

CHAPTER II

THEORETICAL BACKGROUND

2.1 Material Background

2.1.1 Rubber weight by tire component

A tire is manufactured and assembled from several separate components, such as tread, innerliner, beads, belts, etc. Table 2.1 shows which components account for the rubber used in tire making.

Table 2.1 Percentage by weight of rubber in a new radial passenger tire.

Type of components	%
Tread	32.6%
Base	1.7%
Sidewall	21.9%
Bead apex	5.0%
Bead insulation	1.2%
Fabric insulation	11.8%
Insulation of steel cord	9.5%
Inner liner	12.4%
Under cushion	3.9%
Total	100.0%

2.1.2 Reclaimed tire rubber

Reclaimed rubber is normally made from crumb rubber. The most common rubber reclaiming process can be described as follows:

1. Crumb rubber is mixed with water, oil, and chemicals which are expected to devulcanize the rubber.
2. The mixture is heated under pressure.
3. The resulting partially-devulcanized rubber could be formed into slabs or bales and shipped to manufacturers who then process and vulcanize the received material with virgin rubber or plastic resin.

Compared to crumb rubber, reclaimed rubber loses its elastic properties during the reclaim process. The material was capable of forming molecular cross-links with the matrix material. Although, the material did not behave identically to virgin rubber, reclaimed rubber was expected to have more extensive usage than crumb rubber, especially for rubber products. The greatest obstacle for the reclaiming industry was the extensive use of synthetic polymers in the manufacture of new tires. Modern tire compounds contain approximately five different kinds of synthetic rubber and other various chemicals for different cross-linking methods. The traditional reclaiming technique based on the thermal decomposition of carbon-carbon and carbon-sulfur linkages was not always effective with these current synthetic materials. In addition, the tire materials are required to achieve higher performance under extreme conditions. The amount of reclaimed rubber used by the tire industry was approximately 1-2 % of the raw materials. Because of these reasons, the reclaim rubber industry had declined, with fine crumb rubber replacing the material as cheaper supplemental filler. Some studies and trials for developing a new type of reclaimed rubber have been made. The basic concept was more closely related to surface modification of the crumb rubber. The finely-ground rubber (mechanical grinding preferred) was treated with a liquid polymer in order to form cross-links with the base matrix. It was reported that reclaimed rubber had superior bonding properties and imparted extended usage to rubber products. This reclaimed rubber could penetrate the markets of crumb rubber; provide that there was a clear cost advantage.

2.1.3 Types of devulcanization technologies

Methods of devulcanizing elastomers (or rubber) have been researched almost since the time of the discovery of the rubber/sulfur vulcanizing process by Charles

Goodyear in 1839[2]. Many papers have been published on subjects related to devulcanization. Additionally, a number of patents have been issued on topics concerning devulcanization processes. This section describes the results of a review of the status of research and development performed in the area of devulcanization. Devulcanization has been reviewed for different types of elastomers. The purpose of this analysis was to describe the development of devulcanization processes in general and to relate these developments to the potential for devulcanizing waste tire rubber. Waste tires were composed of a number of different constituents, including vulcanized natural and synthetic rubber compounds, steel, fiber, and other materials. The status of devulcanization must also be measured against the potential uses of devulcanized waste tire rubber and the ability of the devulcanization processes to achieve yields and quality of rubber necessary to make devulcanization feasible.

The process of devulcanizing waste rubber can be broken down into two sequential steps. The first (or pre-processing) step is size reduction. The waste is reduced in size so that it can be fed into the system that actually performs most, if not all, of the chemical bond breaking. The second step is the devulcanization process, or the breaking of the chemical bonds which are primarily the sulfur bonds. The output product from the process is a devulcanized rubber. Devulcanization system suppliers may supply only the devulcanization process itself, or in combination with a size reduction process.

2.1.3.1 Pre-processing of feedstock (Step 1)

Regardless of the specific type of devulcanization technology (biological, ultrasonic, etc.), devulcanization systems in general are composed of several subsystems. Nonetheless all devulcanization technologies share a need for a finely sized, vulcanized rubber feedstock. This is because the chemical, thermal, or biological conversion subsystems accept only finely sized feedstock for devulcanization. Additionally, finely sized feedstock provides substantial surface area for devulcanization reactions to take place. Consequently, the developers of devulcanization technologies either assume that their operation will procure appropriately sized feedstock from a third party or they must include size reduction equipment as part of their overall devulcanization system. Generally, a typically

desired particle size of feedstock for the devulcanization process is in the order of 10 to 30 mesh. However, there are exceptions to this generality, as will be discussed later. There are three primary commercial methods of grinding waste rubber:

1. Ambient grinding.
2. Cryogenic grinding.
3. Wet-ambient grinding.

Generally, several stages of size reduction are used to prepare waste tires or vulcanized scrap rubber for devulcanization. The first stage of size reduction typically reduces the rubber feedstock to a nominal particle size of 1- to 2-inch. When processing waste tires, a magnetic separator and a fiber separator are subsequently used to remove the steel and fiber constituents i.e. contamination. The resulting clean, primary-grind product is then further reduced in size using an ambient ground mill, or ground into fine particles while frozen using cryogenic grinding. One method for producing fine-mesh rubber is cooling scrap tires in liquid nitrogen, and then pulverizing the brittle material in a high-speed hammer mill. The ground rubber has a fine particle size, typically in the range of 30 to 100 meshes. Another method of producing finely sized rubber is ambient mechanical size reduction using a high-powered rubber mill set at close nip. This method commonly produces 10- to 30-mesh material. Multiple grinder passes can be used to further reduce the particle size. Wet or solution process grinding can also be used to produce rubber particle size distributions in the range of 200 to 500 meshes.

Grinding processes for tire rubber are well developed. They are widely used for recycling of tire rubbers and rubber wastes. Also, industrial machines are available for breakup and separation of rubber from steel, cord, and fabrics that are present in tires. High industrial rates for production of tire rubber crumbs have been achieved. However waste tire size reduction comes with high energy requirements. This is a significant issue if finely-sized rubber feedstock is needed, as is diminution of rubber properties due to heat generation during size reduction.

2.1.3.2 Devulcanization Processes (Step 2)

2.1.3.2.1 Chemical

Chemical agents have been used to devulcanize scrap rubber since the 1960s. One of early research was performed by the Malaysian Rubber Producers Research Association (MRPRA). Initial studies on low molecular mass compounds paved the way for other researchers to investigate the action of chemical probes. Further studies have been carried out to ascertain which specific bonds, were being cleaved by the chemical processes. Most chemical devulcanization processes are batch processes that involve mixing size-reduced rubber particles and chemical reactants in a temperature and pressure controlled mixer. In general, rubber is fed into a mixer with a devulcanizing agent and then heated. In the case of abandoned technology of the mid-1990s, namely, the De-Link Recycling System promoted by STI-K Polymers, the recommended ratio of chemical agent to a finely sized (for example, 40 mesh) rubber feedstock was approximately 2 to 6 parts by weight chemical to 100 parts rubber. Once the design reaction time has elapsed, the contents are then rinsed, filtered, and dried to remove any remaining unwanted chemical components. The product can then be bagged or otherwise processed for resale. A flow diagram of the process is given in Figure 2.1.

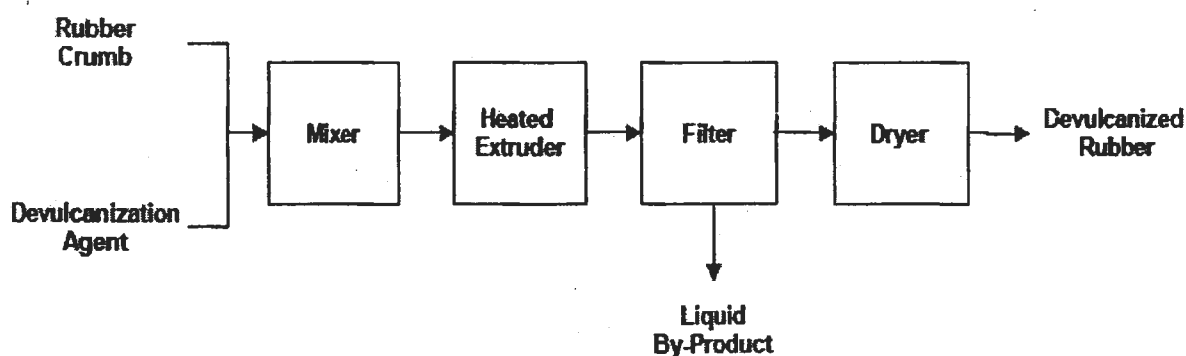


Figure 2.1 Schematic diagram of a chemical devulcanization system

Various chemical agents have been used in the chemical devulcanization processes developed over the years. The agents included petroleum-based solvents

(for example, toluene), thiol amine reagents, hydroxide, disulfide compounds, or chlorinated hydrocarbons. With some chemical agents, a catalyst was also used to promote the desired reactions. The following two chemical devulcanization processes are indicative of the current commercialization efforts, lab-scale systems, or both. POLYMERright, Inc., a California-based company, had been developing a rubber reclaiming process where a measured amount of proprietary devulcanization chemical agent was added to a mixer and heated with a corresponding amount of vulcanized rubber. After the requisite exposure time had been elapsed, the slurry was forced through an extruder at temperatures between 500 ° F and 600 ° F (260 ° C and 315 ° C). Once cooled, the now devulcanized rubber was ready for sale. According to the company, technology of POLYMERright has been demonstrated on a laboratory scale (10 to 15 lb/hr), but it has yet to be demonstrated on a commercial scale. Another company marketing a chemical devulcanization technology is Tires2Oil, Inc. (T2O). The T2O process took place in a mixer or reactor. In the case of tire rubber, granulated rubber (approximately 30 meshes) was separated from the fiber and metal fractions and loaded into a reactor. The rubber is then mixed with a proprietary solvent and treated at thermodynamically critical conditions of temperature and pressure.

