CHARPTER II

Theory and Literature Reviews

In the recent years, the safe disposal and reuse of industrial and post consumer rubber wastes (i.e., tires, tubes, hoses, conveyor belts, etc) are serious challenges to environmental safety and public health. These materials cannot return to the ecological environment through natural biological degradation, hydrolyzation or decomposition like plants or animals, because they degrade very slowly. Rubber wastes posses a crosslinked three-dimensional structure. This cross-links must be sufficiently frequent to prevent chains from sliding over each other but not frequent enough to destroy their essential flexibility [1].

In 1839, Charles Goodyear discovered that heating a mix of rubber, white lead, and sulphur resulted in a highly elastic material which was rubber cured of its problems [2]. Today, whilst curing and vulcanization are used synonymously for the sulphur crosslinking of elastomers. Since Goodyear was so successful and correct in his comments about vulcanized rubber, he also created one of the most difficult materials to recycle, as it will not melt, dissolve or lend itself to the usual methods of chemical decomposition. Interestingly, Goodyear recognized the need for methods of reuse of his spent rubber articles and in 1853 he patented the idea of adding vulcanized rubber powders to virgin unvulcanized material, a process known as regrind blending today. Most vulcanized elastomers can easily be mechanically ground to a fine particle size with minimal agglomeration. Mechanical grinding was one of the first methods developed for recycling elastomers. The quality and gradation of the crumb to be used in a new compound is dictated by the properties of desired finished product. Although the function of recycled crumb rubber in a compound is essentially that of a resilient filler, it does impart the properties of the original scrap to the new compound and is often used to impart elastic properties to plastics and thermoplastic such as asphalt road materials. Many elastomers have only limited utility in the virgin state and must be compounded with reinforcing materials and vulcanized to develop necessary physical properties.

Commercial roll mills are widely used in mechanical grinding for economically reducing vulcanized rubbers down to 50 mesh (250 μm). A proprietary process that will produce a 500 mesh (20 μm) grind has also been developed which, if economically feasible, could expand

considerably the possibilities for using vulcanized crumb rubber. Table 2.1 shows some current applications of recycled crumb rubber [3].

Table 2.1 Applications of recycled crumb rubber[3].

Applicatioin	Quantity	Purpose
Rubber compounding	$3-10^a$	Low cost; improve molding
Brake pads		Prevent fade
Plastics extender	3-50	Filler; increase elasticity
Asphalts:		
Athletic surfaces		
Hot	8-12	Impart resilience
Cold emulsion	20-80	Impart resilience
Road mixes		
Hot plant mix	2	Improve adhesion; reduce rutting and bleeding
Chip seal	20-25	Improve adhesion; reduce brittle point
SAMI	20-25	Strain absorbing membrane
Joint sealers	20-25	Increase softening point; reduce brittle point

^{a} Up to 30 parts at 20 μm fine crumb is possible.

Recently, the importance of recycling waste materials has been increasing for all industries worldwide. Rubber waste is usually generated during the manufacturing process of products for these industries and by disposal of post-consumer (retired) products, mainly including scrap tires.

2.1 Reclamation or Devulcanization – Definition [4]

Reclaiming of scrap rubber is the most desirable approach to solve the disposal problem. Reclamation is the conversion of a three dimensionally interlinked, insoluble and infusible strong thermoset polymer to a two dimensional, soft, plastic, more tacky, low modulus, processable and vulcanizable essentially thermoplastic product simulating many of the properties of virgin rubber. Recovery and recycle of rubber from used and scrap rubber

products can save some precious petroleum resources as well as solve scrap/waste rubber disposal problems.

Devulcanization of a sulfur-cured rubber is the process of cleaving, either totally or partially, of the sulfur cross-links formed during the vulcanization process. These cross-links can be poly-, di-, or monosulfidic in nature. It would be preferable for depolymerization (main chain cleavage) and main chain modification to be minimized during the process.

According to the ASTM ST P 184A, devulcanization was defined as a combination of depolymerization, oxidation, and increased plasticity. Over the years, many processes have been developed, and some have been commercialized, to reuse of vulcanized rubber. Almost all that have been commercialized have been reclaiming processes.

2.2   Early Methods of Devulcanization

As mentioned in the introduction, early methods of devulcanization were described as reclaim, since the intent was simply to reuse the material. The original purpose of reclaiming was to break down the rubber and increase plasticization, in order to reuse the rubber by employing the normal rubber processing equipment to manufacture new products.

However, the problem with reclaimed rubber, was that since the chemicals and/or heat used for the process did not discriminate, all bonds, including carbon-carbon, were attacked, so a lot of mainchain scission occurred. Because serious reduction in physical property levels always accompanies main chain scission, reclaimed rubber acted much like a process aid. Probably there was still some degree of cross-linking present, and a degree of branching indicates attacks by oxygen, and subsequent molecular weight breakdown takes place. Therefore, in the reclaiming process, much main chain scission occurs due to free radicals producing hydroperoxides by the decomposition of oxygen. Methyl substituents attached to the carbon atom, connected by the double bond, enhance the hydroperoxidation at the alpha-methylenic carbon atom. Styrene-buta-diene rubber (SBR) does not contain a substituent group; therefore, the hydroperoxidation proceeds at a different rate. Because oxygen is always present, hydroperoxides can and do form. The rate of attack, by the hydroperoxides, is different for different polymers.

The major reclaiming processes are the thermal, heater/pan, and alkali digester processes, as described in the following sections. These work well if the polymer is NR, but not if it is synthetic.

2.2.1   Thermal process

This is the oldest process and is carried out by heating rubber pieces in a pan, in an autoclave, with steam at 60 psi. The rubber is opened to the steam and air. The full process is carried out over a period of 3 to 4 hours; the temperature is 260°C for 1 hour, after which the rubber mass is cooled with water, removed, and dried, then massed on a two-roll mill, producing sheeted rubber reclaim.

2.2.2   Heater or Pan process

This process is carried out using a single-shell steam autoclave at pressure of 100 to 300 psi. Reclaiming, charring, and wetting agents as well as plasticizer/oils are used. For example, 2% ammonium persulfate or a 20% aqueous solution containing a wetting agent serving as a charring agent is mixed with the rubber pieces. Paraffinic oil (5% by weight) containing 2% each of coconut oil, fatty acid, and naphthenic oil is mixed with the waste. The material is heated in covered, 4-inch-deep pans in the autoclave for 3 hours and 15 minutes at 150 lbs. of steam, including a 15-minute warm-up. After the heating, the material is cooled, dried, and massed on a two-roll mill with 10% of a high-boiling, aromatic petroleum distillate, and strained through a 40 mesh screen.

