

CHAPTER II

THEORETICAL BACKGROUND

2.1 Reclaimed Tire Rubber

2.1.1 Material Background

Tires become disused principally because of wear, separation and breaking of their parts. During service the tired rubber undergoes structural changes, but its properties remain as a rule relatively unchanged. Apart from rubber, the worn-out tired contain textile and metallic reinforcing materials. Hence the scrap tired supply valuable polymeric and other raw materials used by the rubber industry. At the same time they are a long term and steady environmental pollution source on account of their high resistance to the action of nature factors (such as sunlight, moisture, oxygen, microbiological influences). Thus the processing of worn out tired is of great economic and ecological importance. The most profitable way among those being put into execution in the processing of worn out tired consists in obtaining reclaim from the vulcanized rubber contained in tires. Reclaim is a soft material suitable for manufacturing operations and for vulcanization when it is treated by curing agents. It brings a saving of raw rubber and other compounding ingredients by virtue of reclaim usage in rubber compounds. It also lowers the prime cost of rubber articles and has certain processing advantages such as higher rates of mixing, extruding and calendaring the compounds and reduction of their shrinkage; diminished amounts of blistering and undermoulding in the production of moulded goods, with increased rates of cure.

2.1.2 Production of Reclaim

The production of reclaim is a complicated physio-chemical process, owing to the complexity of composition and structure of the substances concerned as well as to the diversity of influences exerted upon these substances during all the production

steps. To obtain the reclaim, various methods are employed which differ not only in character and intensity of effects produced on a rubber vulcanizate in the course of “devulcanization” but in the nature and amount of applied reclaiming agents (softeners, activators, modifiers, substances destroying the textile, etc.). Thus, the physico-chemical processes bringing about rubber degradation in the production of reclaim with different techniques are to a certain extent distinguished between themselves in both a qualitative and quantitative manner.

In general, irrespective of method used, a degradation of the rubber vulcanizate curing network occurs during reclaiming. As a result the reclaim exhibits, compared with the internal rubber vulcanizate, an increased quantity of the rubber hydrocarbon soluble in chloroform (sol-fraction) and a diminished gel-fraction content. In the course of reclaiming a partial degradation of the filler (carbon black) network takes place. As the reclaiming of rubber is carried out in the presence of low molecular products (reclaiming agents), the reclaim also contains more substances of a nonrubber nature which do not enter into the network [5].

2.1.2.1 Change of the Rubber Vulcanizate Structure

Change of the curing network in rubber vulcanizate. Breakdown of hydrocarbon chains are occur. The determination of the crosslinked molecule number in filler-free NR- and SBR- based vulcanizates and in reclaims derived from them has revealed that in reclaiming the rubbers by mechanical (on roll mills), dispersion, thermomechanical and water-cooking methods a degradation of vulcanizate molecular chains occurs; the chains of NR vulcanizates are destroyed in every case more intensive than those of SBR vulcanizates; according to the influence on the chain breakdown of NR vulcanizate the reclaiming methods are arranged in the order: thermomechanical > dispersion >= water-cooking; for a SBR vulcanizate the order is : thermomechanical > water- cooking > dispersion >= mechanical.

By their effect on the chain breakdown of filled vulcanizates the reclaiming methods form a sequence in the same order as that of their influence upon the chain breakdown of filler-free vulcanized. During reclaim production from the

butyl rubber-based vulcanized by the radiation method a breakdown of chains takes place, with the degree of chain degradation increasing with growing absorption dose. Owing to the breakdown of chains the crystallizing capacity of the rubber substance of the reclaim diminishes.

2.1.2.2 Structurization Reactions (Formation of New Network Junctions)

In an unfilled sulphurous vulcanizate, if placed in a vacuum at 180°C, after 15-30 min of heating the structurized begins to prevail over the degradation; sulphur-free vulcanizates are structurized only under these conditions. With growing amount of softener incorporated into the vulcanizate the reversal of degradation falls to become finally almost unobservable. At 150°C the effect of the thermal degradation in a sulphurous vulcanizate is stronger than at 180°C; in the presence of a softener the degradation effect at 180°C exceeds that seen at 150°C. The effect of the thermal structurization of sulphurous vulcanizates diminishes in the presence of a softener; the greater the amount of softener introduced into a vulcanizate, the smaller this effect will be. The effect of the degradation of an unfilled sulphurous SBR vulcanizate in the air at 180°C is at first stronger than that produced in a vacuum. But then the reversal of degradation proceeds so intensively that the vulcanizate heated for 3 hours has the same density of reticulation as has the vulcanizate before heating.

In reclaiming the sulphurous NR, synthetic isoprene rubber (Russian abbr.:SKI), SBR, stereo specific divinyl rubber (Russian abbr.: SKD), vulcanizates by thermal-oxidative technique; the degree of the vulcanizing network degradation and the plasticity increase at the beginning of the process. However, in NR and SKI vulcanizates, if heated further, the degree of network degradation and the plasticity continue to grow though at a lower rate, while in SBR and SKD vulcanizates a reversal of degradation appears which leads to a reduced degree of their network degradation and plasticity. SBR vulcanizates again show an increase, if only a slow one, in plasticity.

In the unfilled sulphurous SBR, SKI, and NR vulcanizates (unlike the unfilled sulphur-free, peroxide and thiuram as well as filled sulphurous ones) the structurization predominates over the degradation at the beginning of the mechanical destruction process on a roll mill. Introducing a softener or activator into vulcanizates causes a suppression of structurization processes.

Thus, when reclaiming the rubber not only by high-temperature methods but also by low-temperature mechanical ones, the reactions of the vulcanizing network degradation are accompanied with secondary structurization reactions.

2.1.2.3 Contents of Total, Free, and Combined Sulphur

During the reclaiming carried out in aqueous and especially alkaline media (including the case of obtaining a reclaim by dispersive technique) the content of total sulphur can diminish, whereas in air medium reclaiming it remains virtually unchanged. The content of free sulphur decreases in the course of reclaiming by every method. The reclaim obtained at high temperatures does not contain any free sulphur. Free sulphur interacts during reclaiming with zinc compounds contained in a rubber vulcanizate to yield zinc sulphide, as well as with hydrocarbon chains. When reclaiming proceeds in an alkaline medium the free sulphur changes partially into a water-soluble state. Small quantities of combined sulphur is removed from the rubber only with the alkaline methods of reclaim production. If the reclaiming of rubber is made by steam, neutral, and thermomechanical methods the content of combined sulphur undergoes no changes. The reclaims produced at high temperatures contain a good deal more zinc sulphide as compared with the initial rubber vulcanizate. In the thermomechanical process reclaim there is more zinc sulphide than in that made with a water-cooking method.

With low-temperature methods of rubber reclaiming e.g., in the reclaim production by dispersion on roll mills, the content of zinc sulphide in the reclaim turns out to be the same as in the initial vulcanizate. The formation of zinc sulphide occurs most rapidly at the beginning of the reclaiming process, and then it

becomes markedly slower. During reclaiming the zinc sulphide is likely to arise primarily by virtue of polysulphide bonds. This is substantiated by the fact that the reclaim produced from rubber vulcanizate having no free sulphur contains considerable more zinc sulphide as compared with the initial vulcanizate. There is a direct relationship between the rate of zinc sulphide formation and the rate of reducing the content of exchangeable (polysulphide) sulphur in vulcanizates at 180°C in a vacuum and in the air. Formation of zinc sulphide in reclaiming the sulphurous rubber vulcanizates from which polysulphide sulphur has been extracted by means of sodium sulphate, as well as the sulphur-free (thiuram) vulcanizates extracted by acetone and chloroform (with chloroform one extracts from a rubber vulcanizate the zinc sulphide can be formed also owing to the sulphur of monosulphidic bonds. This is confirmed by experimental data furnished through the interaction of the zinc oxide and stearate with the dialkene (diallyl) monosulphide.