When the requisite reaction time had elapsed, the mixture was cooled and then gases vented and stored. The oil and solvent fraction were drained from the reactor, and the carbon black was removed for additional processing. The solvent was then separated by distillation or other means or reuse. The sulfur, which has been collected from the mixture and scrubbed from the gases, reportedly could also be sold. Carbon black recovered from the process could also be further processed by T2O for resale. T2O also claims to have developed additional processes that were capable of recovering the other chemical constituents of vulcanized rubber; such as, oils, solvents, and sulfur.

2.1.3.2.2 Ultrasonic

Most companies marketing ultrasonic devulcanization technologies are utilizing very similar technologies involving cold feed extruders and varying physical arrangements of ultrasonic equipment. The recent technologies are continuous processes, as opposed to batch process. Ultrasonic devulcanization

technology is actually composed of a “devulcanization system”— namely, extrusion and ultrasonic processing. Many of the designs are similar. Two key differences in some cases are the equipment and materials used to generate the ultrasonic energy required for the process, and the positioning of the transducer(s) relative to the extruder. Two different arrangements of ultrasonic devulcanization systems are shown in Figures 2.2 and 2.3.

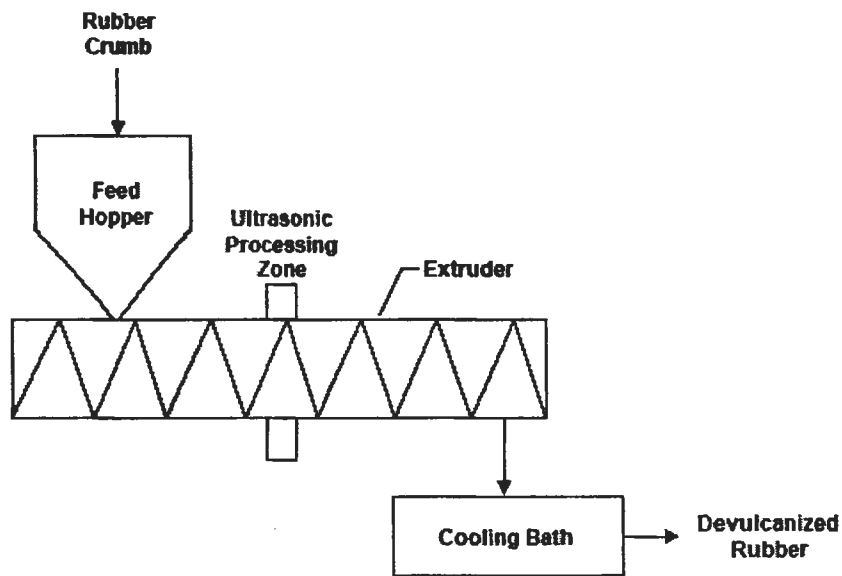


Figure 2.2 Schematic diagram of an ultrasonic devulcanization system showing a mid-extruder location for the ultrasonic subsystem.

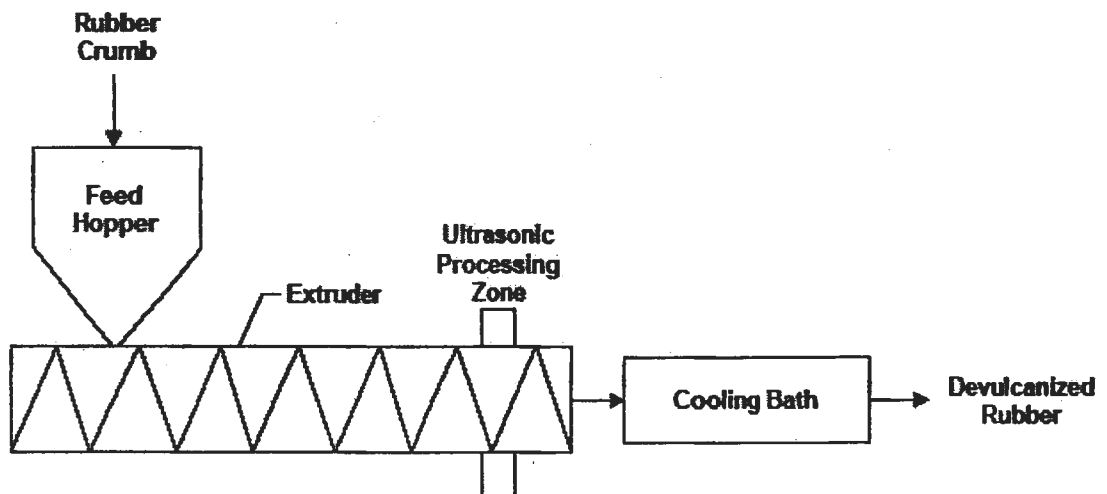


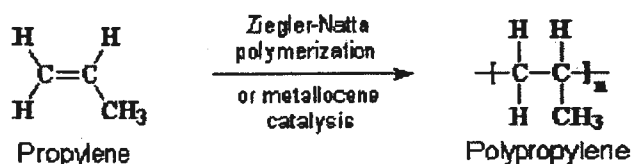
Figure 2.3 Schematic diagram of an ultrasonic devulcanization system showing the ultrasonic subsystem located at the discharge end of the extruder.

In this type of devulcanization system, size-reduced rubber particles were loaded into a hopper and were subsequently fed into an extruder. The extruder mechanically pushed and pulled the rubber. This mechanical action served to heat the rubber particles and softens the rubber. As the softened rubber was transported through the extruder cavity, the rubber was exposed to ultrasonic energy. The resulting combination of heat, pressure, and mechanical mastication was sufficient to achieve varying degrees of devulcanization. The time constant of the devulcanization process takes place in seconds. Essentially all of the rubber entering the process was discharged from the extruder in semi-solid product stream. Process losses would primarily be those due to emissions of fine particulates or of gases, if any, generated due to the mechanical and thermal processes occurring during the devulcanization process. After exiting through the extruder die, the rubber was passed through a cooling bath and then dried.

2.1.4 Polypropylene (PP)

2.1.4.1 General features

A fast growth of PP production, in comparison to other thermoplastics, has been encouraged by significant advances in catalyst and process development and by the attractive combination of features which characterizes this polymer such as low density, heat distortion temperature above 100°C, extraordinary versatility in terms of properties, applications, and recycling in addition to a low cost. PP was a vinyl polymer obtained, by means of organo-metallic catalysts [3], from propylene (CH₃-CH=CH₂) through the reaction shown follow in Scheme 2.1.



Scheme 2.1 Polymerization of polypropylene.

Depending on the organization of CH_3 groups along the backbone, three configurations could be distinguished: isotactic, syndiotactic, and atactic. When all the groups were on the same side of the chain, PP was isotactic. In this case, chains had a very regular arrangement, consequently they could pack easily together in a crystal structure. Thus, the higher the amount of isotactic phases in the polymer, the higher the degree of crystallinity in the solidified PP. In syndiotactic configuration, methyl groups were alternatively on either side of the carbon chain. This structure yielded a highly flexible PP. The side groups were randomly situated on either side of the backbone and therefore the polymer had a very low degree of crystallinity. Compared to isotactic PP, the syndiotactic isomer was believed to exhibit higher impact resistance and improved adhesion on organic surfaces or glass fillers [4]. However, PP was semi-crystalline, which indicated that it always had two phases, an amorphous and a crystalline one. When cooling was slow enough, molecular chains had time to arrange themselves in 'lamellar' fibrils. These structures grew out from a central nucleus in the three dimensions yielding an organization with a spherical symmetry. The whole assembly was called '*spherulite*' and is illustrated in Figure 2.4.

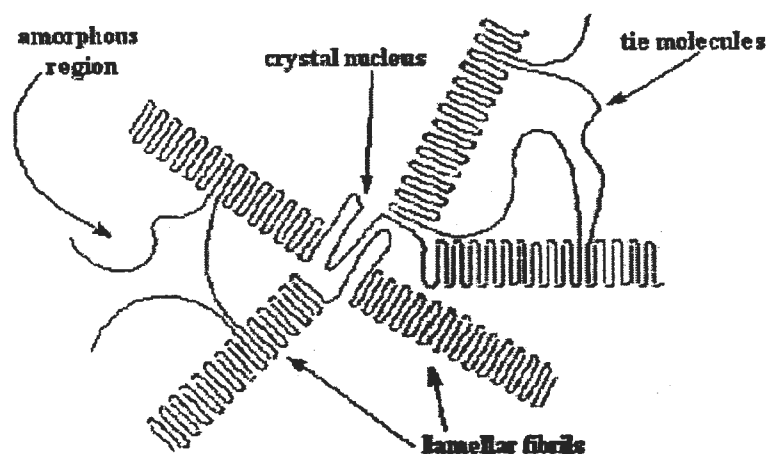


Figure 2.4: Schematic illustration of chains organization in PP spherulites [3]

Thus it was possible to distinguish between spherulites on the largest scale, the lamellar structure on the intermediate level, and the crystal structure on the smallest scale [3]. Moreover, PP was a polymorphic material. This implied that its crystals could be arranged in several forms such as monoclinic, hexagonal, triclinic or

smectic. The formation of a certain crystal form would depend on the crystallization conditions [4]. However PP was usually produced and commercial listed as a copolymer, in which different monomers were used as raw materials. Ethylene was the monomer most commonly copolymerized with propylene. Copolymerization level and type (random, block, alternate) strongly affected the final material properties: for instance if 5% of ethylene was randomly copolymerized, the crystallinity degree was already markedly reduced.