2.3   Later Methods of Devulcanization

The methods of devulcanization developed within the last decade or so are designed to be relatively dry processes that can be done quickly, in a fabrication facility. These processes can be carried out on normal rubber-processing equipment. The devulcanization, in many of the processes, is only regeneration of the surface or close to the surface. Because the user would probably want to utilize the inherent properties of the ground rubber particles when blending them with virgin material, the following devulcanization processes will be discussed: thermal, chemical, mechanical, chemomechanical, thermomechanical, thermochemical, and biological.

2.3.1   Thermal Devulcanization

The process useS high temperatures 180° to 260°C (and sometimes higher) for lengthy periods of time. A strictly thermal process does not work well with SBR, because SBR hardens with heat, compared to NR, which degrades.

In the late 1970s, microwave devulcanization came on the scene. It was felt that if the microwave energy could be controlled closely enough so that only sulfur cross-links would be broken, it would be a viable process. But microwaves cause the material to heat up, so care had to be taken to ensure the rubber did not burn. Microwave devulcanization does not require the use of chemicals. This process was used for a time, but has fallen into disuse, mainly due to cost.

2.3.2   Chemical Devulcanization

The majority of the reclaim rubber industries uses chemical reclaiming agents for the manufacture of reclaim rubbers. These are generally organic disulfides or mercaptans which are exclusively used during mechanical working at elevated temperature. Based on these chemicals many processes have been developed and subsequently patented. Apart from these a few inorganic compounds have also been tried as reclaiming agent.

A process for chemical devulcanization was patented in 1979 and then published in 1982. This process used phase transfer catalysis to carry out the actual devulcanization at temperatures under 100°C for a period of 2 hours. According to the author, most of the cross-links were broken with minimal main chain scission.

2.3.3   Mechanical Devulcanization

Several processes are used, all of which are continuous processes. Fine scrap rubber is mixed with reclaiming chemicals and fed continuously into an extruder in which the rubber is devulcanized at 205°C for about 5 minutes. The heat is partially generated by the electrical heating of the extruder and the friction of the crumb. The devulcanized rubber is extruded from the machine in a dry form ready for refining. The reclaiming chemicals are essentially the same as those used in the pan process.

Yap [5] has patented a method for reclaiming rubber using physical means. Rubber scraps. are milled at high compression pressure and maintained at relatively low

temperature to produce pre-vulcanized state of rubber sheets without the use of any chemical reactants. Temperature of the milling process was below 100°C. The pressure being exerted by the mill rolls at close to zero nip with roll speeds at 1:1.6 ratio. Most preferably, the compression force is equivalent to 200 metric tones in weight. The pre-vulcanized rubber sheets may be moulded and re-vulcanized again using conventional chemicals and method.

Mouri [6] studied method of devulcanized rubber by using high temperature and shearing. Ethylene-propylene-diene terpolymer (EPDM) were devulcanized by using twin-screw extrusion or two-roll mills at a temperature of 180°C-350°C and applying a shearing pressure of 10-150 kg/cm^2. In this research, the use of devulcanizing agent is added to the vulcanized rubber in the devulcanizing treatment. Devulcanizing agent was selected from diallyl disulfide, dixylyl disulfide, thiophenol, and iron oxide, etc. Devulcanizing agent is used to cut sulfuric crosslinking bonds in the vulcanized rubber and to be accomplished at a temperature lower than the normal devulcanizing temperature. Reclaiming oil was selected from paraffinic process oils and naphthenic process oils, etc. Reclaiming oil used to be completed in short period of time. Both of devulcanizing agent and reclaiming oil are preventing the cutting of the main chains of the rubber molecules. The result is heated vulcanized rubber at a temperature higher than 300°C, the network concentration is less than 10%. In addition, the shearing pressure higher than 30 kg/cm^2 is applied to the vulcanized rubber in the devulcanizing treatment , the network concentration is 10% or less compared to the rubber before devulcanizing. Reclaimed rubber products are manufactured by revulcanizing and molding, into desired shapes.

2.3.4   Chemomechanical Devulcanization

The devulcanization was carried out on two-roll rubber mill at relatively low temperatures($< 80^{\circ}$C). Some of these basic rubber chemicals appear to attack the sulfur-sulfur bonds in combination with shear, reducing the cross-link density and increasing the plasticity. Since the process takes place on a two-roll mill in the presence of air, there would, in all likelihood, be a reduction in polymer molecular weight. This reduction in molecular weight would also increase plasticity.

In 1979, work was published on devulcanization using mechanical shear (i.e., a mill). The length of time of the process was quite long at 30 minutes. Thiols and disulfides were used.

Besides main chain breakdown, cross-links were opened and the viscosity was reduced (increased plasticity). This is more like reclaim than straight devulcanization because of the level of polymer chain breakdown.

In 1980, another patent was issued for a process that used many chemicals in virtually the same manner, namely shear(mills and extruders), to chemomechaincally devulcanize. Chemicals suggested were basically accelelators for example diaryl disulfide and 2-Mercaptobenzothiazole. This was done in the presence of air; therefore, main chain scission could occur.