In the presence of activators, e.g. alkyl phenol sulphides, the content of zinc sulphide partially augments on account of the sulphur of and alkyl phenol sulphide. The content in a reclaim (particularly in that obtained by an alkaline method) of sulphur combined with rubber is smaller than in the initial vulcanizate. If sulphurous activators are present the content in a reclaim of the sulphur combined with hydrocarbon chains exceeds as a rule, that in a reclaim produced without any activators.

2.1.2.4 Breakdown of Sulphur Bonds

A rise of temperature along with an increase of process duration in reclaiming an unfilled NR vulcanizate by the water-cooking method will lead to the production of a reclaim with lower-sulphidity bonds. In the reclaims produced from unfilled sulphurous NR and SBR vulcanizates by the water-cooking method in the presence of an activator and a softener there is no sulphur extractable with TPP (triphenylphosphine). Sulphur is also absent for the commodity reclaim made by the water-cooking method (in a reclaim manufactured from a tread SBR vulcanizate under laboratory conditions the sulphur contained in the reclaim)

The absence of polysulphuric bonds in the reclaim originated from a water-cooking process is substantiated by studies on the alteration dynamics of changeable sulphur as well as of mono-, di-, and polysulphide crosslinks in unfilled sulphurous SKI (synthetic isoprene rubber) and SBR vulcanizates extracted with acetone, at 180°C. Polysulphidic links of the vulcanizates are almost totally destroyed after 30 to 60 min, this process occurring most rapidly during the first 15 min of heating (Figure 2.1). The SKI vulcanizates exhibit the destruction of both poly- and disulphide links. In an SBR vulcanizate the breakdown of polysulphide crosslinks is accompanied by a significant increase of the monosulphide crosslink amount; the proportion of disulphide crosslinks changes along the curve with a maximum, which indicates that the processes of formation and breakdown of these bonds proceed simultaneously. Disulphide links remaining in the SBR vulcanizates seem to be bonds of dialkyldisulphide type (Figure 2.2).

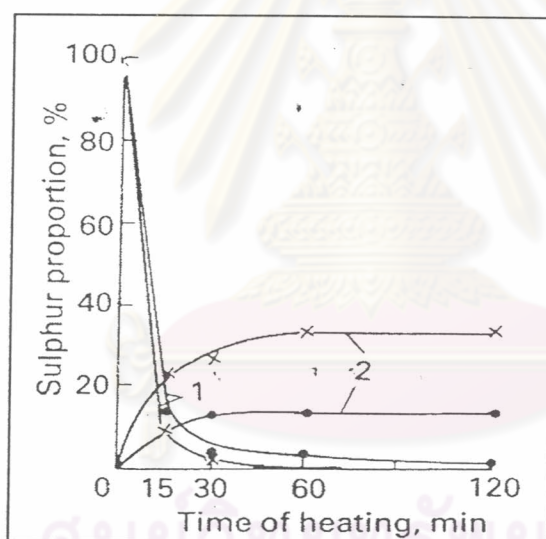


Figure 2.1 Variation in the contents of exchangeable (polysulphide) and sulphide (ZnS) sulphur in SKI and SBR vulcanizates extracted by acetone at 180 °C in air: 1) proportion of exchangeable sulphur, % of its content in the vulcanizates before heating; 2) gain in the proportion of sulphide sulphur in the vulcanizates, % of the exchangeable sulphur content before heating; x = SKI (synthetic isoprene rubber) vulcanizate; • = SBR vulcanizate.

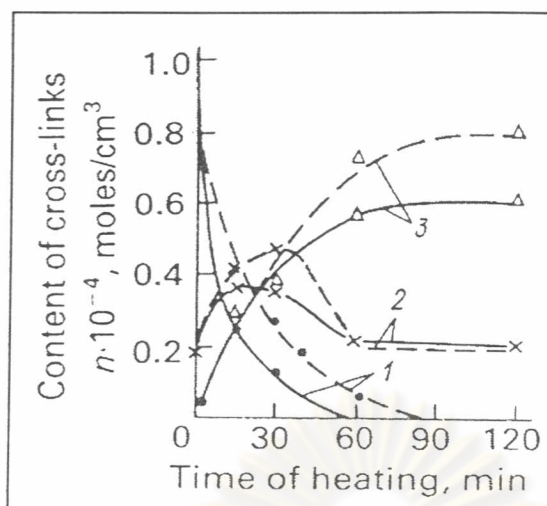


Figure 2.2 Content alteration dynamics of the mono-, di-, and polysulphide sulphur crosslinks in an unfilled sulphurous SBR vulcanizate at 180 °C in vacuum:

1) polysulphide links; 2) disulphide links; 3) monosulphide links; ___ in the presence of 3 parts by weight of trichlorophenol; ___ without additive.

As for the monosulphide links, at the high temperatures that are characteristic of water-digestion and thermomechanical methods they are not only formed but partially destroyed. The breakdown takes place owing both to the interaction of the links with zinc compounds contained in the rubber vulcanizate and to an oxidative destruction of monosulphide links; a product manufactured from a sulphurous SBR vulcanizate at 180°C in air contains less monosulphide and more disulphide bonds than does the product obtained in a vacuum.

When producing reclaim by a thermomechanical method under laboratory; and semi-commercial condition, the amount of sulphur extractable with TPP ranges from 12 to 48% of the organically combined sulphur content in the initial rubber vulcanizate. In a commercial reclaim produced by thermomechanical technique there is no sulphur extractable with, owing to the higher temperature of the process carried out under commercial conditions. Mechanical actions exerted upon the rubber vulcanizate in commercial digesters.

The reclaim produced by a dispersion process on a roll mill at a temperature not higher than 50-60°C contains the sulphur extractable with TPP in proportions only 2-7% less than the initial vulcanizate does. Considering that the main degradation factor in reclaim production by the dispersing technique is the mechanical action, and that mechanical forces affect most intensively; the breakdown of polysulphide cross-links (coupled with simultaneous formation of some disulphide cross-links), the reclaim made by the dispersion process contains somewhat less polysulphuric links compared with the initial rubber vulcanizate.

In a butyl rubber sulphur vulcanizate irradiated by accelerated electrons, the proportion of sulphur extractable with TPP diminishes; it is smaller the greater the absorption dose.

2.2 Crystallization Behavior of Polymers

It is generally accepted that crystalline polymers have superior impact properties to amorphous ones, This is due to the crystallization behavior of the polymers. Nevertheless, in the literature one can find lots of papers claiming a toughness deterioration with increasing crystallinity [6]. On the other hand, Karger-Kocsis [7] assumed that the toughness of semicrystalline polymer goes through a maximum in function of crystallinity.

2.2.1 Crystalline Structure 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. The crystalline phase of polymers consists of thin plates of 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.

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 [8]. 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 crystallization 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.

2.2.2 Crystalline Structure of Polyethylene

It is well recognized that polyethylene is a combination of crystalline and noncrystalline regions. The crystalline region is determined by the molecular structure (i.e., branching, degree of branching, types of branches, both inter- and intradistribution of branches on the molecular scale), by the molecular weight, by the molecular weight distribution, and by the fabrication conditions. The combination of all of these factors controls the crystallization kinetics of the polymer, which in turn controls the morphology. The crystallization process of polyethylene is a combination of nucleation (I) (deposition of the secondary nucleus on the crystal growth surface) and crystallite growth (G) (lateral spreading of the growing crystal on the crystal growth surface).

Variations between these two competing rates lead to three different crystalline growth mechanisms referred to as regime I, regime II, and regime III. When $I \ll G$, the result is regime I, which corresponds to the classical picture in which the spreading rate is much greater than the nucleation rate. Regime II occurs when the two rates are comparable ($I \sim G$), and regime III results when the rate of nucleation is greater than the rate of spreading ($I \gg G$). Since regime I has few nucleation sites relative to the spreading rate, crystals formed in regime I will have time for the molecules to reptate through the molten polymer and thus form large well-formed crystals. This will be the result when the melt of an unbranched polyethylene with a medium molecular weight is slowly cooled. As the molecular weight increases, or as imperfections on the backbone of the chain are added, the spreading rate is decreased. When G approaches I , the crystalline structure is regime II. Branched polyethylenes having low-density normally follow regime II, which results in smaller, less perfect crystals. Regime I polymers tend to have the molecules crystallize in the same crystallite, whereas the regime II polymers tend to have molecules incorporated into multiple crystals resulting in tie-molecules. Cooling rate can also have an effect on the regimes and resulting morphology. Slow cooling, or annealing, favors regime I. Quench cooling, however, retards the ability of the molecules to reptate and thus favors regimes II and III. One can readily see then that quench cooling would lead to more tie-molecules than slow cooling and would tend to give tougher products. This is in fact what is observed.