2.1.4.2 PP properties

'Polypropylene' was a very versatile polymer. An exhaustive discussion of all its features would be too vast and inappropriate in the present work. Moreover, PP was a well known material, hence, in this section, only the properties which might be useful for a deeper comprehension of the subject of this thesis would be briefly outlined. The PP mechanical properties, such as stiffness and ductility, were strongly affected by its crystallinity degree. The latter, though, did not depend only on tacticity but it was influenced by thermal history as well. For example, quenching the polypropylene, the biggest part of polymer will be 'frozen' in an amorphous arrangement, more the few crystals formed would be small. Such a material would be less stiff than the slowly cooled one. Consequently, several variables could be adjusted in order to set the final material properties according to our need. For this reason it was necessary, in listing PP general features, either to state the grade of material currently dealt with or to refer to 'average' values. For a 100% isotactic PP, the significant numbers were [4]:

- Melting temperature:	174°C
- Glass transition temperature:	-17°C
- Amorphous density at 25°C:	0.85 g/cm ³
- Crystalline density at 25°C:	0.95 g/cm ³
- Average tensile yield strength:	30.7 MPa
- Average Young's modulus:	1.9 GPa
- Service temperature up to:	120°C

In general, PP could be considered chemically 'inert'; since very stable structure provided a good chemical resistance, except for aromatic hydrocarbons at elevated temperatures and halogens. It could withstand most inorganic acids, except nitric and sulphuric, and inorganic salt solutions. On the other hand, PP was unsuitable, due to swelling, to be used with most organic solvents [4]. These features, together with water resistance, low density and good price/property ratio, gave PP its great industrial importance.

2.1.5 Additives

2.1.5.1 Polypropylene octene copolymer (POE)

Polyolefin Elastomer (POE) was a premier impact modifier for a wide variety of plastics and thermoplastic polyolefin applications. From polypropylene (PP) to high-density polyethylene (HDPE), POE offered an excellent option for customizing product performance while enhancing the value of offering. Blends using POE resins exhibited significant improvements in impact strength and a better balance of properties with addition levels ranging from 5 to 30%. Compound, injection molders, and extrusion operators usually turned to POE to improve the physical properties of their products. It was normally available in a pellet form which could conveniently be compounded or dry blended with PP, HDPE, or other polyolefin to maximize product performance. Key benefits include:

- Better compound economics due to reduced modifier levels
- Superior impact performance for polyolefin plastics
- Ease of handling, blending, and processing
- Availability in bags, boxes, or railcars
- Improved softness and UV stability
- Reduced weight via lower density products

2.1.5.1.1 Effect of the ethylene-octene copolymer and PP

The best balance of properties in a given application was essential for compound and end users. For impact modification of plastics, the goal

was to achieve maximum flexural modulus while maintaining sufficient flexibility to avoid breakage during practical use. POE was a proven solution that met these needs by improving impact performance. POE was available in a variety of melt indexes, densities, and co-monomers to help users reach their needs. The selection of an ENGAGE POE resin depended on application requirements such as stiffness, ductility, flow, surface appearance, shrinkage, and cost. Figure 2.5 highlights the notched Izod impact and flexural modulus performance when ENGAGE POE is melt blended with a 35 MFR homopolymer PP. The addition levels were 5 to 30% with ENGAGE™ 7270 as the impact modifier. The data demonstrated that ENGAGE POE improves impact performance at low levels with a slight loss in modulus and provided ductility at high levels with proportional loss in modulus [5].

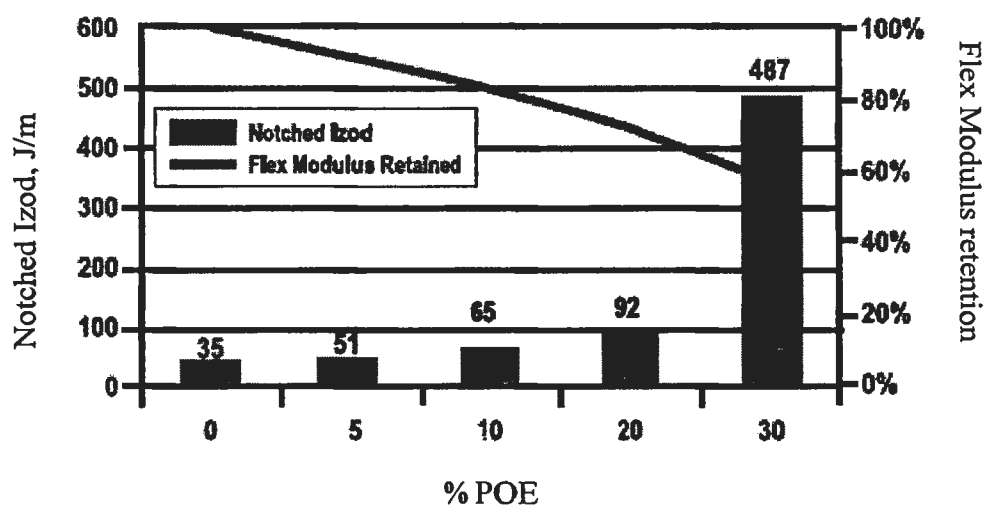


Figure 2.5 Impact Modification of Polypropylene at 25°C

2.1.5.1.2 Effect of the Thermoplastic Base Material (Ethylene-octene copolymer and PP)

The choice of the thermoplastic material could affect the properties of the blend. There were two possible reasons for this. First, the base properties of the thermoplastic were different. Second, the choice could affect the compatibility of the two materials. Since compatibility is important to blend properties, plastic materials that had similar structure and polarity to EPDM could improve the results. Ethylene-octene copolymer (Engage 8100) was chosen to blend

with the recycled EPDM rubber. The resulting ultimate tensile strengths, as showed in Figure 2.6, show a slight improvement over the PP/EPDM blends (0.45 MFI).

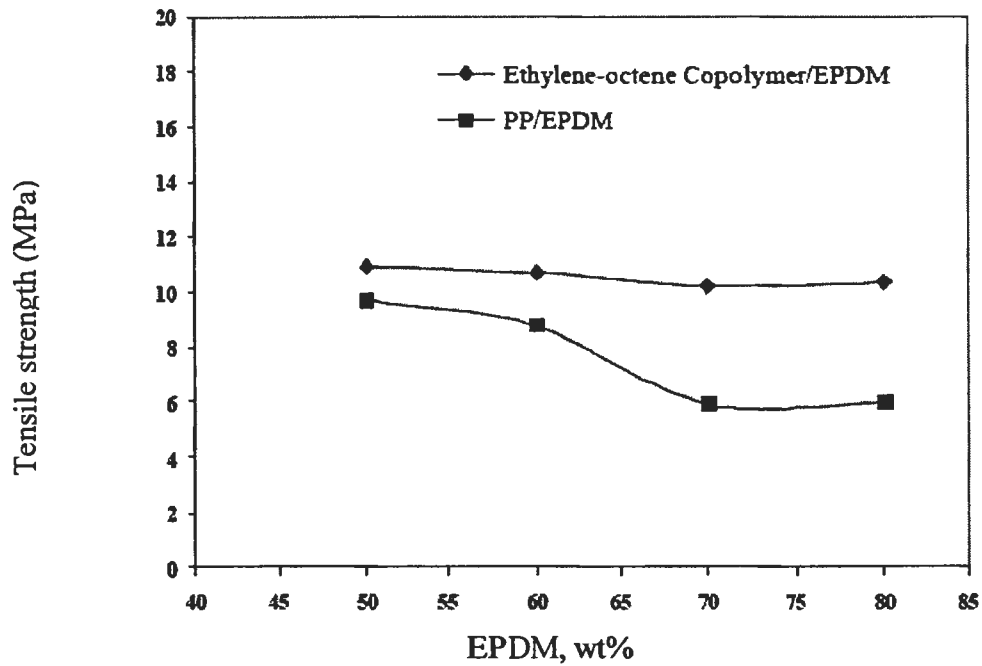


Figure 2.6 Ultimate tensile strength of EPDM rubber blends [5].

The ultimate elongation of the ethylene-octene copolymer blend, shown in Figure 2.7, showed a dramatic improvement over that of the PP/EPDM blend.

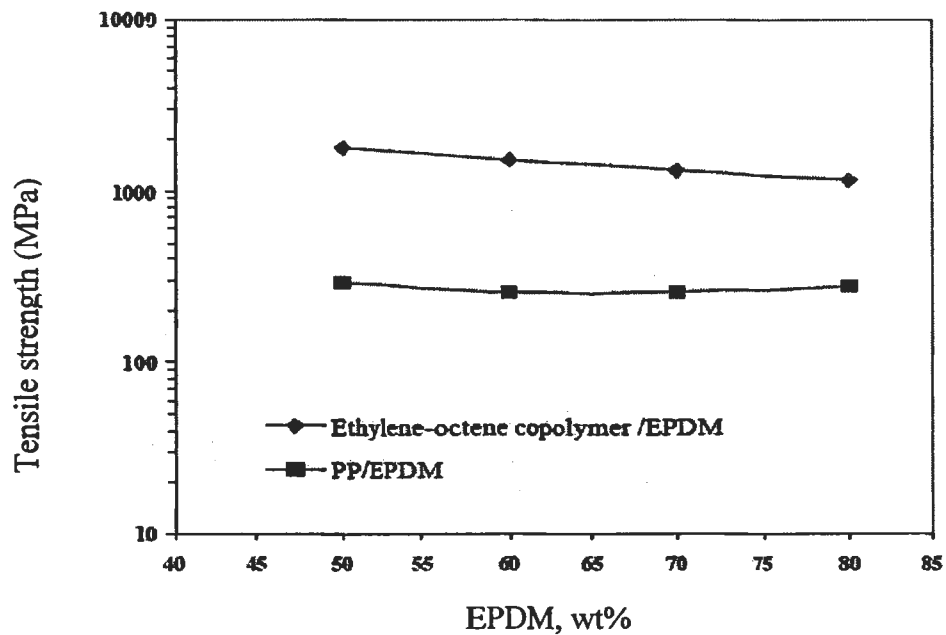
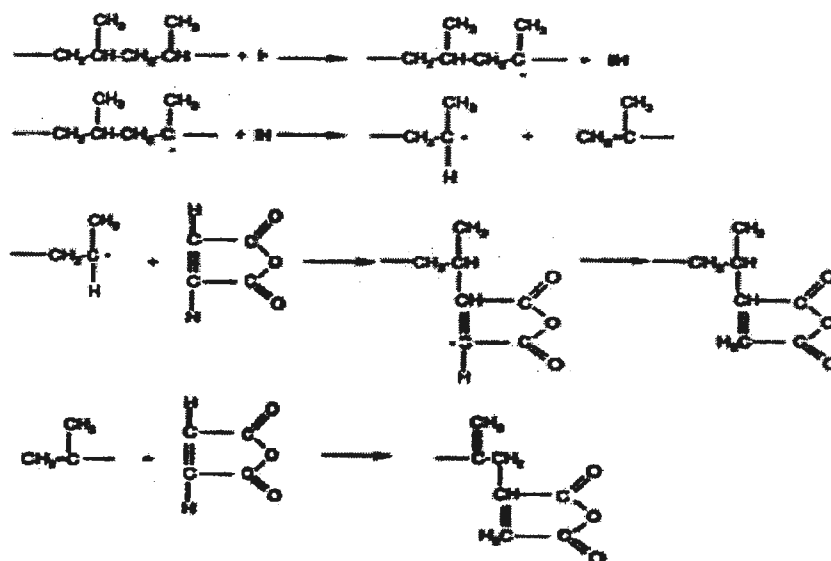


Figure 2.7 Ultimate elongation of EPDM rubber blends [5].