The role of disulfide compounds and thiols used in the reclaiming process is not established till date. Adhikari et al. have proposed the following mechanism of reclaiming of rubber [2].
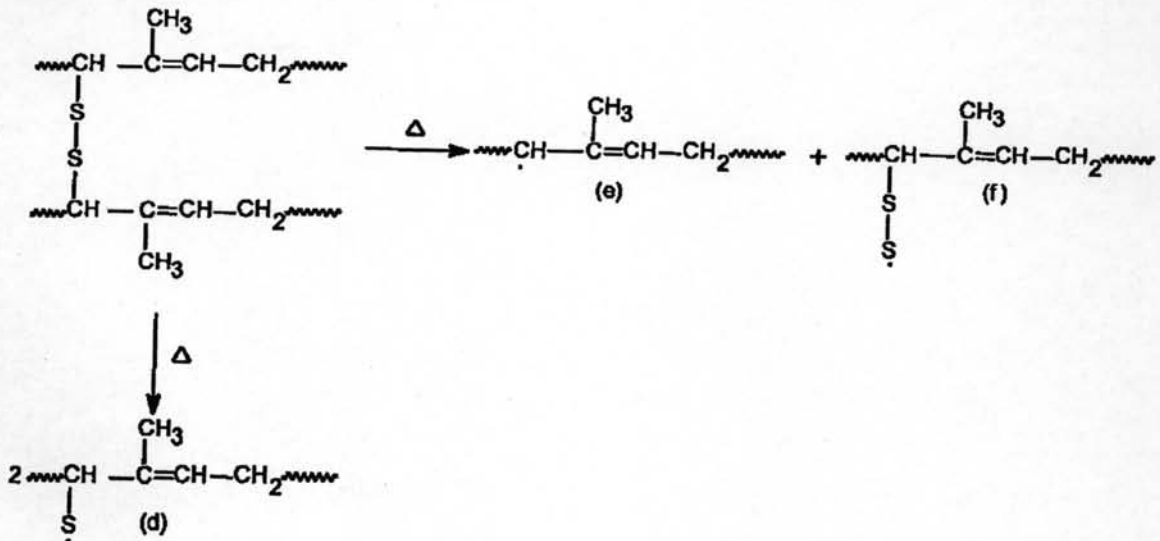
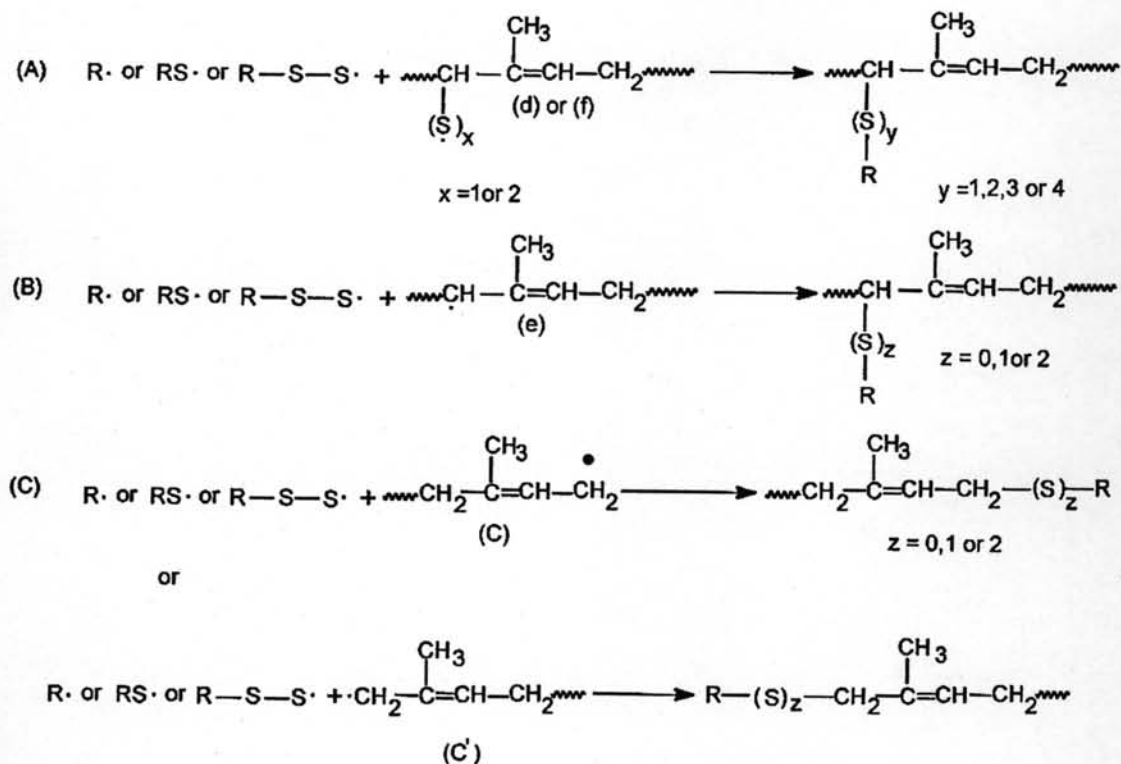Step 1: the hemolytic scission of the disulfide reclaiming agent producing sulfur radicals(a or b).
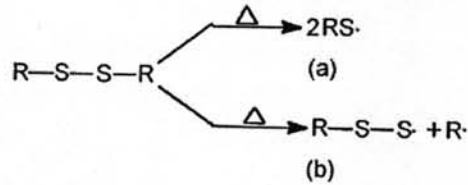
Step 2: depolymerization
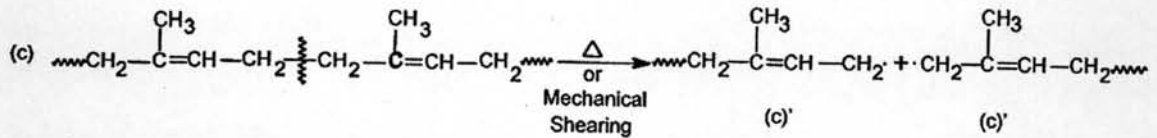
Step 3: thermal scission of sulfur crosslinks

Step 4: radical coupling reaction

(A) R· or RS· or R—S—S· + ~~~CH—C(CH₃)=CH—CH₂~~~ with (S)ₓ· substituent, (d) or (f) ⟶ ~~~CH—C(CH₃)=CH—CH₂~~~ with (S)y—R substituent

$x = 1$ or 2 $y = 1, 2, 3$ or 4

(B) R· or RS· or R—S—S· + ~~~·CH—C(CH₃)=CH—CH₂~~~ (e) ⟶ ~~~CH—C(CH₃)=CH—CH₂~~~ with (S)z—R substituent $z = 0, 1$ or 2

(C) R· or RS· or R—S—S· + ~~~CH₂—C(CH₃)=CH—CH₂· (C) ⟶ ~~~CH₂—C(CH₃)=CH—CH₂—(S)z—R $z = 0, 1$ or 2

or

R· or RS· or R—S—S· + ·CH₂—C(CH₃)=CH—CH₂~~~ ⟶ R—(S)z—CH₂—C(CH₃)=CH—CH₂~~~ (C')

When these reactions have taken place, the disulfide radicals can couple with the rubber radicals by acting as a peptizer, preventing recombination with itself and thereby maintaining the reduced molecular weight. It is not the disulfide alone that is causing the polymer or crosslink scission. Because these processes are open to the air, the oxygen, in combination with the heat and mechanical shear, probably cause the scission of both the polymers and cross-links.

D. De et al. [7] studied the process of mechanical reclaiming of ground tire rubber (GRT) by tetramethyl thiuram disulfide(TMTD) as a reclaiming agent. Reclaimed rubber was prepared by mixing TMTD within two-roll mill and at a friction ratio of 1:2 for various times intervals. The results of this investigation had revealed a definite influence of the concentration of the reclaiming agent and milling conditions on gel content and swelling ratio of the reclaim rubber. When the concentration of the reclaiming agent and milling times increased gel content was decreased swelling ratio was increased. This is due to the breakdown of crosslinks and polymer chains. The breakage of maximum crosslink bonds was obtained at 40 min milling time and for 2.75g TMTD.