Slow cooling will give a higher percent crystallinity, with well-formed crystallites, whereas fast cooling will give lower total percent crystallinity and smaller, less perfect crystallites. Annealing at temperatures slightly below the melting point will give the maximum crystallinity and largest crystallites. For high-density homopolymers the crystallization rate is so fast that it is difficult, if not impossible, to form spherulites. Therefore, the common crystalline structure is that of an axillite, or sheaf. The introduction of a very small amount of comonomer will affect the crystallization kinetics enough to result in the formation of spherulites, even when quenched cooled. At lower densities spherulites are not formed when the resin is quench cooled. Basically, all fabrication techniques for polyethylene quench-cool the fabricated article, with some being much faster than others (cast film is often

extruded at $>500^{\circ}\text{F}$ and cast onto a chill roll at $<100^{\circ}\text{F}$, whereas a thick-walled rotationally molded part may take several minutes to cool). Therefore, it is also obvious that fabrication conditions have a dramatic effect on the final morphology, and thus the properties, of the fabricated part.

There is general agreement that polyethylene crystalline regions are the result of chain folding. As the molecules fold and are incorporated into the crystal, they can either (1) immediately reenter the same crystal, termed adjacent reentry, which results in tight folds; (2) they can enter the same crystal at a nonadjacent location, which results in loops; (3) they can be incorporated into another crystal resulting in tie-molecules; or (4) they can terminate in the amorphous region to form cilia. Crystals grown from solution may have a large percent of adjacent reentry events, whereas crystals formed from quench cooling a melt will have more nonadjacent reentry events. Although there has been much discussion as to which mechanism is present, it is now generally agreed that both can exist depending upon the molecular structure and crystallization conditions. The picture emerging of the molecular trajectory in rapidly cooled bulk systems is therefore one of the molecule remaining as a pseudorandom coil in which the molecule enters and reenter crystals at a myriad of locations and does so in a way which always requires some limited form of adjacent re-entry folding, the remainder of the surface comprising largely tie-molecules, cilia and some non-adjacent re-entry folds.

2.2.3 Amorphous Structure of Polyethylene (Tie-Molecules)

It has become increasingly apparent that to understand the failure mechanisms of polyethylene there must be an understanding of the noncrystalline region. Particularly important is to function of tie-molecules. Polyethylene crystallizes by a chain folding mechanism of polyethylene, as shown in Figure 2.3.

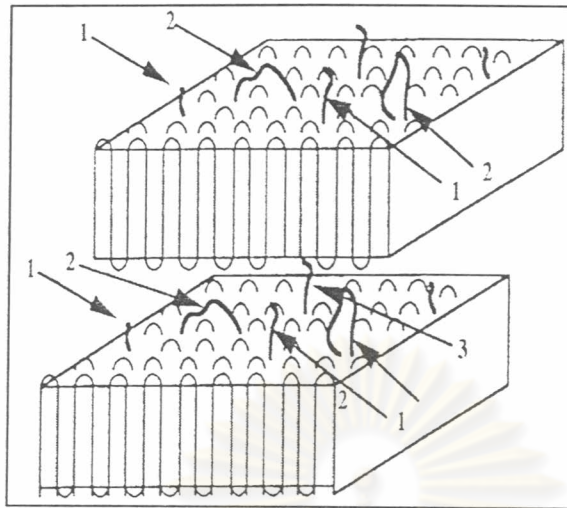


Figure 2.3 Schematic structure of polyethylene crystals: 1) cilia; 2) loops; 3) tie-molecule

As a molecule becomes a part of a crystallite, one portion becomes anchored to the crystallite and the loose end is then “reeled in,” or reptates, through the melt and is incorporated into the crystal. If for some reason a portion of the molecule is rejected from the crystal, it may then find its way into another crystal, make a loop with a molecule from another crystal, and then reenter the original crystal, or it may simply remain in the amorphous region. Molecules that are a part of two crystals or that form loops with molecules of other crystals then become tie-molecules, “tying” the two crystals together. Ends of molecules that reside in the amorphous domains may become entangled with other such molecules and form “weak” tie-molecules. The easier it is for a molecule to reptate through the polymer melt and become part of a crystal the fewer tie-molecules and the weaker the polymer. This is most likely to happen with low molecular weight high-density homopolymers. In fact, it has been shown that high-density polyethylene having a weight average molecular weight of about 20,000 or less has no measurable Izod impact strength.

Separation between adjacent crystallites, or lamellae, either through disentanglement or rupture of the tie-molecules, has been shown to be the dominant

molecular mechanism in the environmental stress cracking of polyethylene, and in slow crack growth. Tie-molecules have also been identified as exhibiting similar mechanisms in impact and tear strengths. Thus, tie-molecules are important to all strength properties of polyethylene. Brown et al. [9] have reviewed slow crack growth in polyethylene. They say that the basic failure process in slow crack growth involves the disentanglement of tie-molecules. The density of tie-molecules is the primary factor that determines the failure time. The most important quantity that distinguishes the different polyethylenes with respect to their resistance to long-time failure is the time for the beginning of brittle failure. For the same stress and temperature the time for initiating brittle failure can vary by a factor of 10^7 depending on the molecular and morphological structure of the polyethylene. They also believe that the molecular motion that controls slow crack growth is the same as that which occurs during the transition measured in the dynamic mechanical test.

Brown et al. [9] have shown that notch opening, and thus failure, is primarily dependent upon branch density. Homopolymer, with no branches, failed in less than 100 min, butene copolymer having 1.2 branches/1000°C failed in about 200 min, and butene copolymer having 2.0 branches/1000°C failed in more than 500 min, the length of the test. Copolymers with ethyl, butyl, and hexyl branches and about the same density of branches were also studied (note that this is the same density of branches, not the same density of the polymers). The activation energy was essentially independent of the length of the branches. The effect of branch density on the density of tie-molecules is related to the fact that the long period decreases as the branch density decreases. In addition to increasing the number of tie-molecules by decreasing the thickness of the lamella crystals, the branches tend to inhibit the motion of the tie-molecules by pinning them. They note that the activation energy Q is about the same for the homopolymer as for the copolymers. This observation suggests that the basic motion of disentanglement is the same. The difference is in the number of tie-molecules and the fact that many tie-molecules are pinned in the copolymer. The greater the number of tie-molecules, the smaller the disentangling force on each one, and thus the greater the strength.

Molecules that are tied by crystals would be expected to resist being disentangled. If the crystals are very thin, they offer little resistance as the tie-molecules either move through the crystal or possibly shear it. If the lamella crystals are very thick, the number of tie-molecules is reduced. Probably the optimum occurs when the spacing between the branches is about equal to the thickness of the lamella, and the molecular weight is great enough to allow the molecules to be in more than one crystal.

The influence of molecular weight on the environmental stress cracking resistant (ESCR) of PE has been shown by Haward et al. [10]. They related the molecular weight to post-yield strain hardening, and in turn related this to ESCR. A PE with $M_n=1.11 \times 10^4$ and $M_w=4.7 \times 10^4$ showed little post-yield strain hardening in a normal tensile test and exhibited a stress cracking time-to-failure T_f of 2hr; a PE with $M_n=1.55 \times 10^4$ and $M_w=1.57 \times 10^5$ showed moderate strain hardening and a stress cracking time of 180 hr, whereas a PE with $M_n=7 \times 10^5$ and $M_w=6.4 \times 10^6$ showed strong strain hardening and a $T_f > 4000$ hr. The circumstantial evidence is that there is a relationship between the degree of strain hardening and ESCR. Since strain hardening is also a function of tie-molecule density, this is additional evidence that tie-molecules are important in the strength properties of PE.