These results could be attributed to the structure of the thermoplastic component. Unlike PP, the ethylene-octene copolymer had a lot of short-sided chains, which led to only 5% crystallinity in the pure ethylene-octene copolymer. Pure PP would be expected to have higher crystallinity and hence lower elongational capability.

2.1.5.2 Maleic anhydride grafted polypropylene (MA-g-PP)

The polar group introduced in the hydrophobic PP backbone to make it hydrophilic was the maleic anhydride which had been reported from a study of Rengarajan et al. [7] to be crucial to promoting the desired phase structure. According to this representation, the MA groups should be randomly grafted or block copolymerized in the PP chain. Nevertheless, this kind of product was usually made by reactive extrusion with a peroxide initiator which caused a free radical formation by scission of the PP chain. Such radical was the reactive site to which the MA group attached. The compatibilizer manufacturer suggested more than one group could react with a broken PP chain leading to a dimer or even trimer formation. This meant that a PP-g-MA represented as a 'surfactant', where a polar head was attached to an aliphatic tail and depicted in Scheme 2.2 below.



Scheme 2.2 Mechanism of chain scission for polypropylene-g-maleic anhydride [7].

In the previous paragraph, it had already been anticipated these existed an optimum in PP-g-MA functionality between a too little functionalized PP, which would be unproductive, and a functionalized PP with an excessive content of MA which, in contrast, would have too large polarity difference with the matrix PP molecules to diffuse in them.

2.2 Compound Processing Characteristics and Testing

The processing of a rubber formulation was a very important aspect of rubber compounding. Also, it was important to understand the rubber properties needed for good processability and the tests required measuring these properties.

2.2.1 Manufacturing process

Uncured rubber, whether natural or synthetic, behaved as a viscoelastic fluid during mixing. Under processing conditions, various rubber chemicals, fillers, and other additives could be added and mixed into the rubber to form an uncured rubber compound. These compounding ingredients were generally added to the rubber through one of two basic types of mixers, the two roll mill or the internal mixer [8].

2.2.1.1 Two roll mill

The two roll mill consisted of two horizontal, parallel, heavy metal rolls which could be jacketed with steam and water to control temperature. These rolls turned towards each other with a pre-set, adjustable gap or nip to allow the rubber to pass through to achieve high-shear mixing. The back roll usually turned at a faster surface speed than the front roll. This difference increased the shear forces. The difference in roll speeds was called the friction ratio. The rubber generally formed a "band" around the front roll. Not so long ago compound preparation was carried out on roll mills only, but nowadays large factories mainly use internal mixers. Nevertheless the roll mill is still an important tool to sheet out and cool down the rubber after internal mixing and to prepare thin sheeted half fabricates for instance for confectioning tires or wrapped hoses. The resulting compound is folded, homogenized, sheeted off and stored for further processing. Mill mixing was the

oldest method of rubber mixing, dating back to the very beginning of the rubber industry; however, it was a relatively slow method and its batch size was limited. Internal mixers overcame these problems.

2.2.1.2 Internal mixers

Internal mixers were first developed by Fernley H. Banbury in 1916. Today, these internal mixers are commonly used because they are much more productive than two roll mills. Internal mixers consist of two rotors or blades turning toward each other in an enclosed metal cavity. These rotors could be either tangential or intermeshing in arrangement (Fig. 2.8). The cavity was open to a loading chute through which rubber, fillers, and various chemicals are placed. Upon completion of the mix cycle, the mixed rubber stock was discharged through a door in the bottom of the mixer. Mixing time was determined by the shape and size of the rotors, the rotor speed, and horse power of the motor turning them. The rotors generally turned at a high friction ratio. Some internal mixers could handle batches in excess of 1000 pounds (greater than 455 kg), and in some cases, could completely mix a compound in less than two minutes. Of course, with so much energy being absorbed by the rubber stock, the batch temperature could rise well above 120 ° C (250 ° F) before it was dumped and cooled. The temperature rise that results from viscous heating of the rubber compound often means the compounds must pass through the internal mixer more than once to disperse fillers and other compounding ingredients. Batches are usually dumped from an internal mixer onto a mill where they may be further worked while being cooled. Sometimes, additional compounding ingredients, such as curatives, were added at this point.

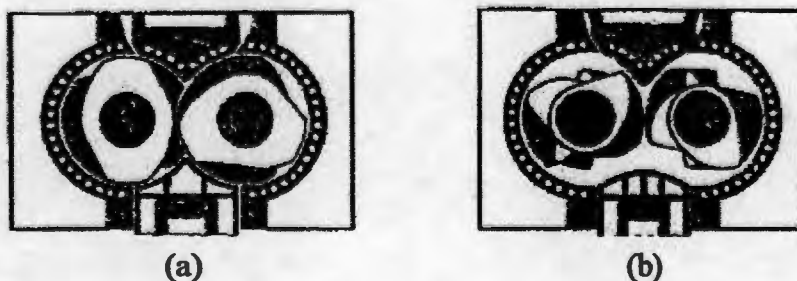


Figure 2.8 a) Tangential vs. b) intermeshing rotors for internal mixers.

2.3 Polymer Blend

Blending of immiscible polymers offered attractive opportunities for developing new materials with useful combinations of properties. However, simple blends often had poor mechanical properties and unstable morphologies. Compatibilization of such blends was necessary. Preformed graft or block copolymers had been traditionally added to act as compatibilizers. An alternative, however, was to generate these copolymer compatibilizers in-situ during melt blending using functionalized polymers. In this review, a variety of reactive polymers that had been utilized in the reactive compatibilization of polymer blends was examined. They were classified into eight major categories according to the types of reactive functionality and the characteristics of blending reactions, namely, maleic anhydride, carboxylic acids, groups capable of interchange reactions, primary and secondary amines, hydroxyl groups, heterocyclic groups, groups capable of ionic bonding, and others. Their preparation methods and applications, and the chemical reactions occurred during melt blending were presented.

2.3.1 Compatibility in polymer blends

There were two widely useful types of polymer blends: miscible and immiscible. Miscible blends involved thermodynamic solubility and were characterized by the presence of one phase and a single glass transition temperature. Their properties could often be predicted from the composition weighted average of the properties of the individual components. Immiscible blends were phase separated, exhibiting the glass transition temperatures and/or melting temperatures of each blend component. Their overall performance depended on the properties of the individual components, but also depended significantly on the morphology of the blends and the interfacial properties between the blend phases. Performance was not easily predictable [9].

In order to achieve miscibility in polymer blends, a negative free energy of mixing must exist which, in turn, required an exothermic heat of mixing, because entropic contributions were negligible. An exothermic heat of mixing might be achieved by the introduction of specific interactions between blend components. The

potentially useful specific interactions ranged from strong covalent and ionic bonding to nonbonding weak interactions such as hydrogen bonding, dipole-dipole, and donor-acceptor interactions, etc. Few polymer pairs form miscible blends. One of the infrequent examples was the commercially important PPE/PS blend. Most polymers, however, were immiscible. But immiscibility was not always undesirable. Blends did not have to be miscible to be useful. HIPS and ABS had proven the importance of phase separation.

The key to make successful blends of this kind was the use of compatibilization to control a resulting morphology. Compatibilization was the result of a process or technique for improving blend performance by making blend components less immiscible. Compatibilized blends were termed "compatible blends" and was characterized by the presence of a finely dispersed phase, good adhesion between blend phases, strong resistance to phase coalescence, and technologically desirable properties. Compatible blends constitute the majority of commercially important blends. The compatibility of these blends might vary widely from one system to another. Compatibility was a measurement of polymer blend immiscibility at chosen scales and criteria.

2.3.2 Strategies for blend compatibilization

There were several methods of compatibilizing immiscible blends, including compatibilization by the introduction of non-reactive graft or block copolymers, non-bonding specific interactions, low molecular weight coupling agents, and reactive polymers.

2.3.2.1 Addition of block and graft copolymers

Suitable block and graft copolymers could be used as compatibilizers for polymer blends. A suitable block or graft copolymer contained a segment miscible with one blend component and another segment with the other blend component. The copolymer segments were not 2 types of reactive polymers used in blending necessarily identical with the respective blend components. Significant amounts of the copolymer were expected to be located at the interface between immiscible blend phases, reducing the interfacial tension between blend components, and reducing the

resistance to minor phase breakup during melt mixing. Thus, this resulted in reduction of the size of the dispersed phase, and stabilization of the dispersion against coalescence. The finer morphology and the increased interfacial adhesion usually resulted in improved physical properties. The effects of a copolymer on the morphology of polymer blends, interfacial adhesion between blend phases, and blend properties depended on such parameters as the type and molecular weight of the copolymer segments; blend compositions, blending conditions, etc.