G. K. Jana et al. [8] found that mechanochemical devulcanization by using thiol acid as a devulcanizing agent and mixing in two-roll mill represented an ideal method for making value added rubber products from waste rubber. Devulcanization of natural rubber vulcanizate containing three different sulfur/accelerator ratios was carried out in 90°C for 10 min with two-roll mill in presence and absence of thiol acid. Revulcanized rubber obtained by devulcanizing with thiol acid offered better mechanical properties. Increase in storage modulus and decrease in loss modulus were observed for revulcanized rubber from DMA study. The revulcanized rubbers obtained from this process had very good mechanicl properties compared with original rubber vulcanizates. The properties of revulcanized rubber markedly depended on the concentration of devulcanizing agent. With incorporation of small amount of acid, it was possible to recover more than 85% of original rubber properties.

2.3.5 Thermomechanical Devulcanization

The recycled rubber crumb is obtained by thermomechanical treatment. No chemical agents are added; the process involves just heat and/or shear. This kind of treatment has evolved into commercial processes. For example, National Rubber Industries(NRI's) process was produced Symar D. NRI investigators have shown that upon regeneration, the sol fraction increased and the average number of cross-links decreased substantially. They also found that as the regeneration proceeded, the molecular weight of the sol fraction increased and conjugated unsaturation began to be observed. These observations indicate that some definite changes are occurring along the main chain of the polymers.

2.3.6 Thermochemical Devulcanization

These methods are basically a reclaim process, but they use agents other than alkali and references therein. In the past, many used an autoclave, either steam or dry, or a kettle to carry out the process. Chemicals were used to soften or plasticize the crumb rubber. Temperature ranges from 140-200°C. All were refined on a two-roll mill after the autoclaved treatment. The length of time was again long up to 4 hour. How much of the reclaiming was due to the initial process and how much was due to the refining afterwards is not known. These processes were also rather messy and none seemed to have become commercially viable. At least not for long. All processes had to deal with the same problems; the chemicals used were

highly toxic, so after the process was completed, disposal of the spent liquor or aqueous reclaiming solution was required, unless the process was a dry one.

2.4   Principle of Microwave

Microwaves are invisible radio frequency or electromagnetic waves, which have properties that enable them to be generated and sent trough space and received or absorbed at a distance.

Another aspect of microwaves is power, which is usually measured in kilowatts. Power is the expression of how much work microwaves can perform, A kilowatt is approximately 1 BTU per second or 3400 BTUs per hour or about 3.4 pounds of stream per hour, or about ¼ calorie per second, One kilowatt of microwave power is able to boil away about three pounds of water at one atmosphere pressure and at room temperature in 1 hour. [9]

Microwave fields have certain properties (Figure 2.1). They are reflected off metals that they do not heat. Therefore, metals are used as conduits for microwaves. These conduits are called waveguides. Metals are also used for the walls of the microwave oven where they confine the microwave to a usable region.

METAL

REFLECTION

Microwave energy is reflected from metals.

Metals, Metals do not heat.

PAPER

TRANSMISSION

Many materials are transparent to microwaves and do not heat.

RUBBER

ABSORBTION

Those materials which absorb microwaves are heated. Polar rubber compounds and carbon absorber.
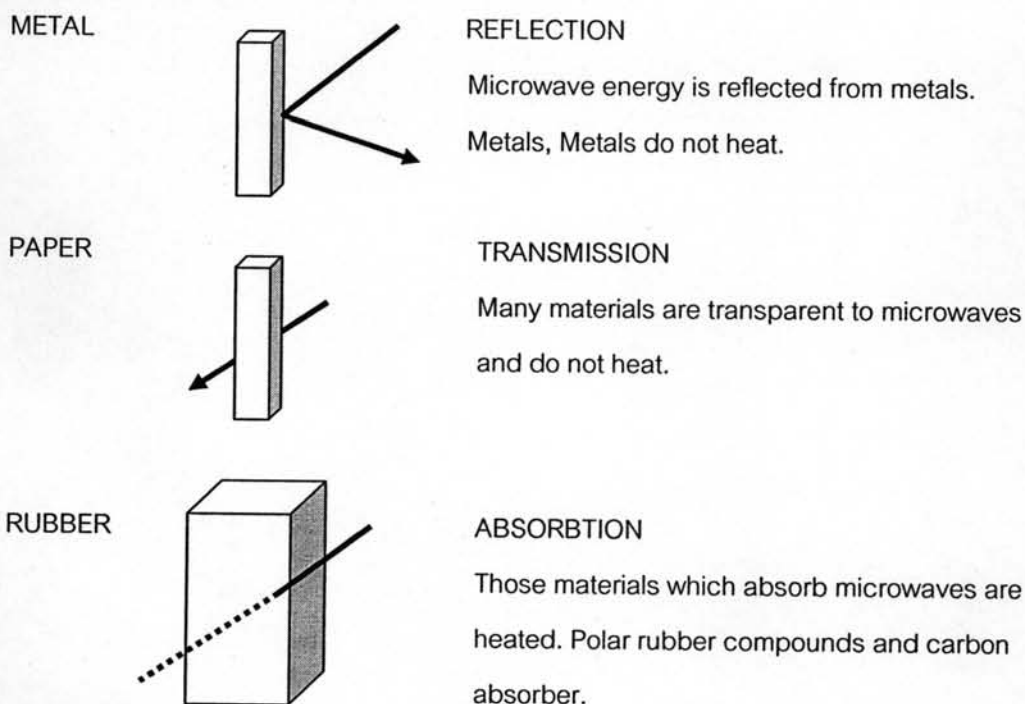
Figure 2.1 Behavior of materials that respond to microwave radiation.

Some materials have the property of transmission in a microwave field. That is, they are transparent to the microwave fields and the fields will pass through as light will pass through glass. Microwave transparent materials neither reflect microwave fields nor do they heat. Such materials are used in microwave ovens as support structure where absorption is not desired such as glass, alumina and some type of polymers (polyethylene and polypropylene).

The most important property of materials in a microwave field is the property of absorption such as water, silicon carbide and carbon black. Materials that absorb microwaves are heated.

There are essentially two mechanisms for the absorption of microwave power by materials. One is that of dipole rotation that would apply to polar materials such as nitrile and neoprene polymers. The molecules of these polar compounds are electrically neutral, but have a spatially separated positive and a negative electric charge. They appear a molecular electric "compass needles" or dipoles which react to field changes and orient and reorient themselves as the amplitude of the field increases from zero in one direction, reaches maximum, decreases back to zero and than increases to a maximum in the opposite direction. The field has both amplitude and direction at 2450 MHz. The field is alternating or reversing its direction at a rate of 2450 million times per second. The polar rubber molecule in this microwave field will attempt to rotate its negative pole in the direction of the field. It will then return to its normal state of disorder as the amplitude move to zero, and then will attempt to rotate its positive pole to the opposite direction of the field and do all this activity at a frequency of 2450 MHz.