2.3 Thermoplastic Elastomers

The emergence of thermoplastic elastomers (TPE) bridges the gap between conventional elastomers and thermoplastics. They have many of the properties of elastomers, but are processable as thermoplastics. The mechanical properties of the blends such as tensile strength, impact strength are inferior to either thermoplastics or elastomers. The growth of the thermoplastic elastomer industry has now reached a high level of commercial importance, involving many new products and industrial participants and a large number of strong academic research groups.

The majority of TPEs are block or graft copolymers. The most commonly applied terminology for block polymers uses A and B represent two different

repeating units. Different block copolymers are distinguished by the number of blocks per molecule, for example,

$AmBp$	$AmBpAm$	$AmBpAmBp$	$(AmBp)n$
Diblock	Triblock	Tetrablock	Multiblock

For the various block copolymers the values of m and p as well as n are average values; thus, there is a distribution of block lengths and number of blocks along the copolymer chain. There is considerable structural versatility possible for statistical and block copolymers in terms of the relative amounts of A and B in a copolymer. For block copolymers there is the additional variation possible in the number of blocks of A and B and their block lengths (value of m and p). For example, a three-block copolymer, poly(styrene-*block*-butadiene-*block*-styrene) is written as S-B-S. If one of the blocks is itself a copolymer (e.g., ethylene-propylene rubber), the block copolymer poly(styrene-*block*-ethylene-*co*-propylene-*block*-styrene) is written as S-EP-S. Graft copolymer is one or more blocks of homopolymer B are grafted as branches onto a main chain of homopolymer A. Graft copolymers are named by inserting graft- in between the names of the corresponding homopolymers with the main chain being named first (e.g., poly A-graft-poly B)[11].



Graft copolymer

These new materials contain physical cross-links rather than chemical crosslinks. A physical crosslink can be defined as a noncovalent bond that is stable under one condition but not under another. Thermal stability is the most important case. These materials behave like cross-linked elastomers at ambient temperatures but as linear polymers at elevated temperatures, having reversible properties as the temperature is raised or lowered. The most important method of introducing physical crosslinks is through block copolymer formation. At least three blocks are required. The simplest structure contains two hard blocks (with a T_g or T_f above ambient temperature) and a soft block (with a low T_g) in the middle. The soft block is amorphous and above T_g under application temperatures, and the hard block is glassy or crystalline [12].

The thermoplastic elastomers depend on phase separation of one block from the other, which in turn depends on the very low entropy gained on mixing the blocks. The elastomeric phase must form the continuous phase to produce rubbery properties; thus the center block has a higher molecular weight than the two end blocks combined. Examples of the thermoplastic elastomers include polystyrene-block-poly-butadiene-block-polystyrene, SBS, or the saturated center block counterpart, SEBS. In the latter, the EB stands for ethylene-butylene, where a combination of 1,2 and 1,4 copolymerization of butadiene on hydrogenation presents the appearance of a random copolymer of ethylene and butylenes. Important applications of the triblock and its cousins, the starblock copolymer thermoplastic elastomers, include the rubber soles of running shoes and sneakers [13] and hot melt adhesives. In the former application, sliding friction generated heat momentarily turns the elastomer into an adhesive, reducing slips and falls. When sliding stops, the sole surface cools again, regenerating the rubber.

The so-called segmented polyurethanes form thermoplastic elastomers of the (AB) type, where A is usually a polyether such as poly(ethyleneoxide) and nB contains aromatic urethane groups [14]. These polyurethanes make excellent elastic fibers that stretch about 30% and are widely used in undergarments under the trade names Spandex and Lycra.

A newer type of (AB) block copolymer, known as the poly(ether-ester) elastomers and sold as Hytrel, contains alternating blocks of poly(butylenes oxide) and butylenes terephthalate as the soft and hard blocks, respectively. Usually, $m=1$ or 2 , and $n=40-60$; thus the soft segment is much longer than the hard segment. Typical sample compositions for the poly(ether-ester)-AB-block copolymer structures. The hard blocks crystallize in this case.

2.3.1 Preparation of Elastomer-Plastic Blends by Dynamic Vulcanization

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 elastomer, 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. The procedures given below are based on the use of either a small Brabender mixer or a Haake Rheomix. In each case the mixer was fitted with cam-type rotors and optimum batch sizes were between 55 and 75 g. In a process he named dynamic vulcanization, Fischer used a dynamic vulcanization process to prepare compositions containing varying amounts of partially vulcanized ethylene-propylene-diene terpolymer (EPDM) elastomer. Large proportion of elastomer were generally used and soft compositions could be obtained. An organic peroxide was used to crosslink the elastomer in the presence of polypropylene, which was greatly damaged by the action of the peroxide [3].

Later, it was found that very strong, elastomeric compositions of EPDM and polypropylene can be prepared by dynamic vulcanization, provided that peroxide curatives are avoided. If enough plastic phase is present in the molten state, then the compositions are processable as thermoplastics. Plasticizers or extender oils and fillers can be used to expand the volume of the elastomer phase. In the molten state, a suitable plasticizer can expand the volume of the plastic or "hard" phase. Thus, the

plasticizer may act as both a processing aid at melt temperatures and also a softener at the lower temperatures of use. The dynamic vulcanization process has been applied to many elastomer-plastic combinations. It can be described as follows. Elastomer and plastic are first melt mixed, usually in an internal mixer. After a well-mixed blend has been formed, vulcanizing agents (curatives, crosslinkers) are added. Vulcanization then occurs while mixing continues. The more rapid the rate of vulcanization, the more intense the mixing must be to ensure good fabricability of the blend composition. It is convenient to follow the progress of vulcanization by monitoring mixing torque or mixing energy requirement during the process. After the mixing torque or energy curve goes through a minimum, mixing can be continued somewhat longer to improve the fabricability of the blend. After discharge from the mixer, the blend can be chopped, extruded, pelletized, injection molded, etc.

2.3.2 Properties of Blends Prepared by Dynamic Vulcanization

Dynamic vulcanization is the process of vulcanizing elastomer during its intimate melt mixing with a nonvulcanizing thermoplastic polymer. Small elastomer droplets are vulcanized to give a particulate vulcanized elastomer phase of stable domain morphology during melt processing and subsequently.

As stated earlier, the effect of the dynamic vulcanization of elastomer-plastic blends is to produce. Compositions that have improvements in permanent set, ultimate mechanical properties, fatigue resistance, hot oil resistance, high-temperature utility, melt strength, and thermoplastic fabricability. Permanent set of these compositions can be improved by only slight or partial vulcanization of the elastomer. Such compositions can be produced either by the partial vulcanization of the elastomer before its mixture with plastic or by dynamic vulcanization (during mixing with plastic) [15]. However, the other improvements can be obtained only (at least in the case of EPDM-polyolefin compositions) by dynamic vulcanization in which the elastomer is technologically fully vulcanized. The term "fully vulcanized" refers to a state of cure such that the crosslink density is at least 7×10^{-5} mol per milliliter of elastomer (determined by swelling) or that the elastomer is less than about 3% extractable by cyclohexane at 23°C [13].

2.3.3 Reactivity of Sulfur Vulcanization

The vulcanization occurred by a free radical reaction initiated with accelerator. The accelerator has an-S-N-bond for which the dissociation energy is 35 kcal/mol, that can be easily dissociated by the heat of vulcanization process over 140°C to produce-S and N- radicals. These radicals attack elemental sulfur with comparatively weak bonds rather than rubber chains to generate a sulfur radical, -Sx. The sulfur radicals attack allylic and benzylic hydrogens in the rubber to make crosslinks. This is simply explained by comparison of the related bond dissociation energies of sulfur, and allylic and benzylic hydrogens are 54, 77 and 77.5 kcal/mol, respectively. Hereafter, in referring to allylic hydrogen we mean allylic and benzylic hydrogen because they have nearly the same dissociation energy. Because it is easier to thermally split the lower energy bond, the accelerator first initiates sulfur radicals that react with rubber molecules successively.

