure 2.10.



**Figure 2.10** Fracture toughness of PP as a function of spherulite size  
(a) Coarse spherulitic, (b) Fine spherulitic morphology [34]

In general, it is believed that the spherulitic nucleation takes place at heterogeneities in the melt such as catalyst residues, dust particles, low-molecular-weight fractions, branch points, stereo-irregular molecules, fillers or specific nucleating agents. The spherulite size is primarily dictated by the volumetric nucleation rate, which depends on thermal history, nature of the surface and degree of undercooling. The amount of crystallinity and spherulite size influences the modulus and strength of PP [34]. Spherulite size and spherulite boundaries significantly influence the yield and failure behavior of polymers. These effects are manifested in the macroscopic nature of the fracture path. The fine spherulitic microstructure produced by adding nucleating agents gives rise to greatly enhanced ductility, yield strength, and impact strength. In general, refinement of the spherulite size by either homogeneous or heterogeneous nucleation or by reducing the crystallisation temperature results in improved ductility and strength. It is clear that large spherulites exhibit cracks at spherulite boundaries, whereas systems with smaller spherulites draw smoothly.

### **2.7.2 Crystallisation of Polypropylene Blends**

The binary crystalline polymer blends and alloys may be categorized in terms of crystalline / crystalline systems, wherein both the component polymers are crystallising, and crystalline / amorphous systems, wherein only one of the components is crystallising. The critical factors governing the extent and direction of change in the rate of crystallization and morphology of a polymer in a blend include miscibility, the glass transition, and melting temperatures of the constituent polymers, their relative melt viscosities, chemical compatibility, inherent crystallisability and phase morphology [35]

The crystallization of a polymer in a blend takes place under conditions different from those involved in its crystallization from those involved in its crystallization from the virgin melt. The physical state of the second component and

the temperature range of crystallisation are determined by considerations such as the difference in the melting points of the component polymers, their glass transition temperatures and miscibility. Depending on the differences in the melting points and the inherent crystallisability, a polymer may crystallise either concurrently with the other component, in the presence of the solidified second component, or in the presence of the melt of the second component [35]. Thus, in LLDPE/HDPE blends, concurrent crystallization of the two components is feasible since their melting points are close and the temperature range of crystallisation are overlapping. However, in PP/PVDF blends, although the melting points of the two polymers are comparable, PVDF will crystallize first in the presence of supercooled PP melt owing to its higher crystallisability; thus PP would crystallise in the presence of solidified PVDF. The presence of a second component either in the molten or solid state affects both nucleation and crystal growth of the crystallising polymer. The effect of blending on the overall crystallisation rate is the net combined effects on nucleation and growth. In general, the presence of the second component physically hinders the transport of the crystallising polymer molecules, thereby adversely affecting crystal growth. The extent of the adverse effect is governed by the blend composition, the relative melt viscosities of the component polymers, and miscibility. The effect of blending on nucleation is more subtle and complex, particularly in the presence of the melt of the second component. However, in the presence of the molten second component, factors such as miscibility, relative viscosity, and inherent crystallisability all influence the formation of critical size nuclei.

In the case of immiscible blends the addition of a second noncrystallising polymer results in significant changes in the spherulitic morphology. The effect of the second phase on the overall rate of crystallisation was found to be either positive or negative depending on the conditions of crystallisation, composition, molecular structure and the molecular weight of the noncrystallising component. The incorporation of one or more diluents in a crystallisable polymer may lead to the following modifications in its crystallisation behavior;

- noeffect on crystallisation rate or morphology,
- retardation of crystallisation with or without change in morphology,
- prevention of crystallisation at high loading,
- acceleration of crystallisation with or without morphological change,
- crystallisation of normally noncrystallising polymer as a result of induced mobility.

## 2.8 Literature Reviews

Pramanik, et al. [35] investigated the impact properties of the thermoplastic composites, LLDPE containing ground rubber tire (GRT) of average mesh sizes 40 (GRT 40) and 80 (GRT 80). The different compatibilizers such as epoxydized natural rubber (ENR), ethylene-co-acrylic acid copolymer (EAA) were added to improve the impact strength of the composites. The impact energies or ductilities of some composites are found to increase with the increase in the ENR content. A combination of the maleic anhydride (MA) and dicumyl peroxide (DCP) shows a significant increase in impact strength along with an increase in the melt viscosity of the composites. The improvement in impact properties is believed to occur as a result of several competing mechanisms, interaction of a compatibilizer at the plastic/rubber interface through the improved surface activity of GRT particles. In other cases, matrix crosslinking appears dominant.

Mennig, et al. [36] studied the properties of the composite which blending between polypropylene and hot grinding of scrap rubber (at 30-70 °C) derived from truck tires by dynamic vulcanization. The best mechanical properties; tensile strength, elongation at break, impact resistant were found when sulfur and cumyl peroxide were used as components of the crosslinking system.

Oliphant, et al. [37] investigated some of mechanical properties of cryogenically ground rubber tires (CGT) / linear low-density polyethylene (LLDPE) and high density polyethylene (HDPE). A blend of 40 wt% EAA (ethylene – acrylic acid copolymer) coated CGT particles with LLDPE is shown to have impact and tensile strengths that are 90% of those for the pure LLDPE, representing increases of 60 and 20%, respectively, over blends with uncoated particles. LLDPE/ground tire bladders demonstrate that even better mechanical properties can be obtained with similar large rubber particle size but somewhat better adhesion. HDPE is shown that with large rubber particles, moderate adhesion is not sufficient to produce useful composites.