The force exerted on the polar molecule is by definition the field strength, which is related to the amount of microwave power available. This action of molecular rotation to orderly align with the microwave field and then return to the normal state of disorder of the molecule forms part of the mechanism of microwave heating. It is instantaneous, uniform and penetrating through out the material. The microwave field has transferred energy to the rubber molecule which has transformed the energy into heat within itself. This instantaneous and deep penetrating effect is the great advantage to microwave processing of rubber since rubber is a thermal insulator. To conduct heat into the rubber in a conventional manner such as hot air is considerably slower than the microwave effect of molecular rotation.

The capacity of a substance to absorb microwave energy is expressed by its dielectric loss factor tanδ, which is represented by the dielectric loss(ε'') and the permittivity (dielectric constant) (ε').

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'}$$

The lower the loss factor, the lower the absorption capacity of the substance. Materials with a low absorption capacity can be used as neutral components, e.g., as vessel material [10].

Different materials have different abilities to absorb microwave energy. This ability is expressed in terms of dielectric loss factor. Polar rubber polymers, on the other hand, generally have the opposite characteristic, that is, in most cases they tend to become more receptive to microwave energy as they are heated. The dielectric loss factor is the important factor to identified absorbility microwave radiation of materials. The absorbility microwave radiation of materials increase when the dielectric loss factor is increase.

The second mechanism of microwave heating is that of ionic conduction. It is commonly known that non-polar rubber such as natural rubber, EPDM, SBR, etc., are not receptive to microwave energy but are made receptive by the addition of carbon black. The heating effect of non-polar rubber with carbon black is due to ionic conduction. Free ions exist at the interface of semi-conductor materials, the interface between the carbon particle and the polymer. These ions are not electrically neutral, but rather are either positives or negatively charged. As such, they are attracted by electric fields and their movement in such field constitutes a flow of current. Their velocity represents kinetic energy given to them by the microwave field. The free ions do not travel very long in the microwave field before they collide with un-ionized molecules giving up their kinetic energy in a randomized billiard ball fashion almost as fast as they obtain it. It should be noted that, as distinguished from dipole rotation, the ionic conduction heating process is not dependent to any great degree on either temperature or microwave frequency. Non-polar rubbers, therefore, which have only the addition of carbon black will tend to remain constant in their ability to receive microwave energy as they are heated. However, rubber compounds contain many ingredients and chemicals. There is, therefore, a complex mixture of materials, some of which are being heated by ionic conduction and other by dipole rotation within a given receipe.

Water, a liquid, and monomers have small molecules, whereas polymers (polar rubber) have quite large molecules. The efficiency, or amount of energy converted into heat by each cycle of dipole rotation is optimum when the time intervals of application and removal of the electric field (the microwave frequency) coincides with the time required for the build-up and decay of the induced order. The higher the temperature, the faster the build-up and decay of order imposed by the microwave field. The temperature dependent and the molecular-size dependent time for build-up and decay are called the relaxation frequency. In small water molecules the relaxation frequency is already higher than the microwave frequency and it moves further from the microwave frequency as the temperature increases, causing a slow down of energy conversion. On the other hand, large molecules, (e.g. polar rubber), have a relaxation frequency that is lower than the microwave frequency, but which gets closer to it as the temperature climbs, resulting in faster energy conversion at higher temperature.

2.5   Microwave Devulcanization [4]

In the microwave technique a controlled dose of microwave energy at specified frequency and energy level in an amount sufficient to cleave carbon-sulfur bonds and sulfur-sulfur bonds is used. Thus in this process elastomer waste can be reclaimed without depolymerization to a material capable of being recompounded and revulcanized having physical properties essentially equivalent to the original vulcanizate. This method is very much useful because it provides an economical, ecologically sound method of reusing elastomeric waste to return it to the same process and products in which it was originally generated and it produces a similar product with equivalent physical properties. The devulcanized rubber is not degraded when the material being recycled which normally takes place in the usual commercial processes currently being practiced. In microwave devulcanization process, the sulfur vulcanized elastomer containing polar groups is suitable.

Tyler et al. [11] have claimed their microwave devulcanization process as a method of pollution controlled reclaiming of sulfur vulcanized elastomer containing polar groups. The microwave energy devulcanization device generates heat at a temperature of 90-125°C. The extrudate can be used per se as a compounding stock. The process involves the impregnation of the waste rubber with an essential oil and then heat treating the impregnated material under reduced pressure with microwave radiation.

The waste material must be polar in order that the microwave energy will generate the heat necessary to devulcanize. Microwave energy between 915 and 2450 MHz and between 41 and 177 W h per pound is sufficient to cleavage all crosslink bonds but in sufficient to sever polymer chain degradation. The tensile properties of microwave devulcanized EPDM rubber, EPDM hose and IIR are shown in Table 2.3. From this table it has been found that the tensile properties of devulcanaized rubber blend is almost comparable. The cost of devulcanized hose and inner tube material waste to refined stock ready for remixing takes place in only five minutes with usually 90-95% recovery of the rubber. Therefore, it appears that this microwave technique is an unique method of reclaiming in terms of properties and fastness of the process.

Table 2.3 Physical properties of microwave devulcanized product [10]

Physical properties	EPDM				IIR			EPDM hose		
	% Devulcanized EPDM				control	50% virgin, DVC Rubber blend	DVC IIR	% Devulcanized EPDM		
	0	18	26	100				0	10	25
Tensile Strength (psi)	1600	1340	1230	1430	1520	1210	1300	1190	1080	1057
Elongation at break (%)	300	375	290	175	835	670	400	300	250	375
Hardness (shore A)	67	70	71	66	55	72	71	65	66	68

Novotny et al. patent [12] investigated devulcanization of rubber by the use of microwave energy. The devulcanization process is accomplished by the application of microwave energy to siz vulcanized rubber waste employing a controlled dose, dose rate, and temperature. The waste material must be polar in order that the microwave energy will generate the heat necessary to devulcanize. This polarity may be an inherent characteristic of the rubber

compound itself as for example polychloroprene, nitrile rubber, or chlorinated polyethylene. In addition, the polarity may be achieved as a result of some other material compounded into the rubber, for example carbon black. The size of the starting product must be reduced to a size where the material is reasonably compact when subjected to the microwave heating. The method and product employed is useful in that it provides an economical, ecologically sound method of reusing elastomeric process waste to return it to the same process and products. The elastomer are not degraded when the material being recycled.