An accelerator can be activated by zinc stearate that is produced from stearic acid and zinc oxide by heat during the mixing process and forms a complex with the accelerator complex forms a higher active complex with sulfur that provides a polysulfide link to the rubber molecule. This polysulfide reacts further to form mono-, di-, and cyclic sulfide bonds during vulcanization via dissociation, recombination, and rearrangement of the sulfur linkages. These various types of the sulfur linkages affect the rubber properties and tire performance.

In general, the reactivity of hydrogen in a carbon chain becomes higher in order of primary < secondary < tertiary carbon, because of the difference of stabilization of the corresponding radicals via hyperconjugation. Hydrogens of allyl and benzyl groups are much more reactive than that of tertiary carbon due to the resonance stabilization. Because NR, SBR, and BR have many allylic hydrogens, sulfur radicals can react with the allylic hydrogen much easier than with any other hydrogens in the rubber molecules. Thus, the vulcanization rate depends upon the number of allylic hydrogens [16].

2.3.4 Crosslinking with peroxides

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.

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.

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.

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.

The effect of peroxide in the melt extrusion of PP and NR could be in opposite directions in terms of a molecular weight change upon extrusion. The chain scission is preferred over crosslinking at low peroxide concentration and higher temperature since chain scission is a monomolecular reaction and has higher activation energy than has crosslinking. Practically, the peroxide-initiated degradation of PP is used for the production of controlled rheology resin with tailor-made properties.

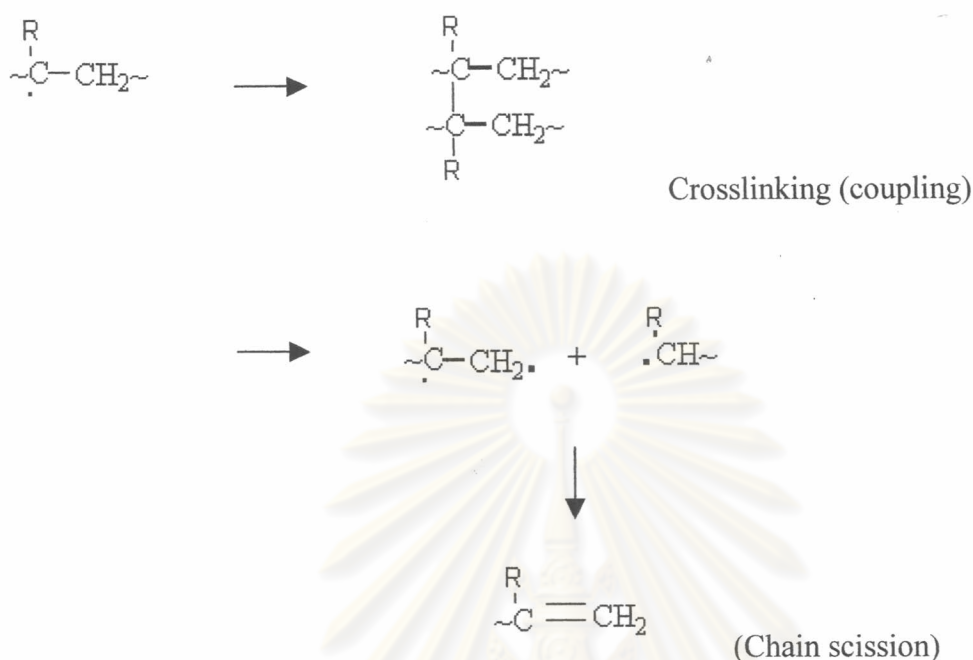
Degradation of peroxide



Generation of macroradical



Macroradical reactions



The crosslinking of PP in the presence of peroxide is facilitated by the addition of a coagent, which is typically a reactive polyfunctional monomer of methacrylate or allyl compounds. The role of coagent seems twofold, i.e., to remove the steric hindrance for coupling and to minimize the β -scission by stabilizing the macroradicals via resonance [17-19].

2.3.2 Technological Compatibilization of NBR-Polyolefin Blends by Elastomer-Plastic Graft Formation

Were it not for their gross mutual incompatibility (in the thermodynamic sense), a combination of a polyolefin resin with NBR might be a good choice of materials from which to prepare oil-resistant thermoplastic elastomer compositions by dynamic vulcanization. Early work with these materials demonstrated only marginal success in obtaining good mechanical properties for such compositions. This was probably due to the large surface energy difference between the two types of polymers. Mutual wetting between the polymers appeared incomplete; relatively large particles of cured elastomer dispersed in polyolefin resin formed during mixing

and dynamic vulcanization. An approach to technological compatibilization, in addition to dynamic vulcanization, was thus sought.

It is now generally accepted that a block copolymer can compatibilize mixtures of the “parent” homopolymers. The block copolymers act as macromolecular surfactants to promote and stabilize the emulsion of the molten homopolymers.

It has been found that a dimethylol phenolic (such as “phenolic resin” curative SP 1045) can be used to technologically compatibilize a mixture of polyolefin and NBR. This compatibilization could be the result of the formation of a block copolymer of the type visualized in Figure 2.4.

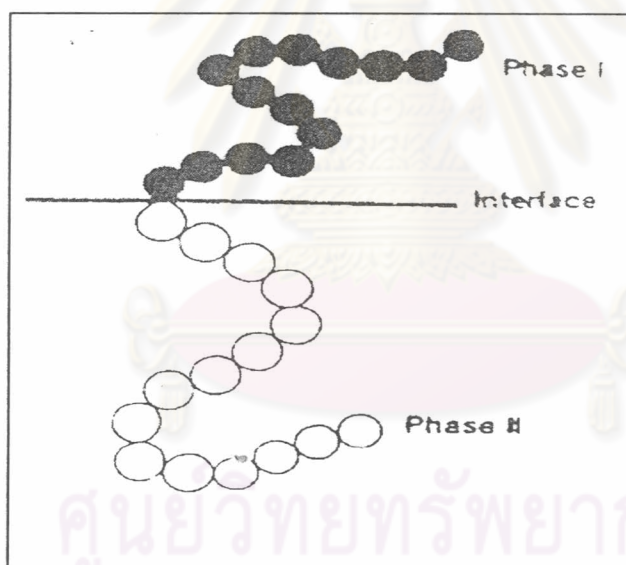


Figure 2.4 Idealized compatibilizing block copolymer molecule.

Such a compatibilizing block copolymer could be formed by the following reaction in Figure 2.5-2.7.

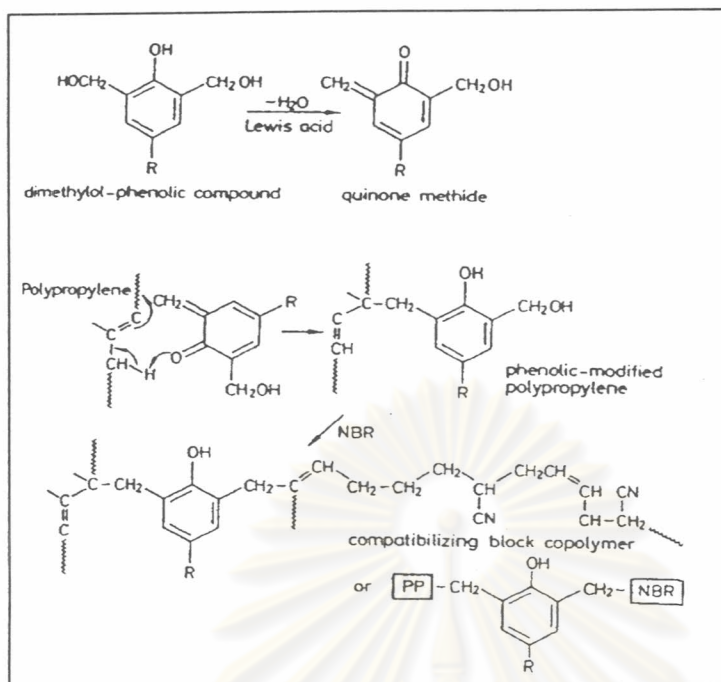


Figure 2.5 The formation of compatibilizing block copolymer from dimethylol-phenolic compound.