2.3.2.2 Utilization of non-bonding specific interactions

Non-bonding specific interactions like hydrogen bonding, ion-dipole, dipole-dipole, donor- acceptor, and π -electron interactions were useful for enhancing the compatibility of polymer blends. Generally, these specific interactions were weak while high concentrations, e.g., one interacting group per repeating unit, were often required for effective compatibilization. In other words, polymers capable of these specific interactions could not, generally, be added only in small quantities into immiscible blends to achieve compatibilization. The addition of large quantities might change the properties of the desired phase constituents and could be uneconomical.

2.3.2.3 Reactive compatibilization

Graft or block copolymers acting as compatibilizers for polymer blends could be formed in situ through covalent or ionic bonding during the melt blending of suitably functionalized polymers [9]. In general, one phase contained reactive groups, while was inherent in the polymer, while the other contained no inherent functionality. Reactive groups could be incorporated into the second phase by adding to it a functionalized polymer miscible. In some cases, both phases might have to be functionalized. The in situ formed copolymer compatibilizers were located preferentially at the interface where they were most needed, hence reducing the size of the dispersed phase, and improving the interfacial adhesion between blend phases and the physical properties of the blends. In situ reactive compatibilization has already been implemented in a number of commercial products and, in many instances, appears to be the method of choice for compatibilization.

2.4 Dynamic Vulcanization

The minor elastomer phase was cross-linked with peroxide used this method to prepare Thermoplastic vulcanized (TPVs) with different compositions. In that work, however, much of the PP was damaged by degradation. Coran et al. [10, 11] found that it was important that the elastomer phase was well mixed before the onset of the vulcanization reaction and that the mixing should continue until the dynamic vulcanization was completed. If the cured elastomer phase was continuous, the resulting compound cannot be processed. The curing technique was improved by Abdou-Sabet et al. who showed that by using a phenolic curing agent, the elastomer could be cured completely [12].

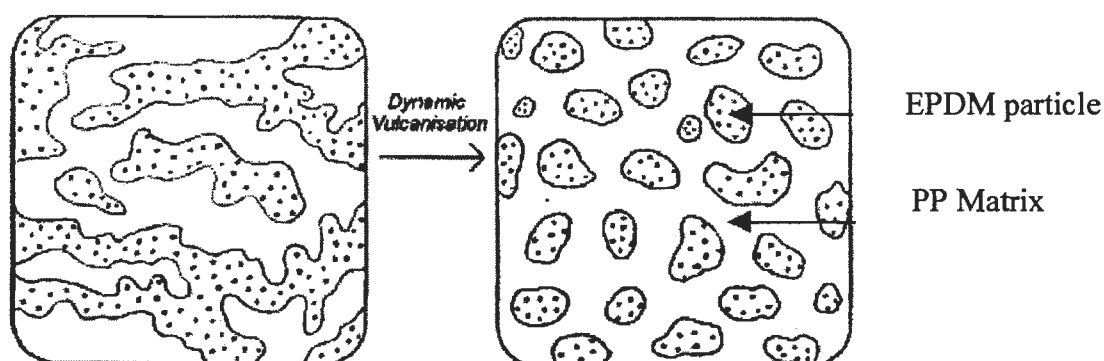


Figure 2.9 Schematic representation of morphology change during dynamic vulcanization [13].

In dynamic vulcanisation, the elastomer phase changed from a viscous fluid to an elastic solid. The elastomer became rigid and could not comply to the applied stress. As a result, this phase broke up into micron-sized elastomer particles [13] (Fig 2.9). Since in most TPVs the elastomer phase was the major component, this phase was continuous in an initial state. Due to the continuing curing and mixing, phase inversion took place and the elastomer became dispersed, even when its volume fraction was very high ($\phi_{EI} = 0.80$). In principle, any curing agent could be used for the crosslinking of the elastomer phase. Curing systems based on peroxides [14, 15], sulphur or phenolic resins were widely used to make TPVs based on PP/EPDM.

Another curing technique was based on silane grafting [16]. The advantages and disadvantages of these curing agents are extensively discussed.

The typical particle-in-matrix morphology depended on both mixing speed and curing rate. Because the curing process was usually very fast, the mixing speed should be sufficiently high to obtain small rubber particles. These conditions could be satisfied in a twin screw extrusion process. The maximum shear rate should be higher than 2000 s^{-1} and the length of the extruder should be larger than 42 L/D. The curing process took less than a minute to complete.

2.5 Polymer rheological properties

2.5.1 Viscosity

Viscosity was defined as the resistance of a fluid, such as rubber, to flow under stress. Mathematically, viscosity (η) was expressed as shear stress divided by shear rate as shown below in equation 2.1.

$$\eta = \frac{\text{shear stress}}{\text{shear rate}} \quad \text{.....(equation 2.1)}$$

Viscosity was significantly dependent on temperature such that at higher temperatures materials were less viscous. The viscosity of rubber could be measured by four methods:

1. Rotational viscometers
2. Capillary rheometers
3. Oscillating rheometers
4. Compression plastimeters
5. Rotational rheometer (Advanced Rheometric Expansion System)

2.5.2 Rotational Viscometers

By far, the most commonly used rotational viscometer in the rubber industry is the Mooney viscometer. Melvin Mooney of U.S. Rubber Co. developed this instrument in the 1930s [17]. Since then, it has become one of the most widely used test method in the industry. It has been used for testing both raw rubber and mixed stocks. This method was described in detail in ASTM D1646 or International Standard ISO 289, Part 1. Two pre-cut rubber test pieces with a combined volume of 25 cm^3 were placed into a two-part compression cavity mold. With the dies closed, a sealed and pressurized cavity was formed, in which a special rotor was imbedded in the rubber. This rotor and the dies were grooved to help prevent the rubber from slipping at the rotor or die interface while the rotor is turning. Usually there is a pre-heat time after the dies are closed to allow the rubber to approach the set temperature of the instrument. Then the test specification calls for the rotor to turn at two revolutions per minute (2 rpm) for a specified time period. The instrument records viscosity in Mooney Units (MU), which are arbitrary units based on torque.

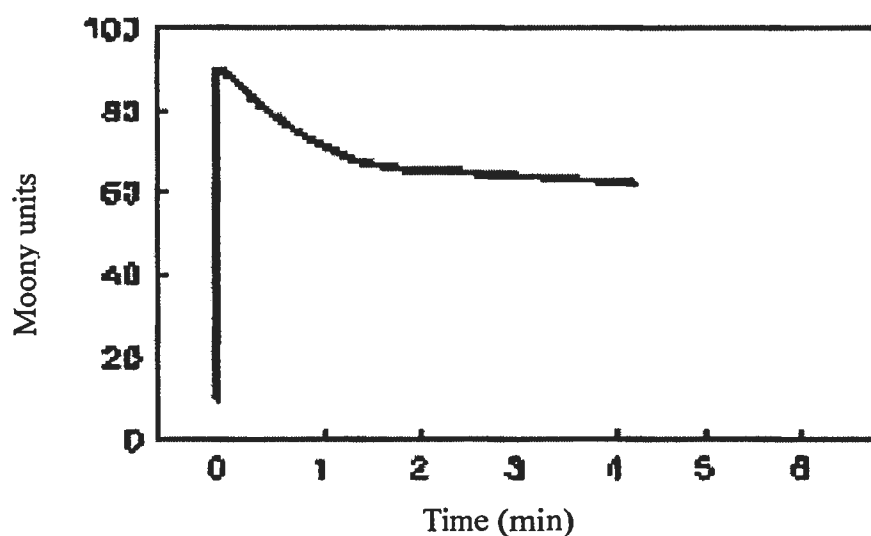


Figure 2.10 Mooney viscosity curve of raw rubber.

Generally, the measured viscosity of the rubber under test decreased with the running time because of the thixotropic effects of the rubber tested. However, depending on the type of rubber and the test temperature, the rate of decrease in the

measured Mooney viscosity with time should gradually slow down as shown in Figure. 2.10.

2.5.3 Capillary rheometer

The capillary rheometer measured the viscosity of mixed rubber stocks at relatively high shear rates. ASTM D5099 describe this method for rubber testing. There was no ISO International Standard for using rubber on the capillary rheometer.

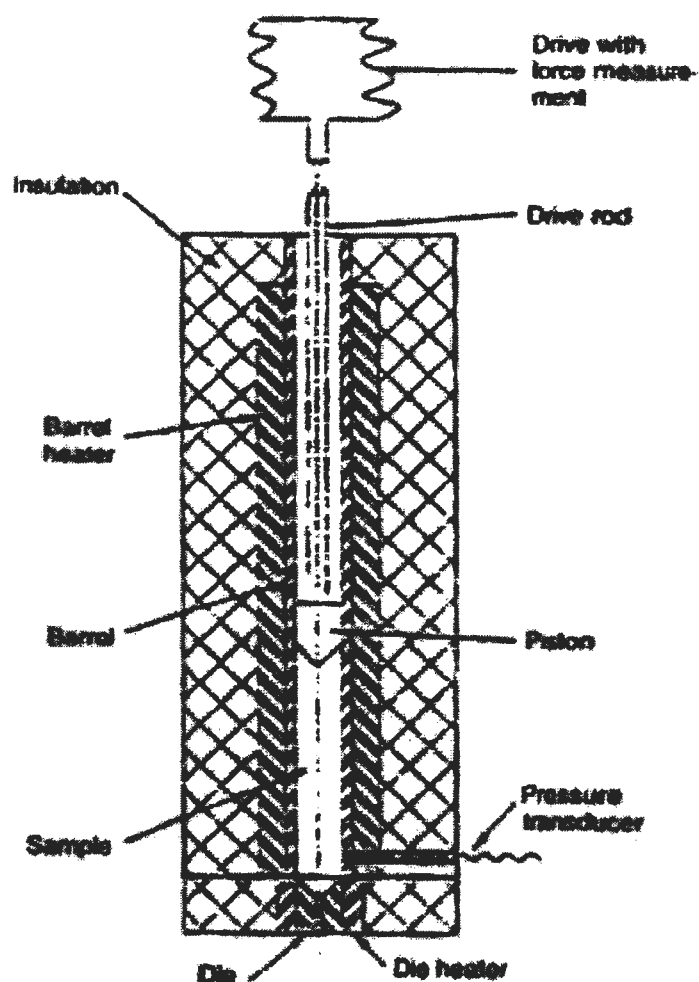


Figure 2.11 Capillary rheometer.