R. Sopakayang [13] compared two types of heating modes, conventional heating and microwave heating, in terms of the consumed energy and time needed for heating the rubber. This research found that microwave heating (volumetric heating) led to more rapid temperature within rubber than conventional heating (Table 2.4). The conventional heating is able to heat only the surface of rubber because rubber is very low thermal conductivity, distributed heat within rubber is not good. Moreover, microwave heating is high penetration ability, rapid, and produce uniform heat within rubber.

Table 2.4 Effect of microwave heating and conventional heating on heatability of rubber.

Factor	Conventional heating	Microwave heating
Initial temperature ($^{\circ}$C)	32	32
Final temperature ($^{\circ}$C)	80	80
Microwave power (W)	300-800	800
Time	5 hrs	6 min

T. Kleps et al. [14] employed thermogravimetry to study the changes occurring in rubber vulcanizates during devulcanization carried out by microwave treatment. Thermoanlytical parameters such as thermal stability, the parameters of thermal destruction, and the composition of vulcanizates before and after devulcanization were determined. The vulcanizates of natural rubber(NR), butadiene-styrene rubber(SBR), and ethylene-propylene-diene rubber(EPDM) were devulcanized by treatment with different quantities of microwave energy. From the results, significant decrease in the initial temperature of decomposition(T_i) and thermal stability index at the temperature of 5% mass loss(T_5) of the vulcanizates before

and after microwave treatment were observed. It follows from the data that the changes in the thermal stability indices. From these the degree of polymer destruction can be estimated during microwave devulcanization and the optimal conditions can be obtained.

2.6   Thermoplastic elastomers(TPEs) [6]

The best way to recycle rubber products would be to devulcanize and reuse them in the rubber industry. Although processes for devulcanization, including chemical, thermal, thermochemical, and ultrasonic, have been worked out, they are costly and not suitable for commercial application. Efforts to recycle rubber by blending it with virgin rubber have met very limited success. The other alternative is to blend the crumb or ground rubber with a material having the ability to flow under heat and pressure, so that it can be shaped into useful articles at a reasonable cost. This can be accomplished by mixing finely ground rubber with plastics, along with necessary additives. Hence, rubber recycling, by blending with thermoplastic and thermoset polymers, has been a subject of interest for quite some time and has been used for manufacturing a variety of consumer products. The advantages of using rubber-plastic blends will be discussed, along with the need for compatibilization and the methods used for achieving that.

Thermoplastic elastomers(TPEs) are thermoplastic polymers which can be melt processed at elevated temperature while possessing elastomeric behaviour at their service temperature. TPEs thus contain a thermoreversible network (also called physical network) structure. This is formed by phase separation in all cases. In segmented (multi) block copolymers the "knots" of the physical network are given either by glassy or crystalline domains. They are referred as "hard phase" dispersed in a "soft" rubbery one. The latter is the matrix that is given by the flexible segments of the block copolymers. Figure 2.2 shows the highest structural diversity of the thermoplastic polyolefin elastomers. They can be directly synthetized or produced by various melt-blending procedures. The appearance of elastomeric polyolefins of different chain build-up is an advent of the metallocene catalysis.
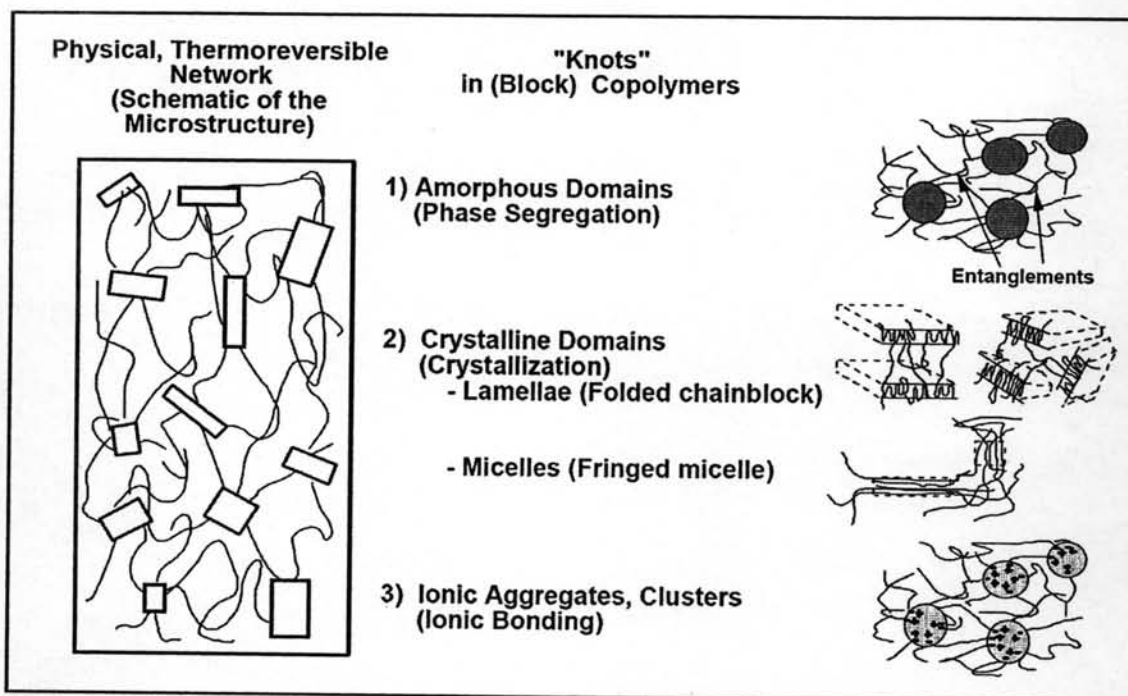
Figure 2.2 Alternative physical network structures in thermoplastic elastomers of (block) copolymer type

Blending of polyolefins with rubbers (NR, EPDM, etc) to produce thermoplastic elastomers has a long history. A further impetus to the related R&D activities was given by the invention of dynamic vulcanization.