The scheme requires the presence of olefinic unsaturation in the polypropylene molecules. Indeed, to satisfy demands of strict polymerization stoichiometry, there is, on the average, one double bond per polypropylene molecule unless hydrogen is used to control molecular weight. The scheme is similar to that proposed long ago for the phenolic-resin curing of diene elastomers.

In practice, the polyolefin resin is treated with about 1 to 4 parts of a phenolic curative (e.g., SP 1045) per 100 parts of polyolefin resin (e.g., polypropylene) in the presence of 0.1 to 0.5 parts of a Lewis acid (e.g., SnCl_2) at a temperature of about 180 °C to 190°C. The phenolic-modified polyolefin is then melt mixed with NBR for a sufficient time for compatibilization to occur with the formation of a blend of improved homogenization. Then with continuing mixing, curative for the elastomer is added. (This can be additional demethylol phenolic resin curative.) If the NBR contains a small amount (ca. 5%) of an amine-terminated liquid NBR, ATBN(e.g., Hycar 1300X16, B.F. Goodrich Co.), then the properties of the compatibilized blend are even better.

The formation of polymer-polymer grafts can be accomplished by a number of other chemical means, in addition to the above use of dimethylol phenolic derivatives. In some cases the results are even better. Such a case is the use of maleic-modified polypropylene to form the block-polymeric compatibilizing agent by reaction with the amine-terminated liquid NBR. In this case, polypropylene is modified by the action of either maleic acid or maleic anhydride in the presence of decomposing organic peroxide. During the process, the molecular weight of the polypropylene becomes greatly reduced as the molecules thereof acquire pendant succinic anhydride groups:

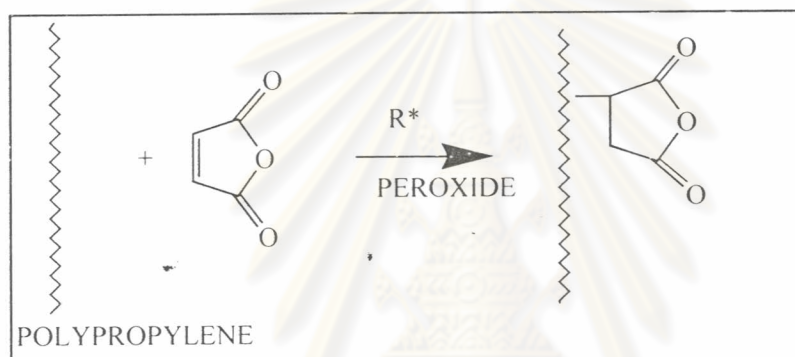


Figure 2.6 The formation of maleic-modified polypropylene.

If part of the polypropylene in a NBR-polypropylene composition is maleic-modified, and if part of the NBR is amine terminated, then compatibilizing amounts of NBR-polypropylene block copolymers form in situ during melt mixing:



Figure 2.7 The formation of compatibilizing block copolymer from maleic-modified polypropylene.

Only a small amount of compatibilizing block copolymer is needed to obtain a substantial improvement in the properties of a blend. Compositions in which 10% of the polypropylene was modified by the action of 5 parts of maleic anhydride in the presence of 0.87 parts of Lupersol-101 peroxide per 100 parts of polypropylene at 180°C to 190°C. Varying amounts of the NBR were replaced by amine-terminated liquid NBR. Since the maleic-modified polypropylene was generally in stoichiometric excess, it can be assumed that essentially as of the amine-terminated elastomer was grafted to some of the polypropylene. After each compatibilized blend was prepared, it was dynamically vulcanized and subjected to the usual treatment for molding and testing [3].

2.3.6 Effect of Compatibilization

The addition of suitably selected compatibilizers to immiscible blends should (1) reduce the interfacial energy of the phases, (2) permit a finer dispersion while mixing, (3) provide a measure of stability against gross phase segregation, and (4) result in improved interfacial adhesion. In polymer blends the physical properties are always affected by the resulting morphology of the compatibilized blends. The effect of maleic anhydride-modified polypropylene and phenolic-modified polypropylene as compatibilizers on the morphology of the 70/30 PP/NBR blend showed that the size of the dispersed NBR phase decreases with the addition of compatibilizers. This reduction in particle size with the addition of modified polymers is due to the reduction in interfacial tension between dispersed NBR phase and the polypropylene matrix.

The average domain size of the compatibilized blend was a function of the compatibilizer concentration. The average domain size of the unmodified blend is 5.87 μm . In the case of MA-PP causes a reduction in domain size of 35%. Further addition of MA-PP does not change the domain size considerably, but a leveling off is observed. In Ph-PP compatibilized blends, the average diameter of the dispersed NBR phase decreases up to the addition of 10 wt % Ph-PP. By the addition of 10 wt % Ph-PP, the domain size is reduced by 77% of the domain size of the unmodified blend. However, further addition of a compatibilizer increases the domain size. The

equilibrium concentration at which the domain size leveled off can be considered as the so-called critical micelle concentration (CMC), i.e., the concentration at which micelles are formed. The CMC has been estimated by the intersection of the straight lines at the low and high concentration regions. The CMC values for MAPP and Ph-PP are 1.5 and 4.5%, respectively. The CMC value indicates the critical amount of compatibilizer required to saturate the unit volume of the interface. The increase in domain size above CMC may be due to the formation of micelles of the compatibilizer at the continuous polypropylene phase. This is schematically shown in Figure 2.8.

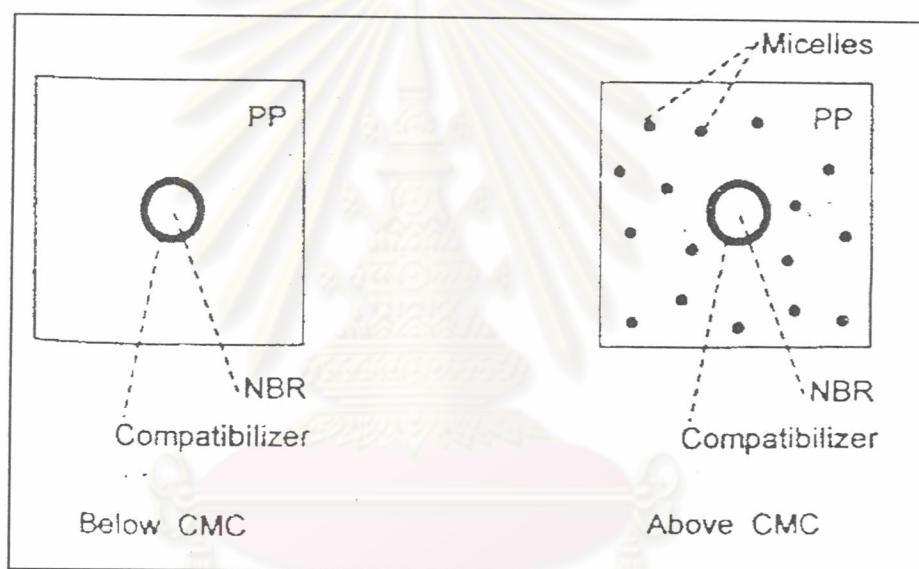


Figure 2.8 Schematic representation of the formation of micelles above critical micelle concentration.

As the micelle formation starts, some of the compatibilizer already at the interface leaves the interface. This leads to an increase in domain size [20].

2.4 Polymer Rheology [12]

Rheology is the study of the deformation and flow of matter. The range of melt viscosities ordinarily encountered in materials is given in Table 2.1. Polymer latexes and suspensions are aqueous dispersions with viscosities dependent on solid

content and additives. Polymer solutions may be much more viscous, depending on the concentration, molecular weight, and temperature.

The temperature dependence of the viscosity is most easily expressed according to the Arrhenius relationship:

$$\eta = Ae^{-B/T}$$

Where T represents the absolute temperature and A and B are constants of the liquid. The Arrhenius equation may easily be shown to be an approximation of the WLF equation far above the glass transition temperature.