The ASTM method consisted of placing (or packing) cut pieces of a rubber sample in a heated barrel. Then, a special piston pushed the rubber out of the barrel through an orifice of a special die with a given capillary length to orifice diameter ratio or L/D to form an extrudate. The apparent shear rate was determined from the

speed of the piston traveling in the barrel the ram speed. The apparent shear stress was determined from the resulting barrel pressure measured by a transducer (Fig 2.11). From Eq. (2.1), the apparent viscosity η_{app} could be calculated. This apparent viscosity could be converted to true viscosity by applying the Rabinowitsch correction to obtain the true shear rate and the Bagley correction to obtain the true shear stress [18]. The main advantage of the capillary rheometer for measuring rubber viscosity was the wide shear rate range which could be applied to the rubber specimen. Many capillary rheometers could measure viscosity shear rates at over 1000 s^{-1} . The disadvantages of these rheometers were that they were difficult to operate, require considerable time to run a single test, and require extensive time to clean the barrel and set up for the next test.

2.5.4 Oscillating rheometers

An instrument called the Rubber Process Analyzer (RPA) by Alpha Technologies [19] measures dynamic viscosity through the application of a sinusoidal strain to an uncured rubber specimen molded in a sealed, pressurized cavity. ASTM D6204 described this unique method for measuring processability. Figure 2.12 shows the instrument used in this method.



Figure 2.12 RPA 2000[®] rubber process analyzer.

Figure 2.13 shows a sinusoidal strain being applied to the rubber test specimen. The complex torque response (S^*) was observed to be out-of-phase with the applied strain because of the viscoelastic nature of the rubber being tested. The phase angle quantified this out-of-phase response.

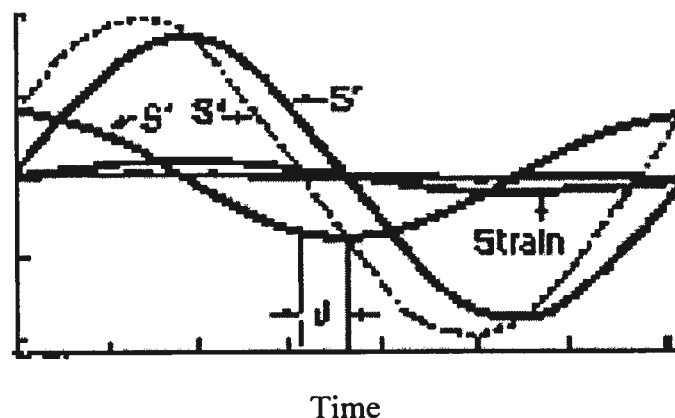


Figure 2.13 Applied sinusoidal strain and resulting stress response.

From the complex torque S^* response and the phase angled, the elastic torque S' (in-phase with the applied strain) and the viscous torque S'' (out-of-phase with the applied strain) could be derived (Fig. 2.14). The elastic response S' was a function of the amplitude of the applied strain while the viscous torque was a function of the rate of change of the applied strain.

The storage shear modulus (G') was calculated as followed:

$$G' = k \cdot S' / \text{strain} \quad \dots\dots \text{(Equation 2.2)}$$

The loss shear modulus (G'') was calculated as followed:

$$G'' = k \cdot S'' / \text{strain} \quad \dots\dots \text{(Equation 2.3)}$$

where k was a constant that took into account the unique geometry of the die cavity.

The complex shear modulus (G^*) was equal to the square root of the sum of G' squared and G'' squared.

$$G^* = [(G')^2 + (G'')^2]^{1/2} \quad \dots\dots \text{(Equation 2.4)}$$

The complex dynamic viscosity η^* was then calculated as followed:

$$\eta^* = G^*/\omega \quad \dots\dots \text{(Equation 2.5)}$$

where ω was the frequency of the sinusoidal strain in radians/second.

The real dynamic viscosity η' was also calculated in the following manner:

$$\eta' = G'/\omega \quad \dots\dots \text{(Equation 2.6)}$$

The complex dynamic viscosity η^* from the Rubber Process Analyzer was analogous to the apparent viscosity (η_{app}) from the capillary rheometer, while the real dynamic viscosity η' was analogous to the corrected viscosity from the capillary rheometer.

Cox and Merz in the early 1950s published the following empirical relationship between capillary rheometer viscosity η_{app} measured under conditions of steady shear rate and dynamic complex viscosity η^* , which was measured through sinusoidal deformation (and constantly changing shear rates) applied by a dynamic mechanical rheological tester [20]:

$$\eta_{app}(\dot{\gamma}) = \eta^*(\omega)|_{\omega=\dot{\gamma}} \quad \dots\dots \text{(Equation 2.7)}$$

where η_{app} was the apparent (uncorrected) capillary rheometer viscosity at a steady shear rate (in s^{-1})

η^* was complex dynamic viscosity measured at an oscillatory frequency of ω (in radians per second).

This empirical relationship was application for most circumstances but should be used with consideration. Sometimes the success of this empirical relationship was based on the nature and concentration of the reinforcing fillers used. The important

advantages of the Rubber Process Analyzer in measuring rubber viscosity over the other methods discussed were its versatility in measuring viscosity at both low and high shear rates, ease of use, and excellent repeatability.

2.5.5 Compression plastimeters

While viscosity was defined as the resistance to plastic deformation, the term plasticity referred to the ease of deformation for a rubber specimen. It could be said that plasticity and viscosity defined the same property, but had the opposite meaning. A plastimeter measured the plasticity of an uncured rubber specimen. Plastimeters were very simple, crude methods for measuring the flow of a rubber sample. The main problem with most plastimeters was that they the test were operated at extremely low shear rate ranges of only 0.0025 to 1 s^{-1} , which were much lower than the Mooney viscometer. To reinforce this point, the Rubber Process Analyzer could be correlated to these methods but only when very low frequencies, i.e. very low shear rates, were applied to the rubber specimen. The principle of plastimeter procedures was basically to measure the deformation of a cylindrically cut, uncured rubber specimen after it had been subjected to a constant compressive force between two parallel plates for a specified time period at a specified test temperature. The initial part of ASTM D 3194 (the standard describing the Plasticity Retention Index for natural rubber) and International Standard ISO 2007 described the use of the Wallace rapid plastimeter method. The Williams plastimeter parallel plate method was described in ASTM D926 and ISO 7323.

2.5.6 Rotational rheometers (Advanced Rheometric Expansion System (ARES))

The Advanced Rheometric Expansion System (or ARES) is a rheometer (mechanical spectrometer) that is capable of subjecting a sample to either a dynamic (sinusoidal) or steady (linear) shear strain (deformation), then measuring the resultant torque expended by the sample in response to the strain. Through this instrument, the rheological properties can be measured. Strain is applied by motor, and a transducer measures the resulting torque. This is truly one of the best rheometers in the world.

In rotation: determination of the dynamic viscosity η for liquids, viscous solutions and melts in rotation by measuring the torque at constant angular velocity (deformation controlled rheometer) or by measuring the angular velocity at constant torque (shear stress controlled rheometer) as function of temperature, time and rotation velocity. Torsion pendulum test: determination of the complex dynamic viscosity and of $\tan \delta$ of liquids, viscous solutions and melts by measuring the amplitudes of torque and angle of rotation as well as the phase shift as function of temperature, time and frequency. Application were determination of the time and temperature dependence of the viscosity of liquids, characterization of curing reactions and characterization of different types of structural viscosities.

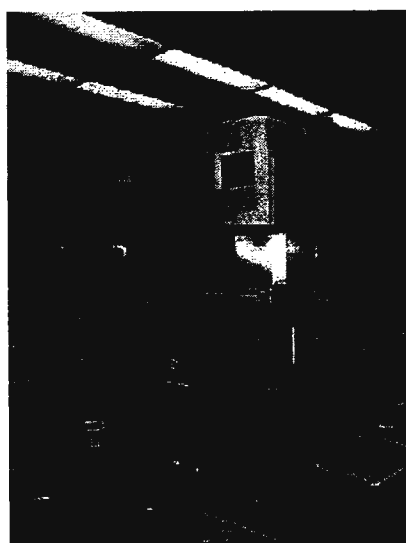


Figure 2.14. The Advanced Rheometric Expansion System.