Thermoplastic dynamic vulcanizates (TDV) are new members of the family of TPEs. TDVs are produced by dynamic curing of blends composed of thermoplastic and crosslinkable rubbers. The term "dynamic curing" means the selective curing of the rubber and its fine dispersion in the molten thermoplastic via intensive mixing/kneading. The microstructure of TDV fundamentally differs from the physical networks formed by phase segregation as shown in Figure 2.2. Note that matrix phase here is given by the "hard" thermoplastic which accounts per se the melt processability. The rubbery properties (recovery) are guaranteed by the non-yielded matrix ligaments (between the crosslinked rubber particles) and their inhomogeneous deformation. It is important to emphasize how fine the rubber particle dispersion in the thermoplastic matrix of the TDV.
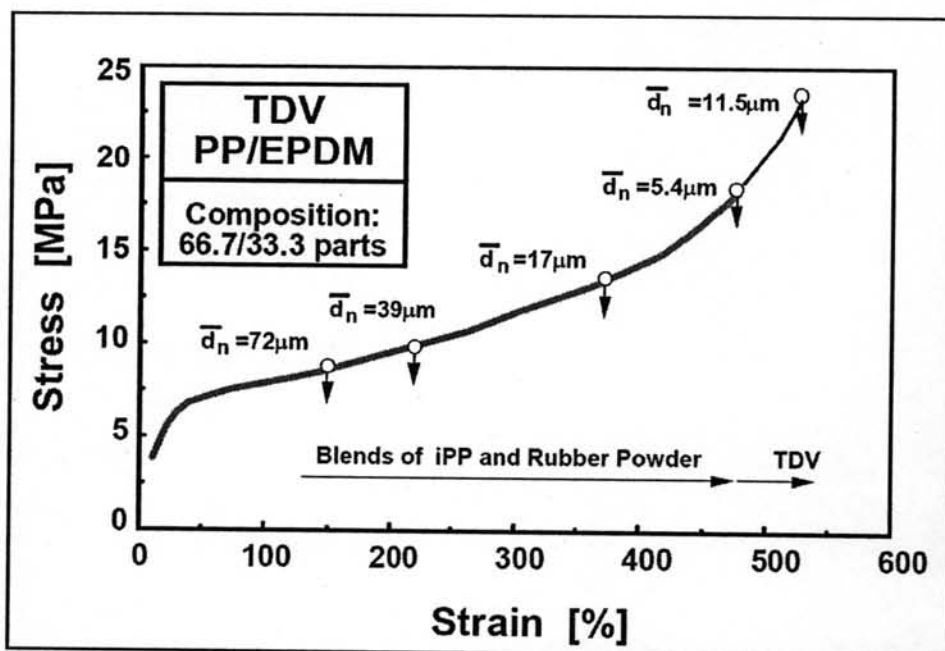
Figure 2.3   Stress-strain behavior of vulcanized rubber particle filled PP and PP-based TDV at the same composition (PP/EPDM = 2:1).

The success with melt blending including the TDV technology forced the researchers to develop TPEs with ground rubber tires (GTR) content. Figure 2.3 already shows that this is not easy task at all as the GTR size (from economic reasons between 100 and 1000 μm) never meets the required one (i.e. < 1 μm). In addition, the good bonding between the in-situ formed rubber particles and matrix, achieved by cahin partitioning (involving co-crystallization phenomena) between the thermoplastic and rubber phases, can also hardly reach with GTR without activation.

Recently, TPEs and TPV have replaced conventional rubbers in a variety of applications including appliance, automotive, medical, engineering, etc. TPEs are made by copolymerization and by blending thermoplastics with a rubbery component. TPV, on the other hand, are made by dynamically vulcanizing the rubber component in a rubber/thermoplastic blend during mixing. Both materials are processed like thermoplastics and are recyclable. Whereas blending of thermoplastics with devulcanized rubber may provide novel TPEs, blending of very fine ground rubber particles from tire waste with a suitable thermoplastic, along with adequate compatibilization, will lead to development of novel, low-cost TPVs. TPVs are currently finding wide application in automotive, electric, appliance, tools, and a variety of

personal products due to their easy processability, elastic properties, and soft-feel appeal. The increasing application of TPVs in the automotive industry is due to faster production cycles compared to vulcanized rubber, lower part weight , elimination of scrap through the use of regrind, reduced material consumption, and better environmental compliance.

In short, there is a great scope for recycling both devulcanized rubber and ground rubber by blending with plastics. Whereas devulcanized rubber will act as a second polymeric component, vulcanized ground-rubber particles will act as a low-cost organic filler or extender. Polymeric in nature, ground-rubber particles provide additional advantage over inorganic fillers such as carbon black, talc, or silica for bonding better with matrix polymer – after suitable chemical or mechanical treatment or in the presence of a compatibilizer.

P. Nevatia et al. [15] investigated physical properties, dynamic mechanical properties, and phase morphology of the thermoplastic elastmers from reclaimed rubber and scrap plastics. The blends of reclaimed natural rubber (NR) and scrap low density polyethylene (LDPE) were prepared over a wide range of compositions from 70:30 to 30:70. The blends were mixed with two-roll mill at a high temperature using steam. They observed that at a very high rubber content it becomes more difficult to process the material because it becomes sticky and the strength is poor. On the other hand, at higher plastic content the blend becomes brittle and loses the thermoplastic elastomer behavior in terms of elongation and set. With the increase in plastic content, the stress at break increases while the elongation at break decreases. A 50:50 rubber/plastic ratio was found to be the best for processability, ultimate elongation, and set properties.

2.7   Compatibilizers[3]

The key to success in blending rubber with plastics is to compatibilize the two components to get satisfactory performance. Since most polymers, including elastomers, are high-molecular weight compounds and are thermodynamically immiscible with each other, their blends undergo phase separation, with poor adhesion between the matrix and dispersed phase. The properties of such blends are often inferior to those of the individual components. At the same time, it is often desirable to combine the processing and performance characteristics of the two polymers, to develop useful products in a cost-effective manner.

Miscibility between the two polymers is best accomplished either by reducing the heat of mixing (ΔHm) or by making it negative. Heat of mixing is reduced when the two polymers are similar and their cohesive energy densities are close to each other. For regular solutions, ΔHm = $K(\delta_1 - \delta_2)^2$, where δ represents the solubility parameter (square root of cohesive energy density) and K is a constant. In other words, a blend can be technologically compatible, if the two polymers have similar intermolecular forces or if they interact or react at the phase interface. Hence, compatibilization may be described as a process that reduces the enthalpy of mixing or making it negative. This is best accomplished either by adding a third component, called a compatibilizer, or by enhancing the interaction of the two component polymers, chemically or mechanically.

The role of the compatibilization is to:

- Reduce interfacial energy and improve adhesion between phases.

- Achieve finer dispersion during mixing. In blending recycled rubber with plastics, smaller particle size of the ground rubber and deagglomeration during mixing play a major role.

- Stabilize the fine dispersion against agglomeration during processing and throughout the service life. The ultimate objective is to develop a stable morphology that will facilitate smooth stress transfer from one phase to the other and allow the product to resist failure under multiple stresses.

In general, compatibilization of two dissimilar polymeric materials is carried out either by mechanical or by chemical methods, or by both simultaneously.