Table 2.1 Viscosities of some common materials [21]

Composition	Viscosity(Pa.s.)	Consistency
Air	10^{-5}	gaseous
Water	10^{-3}	fluid
Polymer latexes	10^{-2}	fluid
Olive oil	10^{-1}	liquid
Glycerine	10^0	liquid
Golden Syrup	10^2	thick liquid
Polymer melts	10^2-10^6	toffee-like
Pitch	10^9	stiff
Plastics	10^{12}	glassy

All real liquids have both viscous and elastic components, although one or the other may predominate. For example, water behaves as a nearly perfect viscous medium, while a rubber band is a nearly perfect elastomer. A polymer solution of, for example, polyacrylamide in water may exhibit various ranges of viscoelasticity, depending on the concentration and temperature. When an elastic liquid is subjected to simple shear flow, the shear stress characteristic of ordinary viscosity was considered.

2.4.1 Shear Dependence of Viscosity

Any liquid showing deviation from Newtonian behavior is considered non-Newtonian. As soon as reliable viscometers became available, workers found departures from Newtonian behavior for polymer solutions, dispersions, and melts. In the vast majority of cases, the viscosity decreases with increasing shear rate, giving rise to what is often called “shear-thinning”.

An example for Xanthan gum solutions is given in Figure 2.9. Note especially the wide range of shear rates obtainable.

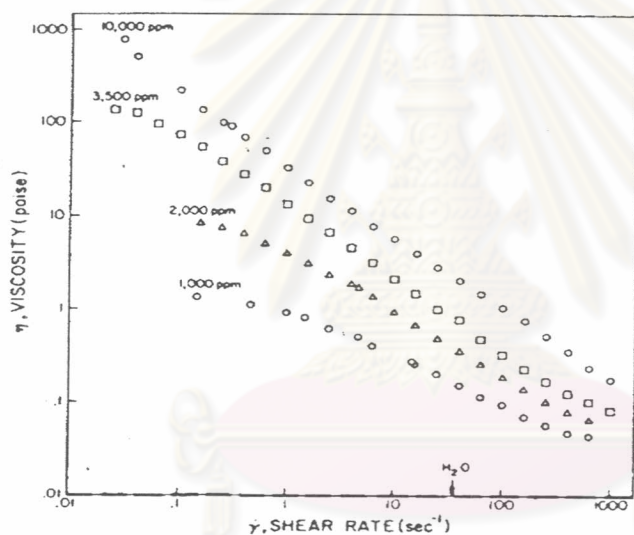


Figure 2.9 Viscosity of polymer melts and solutions.

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Table 2.2 Typical power-law parameters of a selection of well-known materials for a particular range of shear rates.

Material	$K_2(\text{Pa s}^n)$	n	Shear rate range(s^{-1})
Ball-point pen ink	10	0.85	10^0 - 10^3
Fabric conditioner	10	0.6	10^0 - 10^2
Polymer melt	10000	0.6	10^2 - 10^4
Molten chocolate	50	0.5	10^1 - 10^2
Synovial fluid	0.5	0.4	10^1 - 10^2
Toothpaste	300	0.3	10^0 - 10^3
Skin cream	250	0.1	10^0 - 10^2
Lubricating grease	1000	0.1	10^1 - 10^2

Xanthan gum is a high-molecular-weight polysaccharide ($MW=7.6 \times 10^6$ g/mol), a biopolymer used in food applications, oil recovery, and textile printing. Less than 1% of xanthan increases the viscosity of water by a factor of 10^5 at low shear rates, yet only by a factor of 10 at high shear rates. The viscosity reduction is caused by the reduced number of chain entanglements as the chains orient along the lines of flow. Note that water has 0.01 poise (1×10^{-3} Pa . sec), shown as the base line in Figure 2.9.

The general case of shear rate dependence includes a limit of constant viscosity at very low shear rates, and a lower constant viscosity at the limit of very high shear rates. While this is not often observed with polymeric materials, a suggestion of both limits can be seen in Figure 2.9. The reason is that, even at the lowest shear rates, the chains begin to orient, and entanglements slip easier. At the limit of very high shear rates, polymers degrade. An extremely useful relationship is the well known “power-law” model.

$$\eta = K_2 \dot{\gamma}^{n-1}$$

Where $\dot{\gamma}$ is the shear rate, n is the power-law index, and K_2 is called the “consistency.” When n equals zero, a form of Newton’s law is generated. The quantity $\dot{\gamma}$ is identical to ds/dt with units of reciprocal seconds. Typical values of n and k_2 for a number of materials are given in Table 2.2. Many practical materials, such as skin creams and inks, contain polymers.

Mousa et al. [40] investigated the effect of apparent shear rate on apparent shear stress for crosslinked PVC/ENR (epoxidized natural rubber) TPE. They found logarithmic plot of the shear stress versus shear rate flow curves are linear. The uncured and cured TPE may be said to follow the power law. This may be written as:

$$\tau = K(\dot{\gamma})^n$$

Where τ and $\dot{\gamma}$ represent apparent shear stress and apparent shear rate, K and n represent melt flow index and constant. The apparent shear stress increases with apparent shear rate. As the blend is cured, the apparent shear stress increased accordingly, i.e. at a fixed apparent shear rate. The addition of curatives inevitably increases the overall apparent viscosity of the melt. The increase in viscosity might be due to the influence of the curative system which results in crosslink formation. They also found the apparent viscosity decrease with an increase in apparent shear rate indicating pseudoplastic behavior of the PVC/ENR blend. The pseudoplastic nature of the PVC/ENR blends implies that the required shear stress to cause flow becomes smaller as the rate of shear increases. This also suggests that the pseudoplastic behavior might be related to the fact that molecules are progressively aligned with increasing shear rates.

2.5 End-Use Application

New techniques of melt-mixing blends of elastomers and plastics, dynamically vulcanized, and employing compatibilizing agents have greatly expanded the number of useful thermoplastic elastomers. It is probable that this expansion will continue and accelerate. Potential and proven applications of these more recently developed thermoplastic elastomers are listed here.

For mechanical rubber goods applications: caster wheels, convoluted bellows, flexible diaphragms, gaskets, seals, extruded profiles, tubing, mounts, bumpers, etc.

For under-the-hood automotive applications: air conditioning hose cover, fuel-line hose cover, vacuum tubing, vacuum connectors, seals, electrical components, etc.

For industrial hose applications: hydrolic (wire braid), agricultural spray, paint spray, plant air-water, industrial tubing, etc.

For electrical applications: plugs, strain relief, wire and cable insulation and jacketing, bushing, connectors, etc.

2.6 Literature Reviews

Kim and Burford [4] reported the use of GRT by adding to a nonpolar matrix compound based on natural rubber (NR) and to a deliberately different porality elastomer (NBR) with surface chlorination on GRT. As the GRT was already vulcanized, difficulties in blending it with other polymers exist. The difficulty leads to a decrease in mechanical properties of the filled polymer composite. Surface chlorination of GRT was used. This enhanced the mechanical performance of GRT modified NBR but reduced the properties of the NR compounds.

Rajalingam et al. [5] 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 studies 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.

Chough et al. [16] investigated the relationship between vulcanization reactivity and chemical structure using a rheometer and DSC for natural rubber,

butadiene rubber, styrene butadiene rubber and their blends. They found that the overall rate of the vulcanization was $SBR > BR > NR$. This was the same trend as the number of allylic hydrogens in the statistical repeat unit of the rubber used. The higher the content of allylic hydrogen, the lower the overall apparent activation energy is in the vulcanization. Because NR has a higher number of allylic hydrogens, implying that it is more easily attacked by a sulfur radical during the vulcanization, this rubber shows a high vulcanization rate in the early stage of the reaction.