Linear viscoelastic material behavior is described by a multi mode Maxwell model [8]

$$\dot{\tau}_i + \frac{1}{\lambda_i} \tau_i = G_i \dot{\gamma}, \quad \dots \dots \text{(Equation 2.8)}$$

where τ_i is the shear stress contribution of mode i with the relaxation time λ_i and modulus G_i . $\dot{\gamma}$ is the applied strain rate. The total stress (τ) is the sum of the stress contributions of all (n) modes:

$$\tau = \sum_{i=1}^n \tau_i. \quad \dots \dots \text{(Equation 2.9)}$$

A frequency (ω) dependent input $\gamma = \gamma_0 \sin \omega t$ will lead to a sinusoidal shear stress

$$\tau = G_d \gamma_0 \sin(\omega t + \delta), \quad \dots \dots \text{(Equation 2.10)}$$

where G_d is the dynamic modulus and δ the phase shift. The response can be written in an in-phase and out-of-phase wave: $\tau = \tau' + \tau'' = \tau'_0 \tau \sin \omega t + \tau''_0 \cos \omega t$. From this one can compute the moduli.

$$G' = \tau'_0 / \gamma_0 = \sum_{i=1}^n G_i \frac{\lambda_i^2 \omega^2}{1 + \lambda_i^2 \omega^2}, \quad \dots \dots \text{(Equation 2.11)}$$

$$G'' = \tau''_0 / \gamma_0 = \sum_{i=1}^n G_i \frac{\lambda_i \omega}{1 + \lambda_i^2 \omega^2}, \quad \dots \dots \text{(Equation 2.12)}$$

where G' is the storage modulus, representing the elastic part of the behavior and G'' is the loss modulus, representing the viscous part of the behavior. The two moduli, G' and G'' , form the complex dynamic modulus $G_d = G' + iG''$. The phase shift δ is a measure of viscous versus elastic material behavior and is related to 2.11 and 2.12 as follows:

$$\tan \delta = \frac{G''}{G'}. \quad \dots \dots \text{(Equation 2.13)}$$

All shear experiments should be performed in the linear viscoelastic regime of the tissue. The linear regime is the strain range in which the material properties are assumed to be constant. This regime is determined using oscillatory shear experiments with constant frequency and varying strain (strain sweep). A constant strain within this linear regime is chosen for the subsequent frequency sweeps. The frequency in the latter experiments is increased stepwise from 0.1 to 100 rad/s

2.5.7 Shear thinning behaviour

Shear thinning behaviour was the characteristic of non-Newtonian fluids (such as rubber compounds) to a decrease in measured viscosity with an increase in applied shear rate. Not only was it important to measure the compound viscosity, it was also

important to know how rapidly viscosity decreased with an increasing shear rate. All rubber compounds were non-Newtonian in their flow characteristics and their viscosity usually decreased according to the power law model. If the log of viscosity was plotted against the log of shear rate, a straight line was usually resulted. Rubber compounds with different reinforcing filler systems had different log-log slopes. These different slopes could be quite important because compounds were commonly processed at different shear rates. As shown in Fig. 2.15, the ordinal relationship of Compound 1 vs. Compound 2, for example, could change between a low shear rates to high shear rate. Therefore, compound 2 might have higher viscosity than Compound 1 in an injection molding operation, but Compound 2 might have lower viscosity than Compound 1 in the mold after injection. Two effective methods of measuring shear thinning behavior were the capillary rheometer and oscillating rheometer.

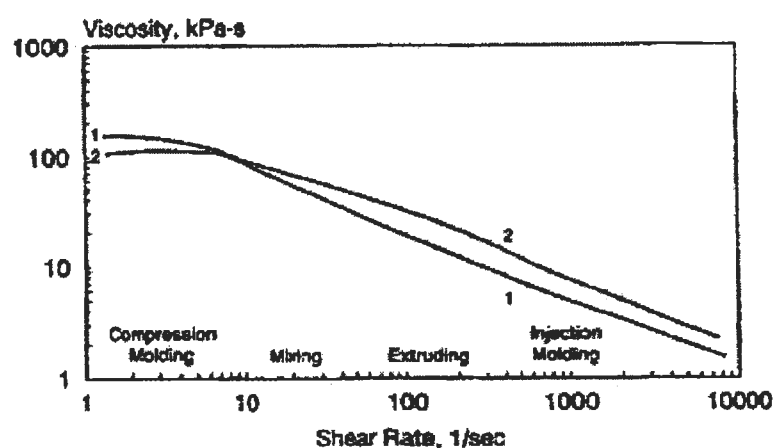


Figure 2.15 Comparison of two compounds with different shear thinning behavior profiles from capillary rheometer viscosity measurements with increasing applied shear rates.

2.5.7.1 Shear thinning behavior by Capillary rheometer

The capillary rheometer could apply a wide range of shear rates. As discussed earlier, according to ASTM D5099, the piston could be programmed to travel in the barrel at a series of increasing speeds which would result in higher applied shear rates. The applied shear rate for a capillary rheometer could be more than 1000 s^{-1}

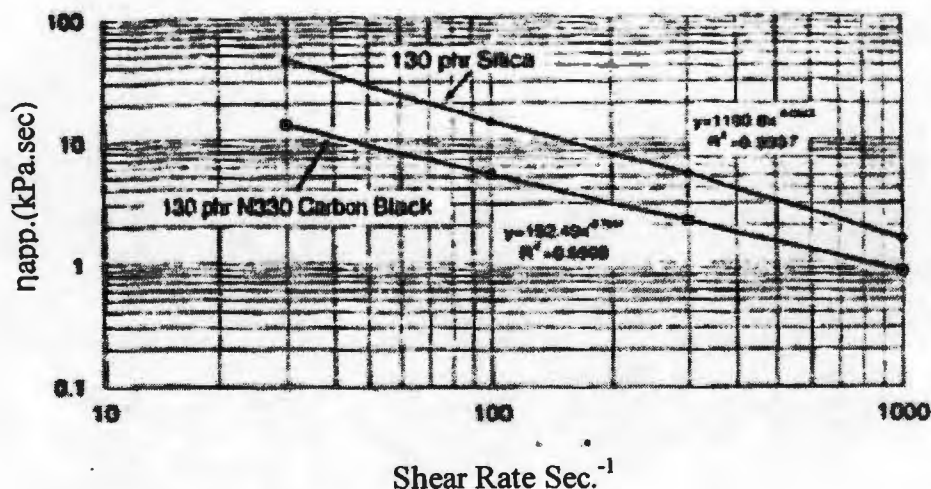


Figure 2.16 The log-log plot for a capillary rheometer.

2.5.7.2 Shear thinning behavior by Oscillating rheometer

As discussed earlier, the Rubber Process Analyzer (which was defined in ASTM D6204) increased shear rate by increasing the frequency of the sinusoidal strain. Figure 2.16 shows a log-log plot of the complex dynamic viscosity vs. shear rate (frequency was in radians/ second) for the same set of compounds shown earlier in the Figure 2.11 for capillary rheometer measurements. It can be seen that Figure 2.17 showed how the power law slopes from these measurements for capillary rheometer vs. Rubber Process Analyzer agreed quite well. Shear rate with the Rubber Process Analyzer could also be increased by using a higher applied strain. Occasionally applying higher strains to achieve higher shear rates might have some advantages over higher frequencies because these higher strains might be more effective in destroying carbon black aggregate-aggregate networks which formed in the rubber compound while in storage. Figure 2.18 showed the very good correlation was achieved between a capillary rheometer shear stress values measured at 100 s⁻¹ and Rubber Process Analyzer (RPA) G' values at very high applied strain.

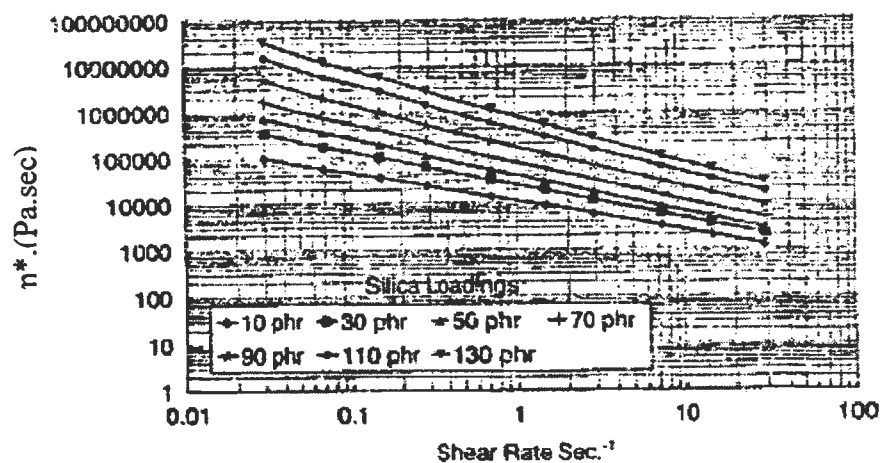


Figure 2.17 Log-log plot of RPA dynamic complex viscosity η^* vs. shear rate rad/s (frequency sweep).

R^2 Power Law slope for MPT from Shear Thinning behavior

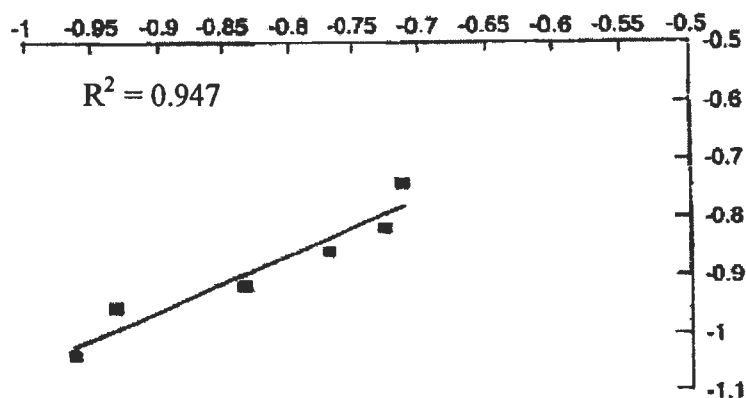


Figure 2.18 Comparison of power law slopes for shear thinning behavior as measured with a capillary rheometer vs. an oscillating rheometer (RPA).

The Rubber Process Analyzer was very simple to operate and versatile in applying different shear rates by either varying the frequency or varying the strain. It was a unique instrument because it could apply very high strains to an uncured rubber specimen in a sealed pressurized cavity and very repeatable results were achieved. Also, the Rubber Process Analyzer had an advantage over the capillary rheometer that

it could more effectively test raw rubber samples for shear thinning behavior and achieve better repeatability in results.

2.6 Literature Reviews

Radheshkumar et al. [21] investigated the use of thermomechanically reclaimed GRT composed of LDPE, fresh rubber (SBR or NR or EPDM). During blending dynamic curing was achieved using sulphuric, phenolic, and peroxide curing agents. They found sulphuric and phenolic curing agents proved to be most suitable for dynamic curing. Thermoplastic vulcanizates with the best mechanical performance contained SBR and EPDM rubber. The observed improvement in mechanical performance were attributed to chain entanglement and co-crosslinking in the interphase between the thermomechanically reclaimed GRT particles and the surrounding matrix (i.e., with the fresh rubber and/or LDPE).