Lee Keun Yoon, et al. [38] studied the effect of peroxide (1,3 – bis (t- butyl peroxy) benzene) and coagent (trimethylolpropanetriacrylate; TMPTA) content in terms of melt index (MI), melt viscosity, morphology, thermal, and mechanical properties on the reactive extrusion blending of polypropylene (PP) / natural rubber (90/10). At a constant content of the coagent, melt viscosity increased at a low and decreased at a high content of the peroxide. On the other hand, melt viscosity increased monotonically with the coagent concentration at constant peroxide content. The increase and decrease of viscosity were interpreted in terms of crosslinking and chain scission of PP, which governed the rubber domain size and mechanical properties of the reactive blends.

Choudhury, et al. [39] investigated the compatibilization of ground rubber tire (GRT)/low-density polyethylene (LDPE) blend. Chlorinated polyethylene (CPE) was chosen as compatibilizer. All the compatibilized blends showed improved mechanical properties, such as tensile, elongation and impact over the control 70:30 GRT–LDPE blend. The compatibilizer had better adhesion with the plastic and rubber phases. The melt flow index (MFI) decreased approximately with the concentration of compatibilizer for all the ternary blends, indicating better adhesion of CPE with the component phases.

Phadke, et al. [40] investigated the influence of cryo-ground rubber (CGR) on melt flow and mechanical properties of polypropylene. CGR was incorporated in the PP matrix (a) in powder form and (b) as masterbatch with natural rubber (NR), dispersing agent. CGR in the powder form shows poor adhesion to PP matrix and, therefore, decreases the impact strength at higher loading. Addition of masterbatch of CGR and NR improves the impact strength of PP.

Michel, et al. [41] studied the reactive blending of 10-60 wt% ground scrap rubber with linear low-density polyethylene (LLDPE). Prior to blending the rubber phase and the LLDPE phase were modified with small amounts of chemical functionality capable of interacting in the melt blending process. Impact and tensile properties of these reactive blends were compared with simple mechanical melt blends of similar compositions. All blends, whether reactive or unreactive, showed a decrease in overall mechanical properties at all proportions of rubber phase content, but the former exhibited impact and tensile strength improvements of up to 58 and 47%, respectively, over the latter.

Rajalingam, et al. [42] studied the melt blending of LLDPE/different ground rubber tire (GRT) which used a coupling agent (IB'E', ethylene glycidyl methacrylate copolymer). The effects of the GRT particle size, particle sizes distribution and shape, the mode of grinding, and the oxygen surface concentration was analyzed. The wet-ambient-GRT based composites show higher surface oxidation and give better impact energy than cryo-ground and normal air-GRT based composites. Smaller GRT particle size results in a small increases in the impact property of the composite and a greater influence on the melt processability of the composites. Of the different GRT surface modification techniques studied for improved composite interfacial adhesion and impact properties the composites from electron beam radiation treated GRT yield higher increases in impact energy in comparison to corona and plasma treated GRT based composites.

Tuchman, et al. [43] blended untreated crumb from the cryogenic grinding of tires with polystyrene. The impact strength increased with increasing crumb particle size, this being attributed to greater crack deviation. And found that grafting even a small amount of plastic to the surface of the crumb led to greater impact strength.

Arroyo, et al. [44] investigated the crystallization kinetics and tensile behavior of EPDM / PP blends. The results have shown that PP / EPDM blends are immiscible in the melt, and, at low EPDM percentages in the blend (<25%), the particles of EPDM act as nucleating agents and co-crystallize with PP. However, at higher percentages, the EPDM obstructs the mobility of PP chains and hence decreases the PP crystallization rate.

Naderi, et al. [45] studied the effects of the compositions and dynamic vulcanization of the blending on the physical and mechanical properties. Polypropylene (PP) was modified with dimethylol-phenolic resin and then it was melt-mixed with acrylonitrile-butadiene rubber (NBR) for several weight ratios. After sufficient mixing time additional phenolic resin was added to mixing chamber and the blend were dynamically vulcanized. The results show that dynamically vulcanized blends have higher tensile strength, elongation at break, solvent and oil resistance.

Nomura, et al. [46] studied the relationship between the morphology and impact strength for the blends of PP with two kinds of ethylene-propylene (EPR) having different propylene contents. The PP / EPR blend with less than 30 wt% EPR have the PP matrix-domain structure, whereas those with more than 40 wt% EPR have the interpenetrating co-continuous structure produced by the liquid-liquid phase separation process resulting from the spinodal decomposition. The blends of PP/EPR having a high propylene content resulted in the thickening of the interfacial region between PP domain and EPR one, because this EPR has good compatibility to

PP. This thickening of the interfacial region caused the enhancement of impact strength.

Jang B.Z. [47,48,49] reported that the deformation mechanism of impact toughened polypropylene depended very sensitively on strain rate and temperature. High temperature and low strain rate favored shear yielding, whereas low temperature and high strain rate favored crazing.

Jacocy P., et al. [50] have produced different levels of the  $\beta$  - form PP by adding a small amount of a quinacridone dye nucleating agent. They reported that PP which contains high levels of the  $\beta$ -form exhibits lower values of the modulus and yield stress, but higher values of the impact strength and elongation at break.

Tjong S.C., et al. [51] have conducted a preliminary study on the impact behavior of such high  $\beta$  - form material. They also confirmed that the  $\beta$ -form sample exhibits a much higher Izod impact strength than that of an  $\alpha$ -form sample. The above behavior is related to a difference in the spherulitic morphologies between the  $\alpha$ - and  $\beta$ -crystallites. The  $\beta$ - spherulite exhibits a sheaf-like structure, whereas the  $\alpha$ -spherulite consists of an aggregate of lamellae growing and braching from a central nucleus. The greater impact toughness observed in the  $\beta$ - form PP specimen is due to the larger energy dissipation, which is associated with the formation of microfibrils.