George et al. [20] investigated the effect of compatibilization and dynamic vulcanization of PP/NBR blend at different temperature on dynamic mechanical properties. They found that the storage modulus of the blend decreased with increase in rubber content and show two T_g 's indicating the incompatibility of the system. The addition of phenolic modified polypropylene and maleic modified polypropylene improved the storage modulus of the blend at lower temperature, which indicate an increase in interfacial adhesion on the addition of these compatibilizers. At a higher concentration of these compatibilizers, the storage modulus decreases due to interfacial saturation. The enhancement in storage modulus was correlate with the change in domain size of dispersed NBR particles. The effect of dynamic vulcanization using sulfur, peroxide and mixed system on viscoelastic behavior was also studied. Among the vulcanized systems, the peroxide system shows the highest modulus, and sulfur system exhibits the lowest. The mixed system showed an intermediate behavior.

Oliphant et al. [22] reported the effect of cryogenically ground rubber tires (CGT) on some of the mechanical properties of the blends with LLDPE and HDPE. They found that the addition of CGT to LLDPE and HDPE resulted in a substantial drop in mechanical properties. Reducing the CGT particle size (from $300\mu\text{m}$ to $150\mu\text{m}$) improved mechanical properties, but generally was associated with higher grinding costs. For LLDPE, the reduction in properties can be largely overcome by precoating the CGT particles with an ethylene acrylic acid copolymer. In this manner, blends of LLDPE with 40 to 50% CGT are obtained that have impact properties approaching those of the pure PE while retaining adequate processability. These property improvements are believed to be due to an interaction between the

carboxylic acid groups on the EAA copolymer and functional groups on the CGT surface, which result in increased adhesion and greater ductility.

Naskar et al. [23] reported that blending of GRT/EPDM/acrylic modified HDPE with high rubber content (70:30 rubber/plastic and above) show poor processability and physical properties, while the compositions with higher plastic content behave like toughed plastics. However, the 60/40 rubber/plastic blend shows thermoplastic elastomer behavior. It was found that 50% of EPDM could be replaced by rubber hydrocarbon of GRT without adverse effects on the processability and physical properties of the blend.

Tsenoglou et al. [24] studied restabilization and multiple extrusion cycles at different reprocessing temperature of post used high density polyethylene, almost devoid of any stabilizing agents. They found that the process induced material degradation, attributed primarily to chain branching, was monitored by an increase in viscosity and evaluated quantitatively from melt flow rate measurement on the basis of a approximate expression derived in this study by using fundamental precepts of macromolecular rheology.

Miller et al. [25] investigated the rheological and mechanical properties for blends of recycled high density polyethylene and virgin polyolefins and attempts to correlate relative shear viscosity and relative stiffness for these blends. They found that branching content and type of branching is important, particularly for viscosity ratio. Blends with long chains, such as high flow injection molding grade materials, displayed significant variation in the viscosity ratio compared to those with short chains, such as the low flow film blowing grade materials. The PE/PP blends were either stiffened by a higher viscosity material or rendered more flexible by a lower viscosity material. The PE/PP blends were reinforced by the addition of a lower viscosity material.

Sombatsompop et al. [26] 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 recycle. 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.

Zhang et al. [27] studied the contribution of thermal volume expansion to electrical properties for high density polyethylene/ carbon black composites. They found that the volume expansion of the polymeric matrix could induce the decrease of the carbon black volume fraction, thus increasing the resistivity. However, when irradiated at different doses and temperatures, the samples showed distinctive differences in resistivity temperature behaviour, even if they contained the same carbon black volume fraction and possessed the same thermal volume expansion. HDPE crosslinking in the composites produced by electron beam irradiation limited the movability of carbon black and macromolecule chains.

Thongruang et al. [28] investigated effect of volume exclusion in HDPE blends filled with carbon black, graphite, or carbon fiber. They found that double percolation of small inorganic fillers (e.g., carbon black and graphite) in a segregated polymer phase can be achieved in blends of HDPE and ultrahigh molecular weight polyethylene. At blend composition in the vicinity of 70-80 wt% UHMWPE, the conductivity can increase by more than an order of magnitude at constant filler concentration. Similar, but less pronounced, results are realized in carbon fiber composites, which exhibit a relatively broad conductivity maximum closer to 25 wt% UHMWPE.

Lee et al. [29] investigated the electrical resistivity of HDPE loaded with carbon black blends as a function of blending time and the melt index of HDPE. They found that the positive temperature coefficient effect was improved with an increase of mixing time when the compounds are mixed for long time during the preparation process. The increment of the bound polymer, which is the physical and chemical absorption of the polymer on the carbon black surface, makes the room temperature resistivity of the compound increase. Radiation crosslinking significantly improves

the reproductivity and makes the negative temperature coefficient effect vanish for carbon black filled HDPE.

Naskar et al. [30] investigated chlorinated ground rubber tire particles were used 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 increases in the level of chlorination and reaches a maximum at an optimum degree of chlorination, beyond which it decreases. Chlorinated GRT, when molded, forms a biphasic morphology consisting of the rubbery phase and hard phase, which is formed by the dipolar interaction. In spite of the very lossy nature of GRT and chlorinated GRT (as compared to the PVC compound), their blends with the plasticized PVC compound do not show a high dielectric loss factor. This indicates that the blends can be used as dielectric material.

Naskar et al. [31] also investigated 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 exists 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 is replaced by the rubber hydrocarbon content of GRT, imparts greater physical properties than the nonmaleated counterpart. The composition containing acetone extracted GRT shows higher tensile strength, Young's modulus, and 100% modulus but lower ultimate elongation and tear strength than the corresponding nonextracted counterpart because of the removal of the oils and stearic acid acting as a plasticizer in the blend.

Radheshkumar et al. [32] 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).

Oderkerk et al. [33] investigated morphology development by reactive compatibilization and dynamic vulcanization of Nylon 6/EPDM blends with a high rubber fraction. They found that binary nylon 6/ rubber blends with 50 or 60 weight percent of an EPDM rubber exhibit co-continuous morphologies and thereby relatively poor mechanical properties. Using a suitable compatibilizer EPDM-g-MA and by 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 and exhibit good elastic properties with a thermoplastic processability.

Tripathy et al. [34] studied differential scanning calorimetry and differential thermogravimetry techniques to determine the ratio of blend components in reactive chlorinated elastomer blends. They found that determination of the blend ratio of Cl-containing elastomer blends by TGA-DTG technique is very difficult or impossible because of the common moiety of chloride 'as well as amorphous hydrocarbon structure of the elastomers. Polymer identification in the product, using TGA-DTA technique, is a futile exercise in Cl-containing elastomer blends particularly when compounds contain alkali ingredients like Calcium carbonate and Barytes as fillers. The high temperature DSC technique can successfully be used in this type of blend ratio. The concept of best curve fit would be utilized successfully, with minimum error, for the blend ratio determination of the unknown commercial samples containing highly polar groups in the presence of reactive carbon black as filler.

Sombatsompop et al. [35] examined the effect of addition of tired 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.

Tantayanon et al. [36] 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 were 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.

O.P. Grigoryeva et al. [37] investigated structure and property relationships of High-performance thermoplastic elastomers (TPEs), based on recycled high-density polyethylene (HDPE), olefinic type ethylene-propylene-diene monomer rubber (EPDM), and ground tire rubber (GTR) treated with bitumen, were prepared by using dynamic vulcanization technology. It was established that special pretreatment of GTR by bitumen confers outstanding mechanical properties on the resulting TPEs. TPEs containing GTR pretreated by bitumen, exhibit thermal behavior similar to that of the HDPE/EPDM basic blend in the temperature region up to about 340 °C. Rheological measurements showed that bitumen acts as an effective plasticizer for the GTR-containing TPEs. SEM, DSC, and DMTA results revealed improved adhesion

between the particles of GTR treated by bitumen and the surrounding thermoplastic matrix, compared to that of the untreated GTR particles. It was concluded that bitumen acts as an effective devulcanizing agent in the GTR treatment stage. In the following steps of TPE production, bitumen acts simultaneously as a curing agent for the rubber components (EPDM/GTR) and as a compatibilizer for the blend components. GTR-containing TPEs, prepared by extrusion technology, were reprocessed (by passing through the extruder six times) without any observable changes in their tensile properties, thermal stability, and melt viscosity.



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