Tantayanon et al. [22] studied the dynamic vulcanization of reclaimed tire rubber (RTR) and homopolypropylene (PP) by using a sulfur crosslinking agent, maleic anhydride (MA), dicumyl peroxide (DCP), or the combination of MA and DCP. They found that the RTR/PP blend with sulfur crosslink agent had the highest impact strength at the ratio of 30/70. This could be attributed to the limitation of carbon black in the blend. When the combination of MA and DCP was applied, the result was higher impact strength of the blend at the same ratio. This could be attributed to not only the cohesion between the polymer chains in each phase, PP phase and rubber phase, but also the interfacial adhesion between PP and RTR chains in these two phase. For comparison, the GRT/PP blends with and without sulfur crosslinking agent was prepared as well. All these blends showed low impact strength, which was nearly the same as that of PP. It can be concluded that RTR plays an important role in toughening of PP by thorough dispersion into the PP matrix. Furthermore, during dynamic vulcanization by MA/DCP, the crosslinked rubber phase become finer and is uniformly distributed in the PP matrix thus attaining a stable morphology.

Punnarak et al. [23] studied a dynamic vulcanization of reclaimed tire rubber (RTR) and HDPE blends. The effect of blend ratio, methods of vulcanization, i.e.,

sulphur, peroxide, and mixed system and the addition of compatibilizer on mechanical, thermal, and rheological properties were investigated. The blend with highest impact strength was obtained from 50/50 RTR/HDPE vulcanized by sulphur. Increasing the RTR content to more than 50% resulted in a decrease in the impact strength of blend, most likely due to the increasing carbon black content. For tensile strength, the presence of rubber and carbon black, however, unavoidably caused a drop in this property. Comparing among three methods of vulcanization, sulphur system seems to be the most effective method.

Liu et al. [24] studied a thermoplastic vulcanizate (TPV) of ethylene-propylene-diene (EPDM) and polyamide (PA) with excellent mechanical properties prepared by dynamic vulcanization. The effects of the vulcanizing agents, compatibilizer, PA content, aging and reprocessing on mechanical properties of EPDM/PA thermoplastic vulcanizate were investigated. Thermoplastic vulcanizate of EPDM and PA compatibilized by chlorinated polyethylene (CPE) was prepared by dynamic vulcanization. The experimental results show that CPE has a better performance for compatibilizing the EPDM/PA TPV. EPDM/PA TPV using sulfur as a vulcanizing agent has higher tensile strength and elongation than that of the TPV using brominated *tert*-phenolic resin or peroxides as a curative. Tensile strength and elongation of the EPDM/PA TPV increase with increasing the PA content. The most suitable PA content is 35wt% for the TPV having the characteristics of an elastomer. The result of DMTA indicates that the EPDM/CPE/PA is still a immiscible blending system. The T_gs of the components of EPDM/CPE/PA TPV remains largely unaltered but the T_g of PA was shifted with increasing CPE content towards higher temperature, and the T_g of EPDM and CPE have a slight trend to shift towards lower temperature. The average diameter of the dispersed particle is about 2 μm. The EPDM/CPE/PA TPV has good aging and reprocessing properties.

Liu et al. [25] studied the blends of ethylene propylene diene terpolymer (EPDM) rubber with thermoplastic polyolefin such as low-density polyethylene (LDPE), high-density polyethylene (HDPE), high molecular weight polypropylene (PP), and polypropylene random copolymer grade (PP-R) were prepared by melt mixing. Tensile strength and hardness values increase, whereas elongation at break percentages decrease with increasing PP-R thermoplastic content in the EPDM

blends. EPDM/PP-R blend in 20/80 w/w% shows the highest physico-mechanical properties with improved retained tensile strength. EPDM/LDPE blend in 80/20 w/w% imparts the highest retained elongation at break. EPDM/PP-R blend in 20/80 w/w% shows excellent retained equilibrium swelling in benzene.

Li et al. [26] studied the effect of elastomer polarity on the morphology and mechanical properties of high-density polyethylene (HDPE) and scrap powder (SRP) composites containing a polar or non-polar elastomer was investigated. The elastomer polarity influences the morphological structure of HDPE/SRP/elastomer composites. The HDPE/SRP composite containing polar EVA shown separate dispersion of SRP and EVA. The non-polar ethylene octene copolymer results in an encapsulation structure in the HDPE/SRP/POE composite.

Pracella et al. [27] studied the compatibilization and the chemical-physical characterization of blends of PET and polyolefins (HDPE, PP) obtained from post-consumer packing materials were presented. The compatibilization effect of the various functionalized polyolefins was depending on the type and concentration of functional groups and was strictly related with their reactivity toward PET in the melt. The good compatibilizing effectiveness of ethylene-glycidyl methacrylate copolymer (E-GMA) was supported by the results of mechanical tests which indicate that a considerable improvement of tensile and impact resistance could be obtained for R-PET/R-PE blends (with PET matrix) by addition of a low amount (<5pph) of E-GMA.

Abbas et al. [28] studied the recycling of rubber scrap via grinding, and identifying utilization methods that may be effective in solving the rubber scrap problem. These methods were devulcanization, surface modification, use of rubber powder in asphalt paving, or as extender, or to produce filler to reduce the cost. The scrap rubber powder could be reclaimed by the mechanochemical method. The obtained reclaims were of good quality and could be used in rubber industry. The obtained reclaims could replace 10-30% of the virgin rubber without sacrificing the basic properties of the rubber vulcanized. The surface treated scrap rubber powder improves the physicomechanical properties of rubber vulcanized to some extent and could replace 20-40% of the carbon black without sacrificing the main properties of the vulcanization. The sulphonated rubber powder could be used as ion exchanger to

clear the industrial water from was higher than acid form. The modified asphalt by fine scrap rubber powder greatly improves the performance of road pavement, especially the chemically modified rubber powder asphalt.

Scaffaro et al. [29] studied the possibility to produce secondary materials by blending recycled polyethylene (RPE) coming from greenhouses and post-consumer ground tire rubber (GTR) has been studied. The results suggest that good processability and mechanical performance can be achieved minimizing the amount of GTR in the blend and indicate that the filler-like effect and the destructuring of the GTR act on the blends as previously remarked. Finally, the injection molded samples display; in general, better mechanical properties than compression molded samples. As a general conclusion, it has been demonstrated that the thermo-mechanical activation of the destructuring of the GTR is possible even if the process could be further improved. In some blends, in fact, GTR behaves as filler with relatively low interactions with the matrix.

Nomura, et al. [30] 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 blends with less than 30 wt% EPR had the PP matrix-domain structure, whereas those with more than 40 wt% EPR had 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.

Rajalingam et al. [31] investigated the effect of GRT characteristics on toughness of LLDPE/ GRT composites. They found that the wet ambient ground GRT based composites show higher surface oxidation and gave better impact energy than cryo-ground and normal air ground GRT based composites. Smaller GRT particle size results in a small increase 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.

Sombatsompop et al. [32] investigated the effect of adding recycle PVC pipe into two commercial PVC virgin grades (virgin PVC pipe compound and virgin PVC bottle compound) on the thermal property of the PVC blends. They found that degradation temperature gradually increased with increasing PVC recyclate. For a given recycle PVC pipe loading, the degradation temperature of the virgin PVC pipe system was much higher than that of the virgin PVC bottle system. The change in the decomposition temperature value was thought to be caused by the particle compaction and densification.

Naskar et al. [33] investigated chlorinated ground rubber tire particles as filler in a plasticized polyvinylchloride to develop a melt processable rubber composition. They found surface chlorination of GRT enhances its dielectric constant. The dielectric constant of chlorinated GRT went up in the level of chlorination and reached a maximum at an optimum degree of chlorination, beyond which the value decreased. Chlorinated GRT, when molded, formed a biphasic morphology consisting of the rubbery phase and hard phase, which is formed by the dipolar interaction. In spite of the very loss nature of GRT and chlorinated GRT (compared to the PVC compound), their blends with the plasticized PVC compound did not show a high dielectric loss factor. This indicated that the blends could be used as dielectric materials.

Naskar et al. [34] also carried out an investigation in which GRT powder was maleated in an internal mixer using maleic anhydride and dicumyl peroxide at 160° C. They found that the maleic anhydride moiety in the grafted GRT existed mainly in the ionic form because of salt formed by the interaction between the unreacted ZnO remaining in GRT and the acid anhydride of the modified GRT. Maleated GRT in the thermoplastic elastomeric composition based on 60:40 EPDM: A-HDPE, where 50% of the rubber phase was replaced by the rubber hydrocarbon content of GRT, imparted greater physical properties than the nonmaleated counterpart. The composition containing acetone extracted GRT showed higher tensile strength, Young's modulus,

and 100% modulus. However, ultimate elongation and tear strength were found to be lower than the corresponding non-extracted counterpart because of the removal of the oils and stearic acid, which acted as a plasticizer in the blend.

Oderkerk et al. [35] investigated morphology development by reactive compatibilization and dynamic vulcanization of Nylon 6/EPDM blended with a high rubber fraction. They found that binary nylon 6/ rubber blends with 50 or 60 weight percent of an EPDM rubber exhibited co-continuous morphologies and thereby had relatively poor mechanical properties. Using a suitable compatibilizer EPDM-g-MA and slightly crosslinking the rubber phase with peroxide during melt-mixing, it was possible to disperse up to 60 wt% rubber in the Nylon matrix and to improve the mechanical properties markedly. These materials are called thermoplastic vulcanizates because they generally possessed good elastic properties with a thermoplastic processability.

Sombatsompop et al. [36] examined the effect of adding tire tread reclaimed rubber on the properties of two different grades natural rubber compounds with respect to the reclaimed rubber concentration and mastication time. They found that Mooney Plasticity and shear viscosity increased with reclaimed rubber content, but decreased with mastication time. The greater the molar mass of the natural rubber the higher sensitivity to change in compound viscosity due to mastication and reclaimed rubber content. The die swell was more dependent on the reclaimed rubber than the molar mass of the rubbers. For vulcanized rubber, it was also observed that 100% modulus of the rubber increased with reclaimed rubber content, but this was not the case for tensile stress and elongation at break.