An external plasticizer or a polymeric material such as a copolymer (preferably a block copolymer, which has chain units similar to both components of the blend) is added to the blend to achieve compatibilization. Di-block copolymers are preferred over single polymers or copolymers, although in many instances tri-block copolymers (such as styrene-ethylene-butylene-styrene) have also been used, as have random and graft copolymers. Block and graft copolymers reduce the interfacial tension by spreading at the interface and mixing with both phases through their component parts, which are similar to one phase or the other. Moreover, block and graft polymers, formed in-situ during mixing of the two components, assist in compatibilizing the blend.

Rajalingam et al. [17] have used precoating of GRT with functional polymers to improve the compatibility and impact resistance of GRT/PE blends. They used four different polymers: ethylene acrylic acid copolymer, SEBS terpolymer, EVA, and maleic anhydride-grafted PE as coupling agents. The GRTs were precoated with coupling agents in a Haake-Buchler Rheomix batch mixer under high shearing conditions for 3 minutes at 180°C and 150 rpm. Coated and uncoated GRTs were blended with linear low-density polyethylene(LLDPE) and HDPE at 180°C and 100 rpm. Test specimens were prepared by injection molding and were tested for impact resistance by a Rheometrics RDT-5000 instrument. Control blends of LLDPE and HDPE with functional polymers were made under similar conditions. The concentration of functional polymers varied from 0 to 15 wt% for LLDPE. Almost all blends showed maximum impact energy at a concentration of 6.7 wt% of the reactive polymer. The blend containing maleic anhydride-grafted styrene-ethylene-butylene-styrene block copolymer (SEBS) showed maximum increase. However, addition of the same coupling agents with HDPE showed either zero or a small improvement in impact energy, as shown in Table 2.4.

Table 2.4 Effect of functional polymers on the impact energy of treated PE blends.

	LLDPE		HDPE	
Blend Composition	Impact energy (J)	% Increase	Impact energy (J)	% Increase
LLDPE	14.9	-	20.6	-
PE/ethylene coglycidyl MA	16.6	4.1	20.6	-
SEBS terpolymer	16.8	5.5	20.6	0
Ethylene covinyl acetate	18.4	15.0	21.9	6.4
Maleated SEBS	18.7	17.0	21.2	3.2
Maleated PE	16.9	6.2	20.8	1

Goncharuk et al. [18] studied mechanical properties of modified thermoplastic elastomers based on used tire rubber powder and low-density polyethylene. The investigators used compatibilizing agents such as ethylene vinyl acetate(EVA) and a cross-linking agent such as dicumyl peroxide to improve the interfacial adhesion between rubber powder and LDPE. The composites containing 60 wt% rubber and 40 wt% LDPE were made by first melt-mixing

rubber with additives followed, by melt-mixing with LDPE. They reported that elastic modulus and elongation at break of 60/40 tire rubber/LDPE composites containing different amounts of EVA were improved due to the reaction of polar vinyl acetate groups and reactive groups on the surface of the rubber. Tire rubber/LDPE composites made with dicumyl peroxide resulted in an increase of both tensile strength and elongation at break, without sacrifice in elastic modulus. They believed that the improvement in mechanical properties was due to chemical bonding between polymer matrix and rubber at the interface and because of cross-linking with LDPE.

2.8.1 Carbon black [1]

Carbon black is an amorphous carbon of quasi-graphitic structure. The primary purpose for using carbon black with rubber is to reinforce it. By reinforcing is meant the enhancement of tensile strength, modulus, abrasion, and tear resistance obtained by adding the material. The excellent wear resistance of rubber with carbon black was first noticed in England in about 1912.

Carbon blacks are hygroscopic and high surface area. A common value used for the density of carbon black in rubber is 1.8 g/cm^3. This may not be accurate enough for some highly specified products.

Properties that have the most influence on rubber processing and vulcanizates are particle size, surface area and character, and structure. When formed in the furnace, carbon black particles are spherical. This spherical configuration largely carries through for thermal carbon blacks to the end product. Other carbon blacks, especially the popular furnace blacks, tend to form chains or networks of these particles fused together. Probably the most important property of a carbon black is the surface area that is accessible for reaction with rubber molecules per unit of weight, usually in square meters per gram. The term "accessible" is used because some blacks have pores whose area is included in surface area measurements but cannot be reached by rubber molecules. The chemistry of the carbon black surface is complex, and much more research must be done before its influence on mixing, curing, and vulcanizate properties can be well understood. Surface area determination is probably more important, as theories suggest that reinforcement varies directly with the surface area available for rubber-black interaction.

The dramatic increase in properties like modulus, hardness, tear strength, and abrasion resistance that appears when carbon black is added to rubber has caused many researchers to try and find the reason for this reinforcement.

Carbon black is an excellent microwave absorber, and can be heated quickly by microwave energy even if it is on a microscopic scale.

Clarke et al [19] investigated the effect of carbon black on improvement of microwave heatability of high-density polyethylene (HDPE). Blend of HDPE and between 3 and 50% w/w carbon black were prepared. Blend can be heated quickly once a certain threshold content of carbon black has been reached. The threshold content is power dependent, with values of 8.5, 6.4 and 2.2%w/w corresponding to 100 W, 200 W and 400 W of microwave power. When the carbon black content is less than 13% both tensile strength and modulus remain constants, but with further increasing content of carbon black both properties increase. Considering the balance between mechanical properties and microwave heatability, it is concluded that a composite of HDPE containing between 7% to 10%w/w carbon black is acceptable for these materials. When the composites is exposed to the microwave field, the carbon black particles are heated and can transfer their thermal energy to the matrix nearby. Therefore, if the number of particles is large enough the whole specimen can be heated.

2.10 Processing Equipments

Most of processes use some type of two-roll mill or extruder, either alone or in conjunction with chemicals and heat. Both single-screw and double-screw extruders have been used. These types of extruders produce high shear at a relatively high screw speed and high barrel temperatures. These processes are designed for high throughput.

The major problem with all these processes is not simply the high shear and high temperatures involved but rather, that the processes were carried out in the presence of air. Air causes major main chain scission and modification, which, in turn, cause a severe reduction in the physical property level of the material. Using equipment as described means that air will always be present. So radicals will be formed that attack not only the sulfur-sulfur cross-links, but also the polymer main chain; therefore, property values will always be reduced.

2.10.1 Ball Mill

A ball mill, a type of crusher, is a cylindrical device used to grind or mix materials like ores, chemicals, ceramics, and paints. Ball mill rotates around a horizontal axis, partially filled with the material to be ground plus the grinding medium. Different materials are used for media, including ceramic balls, flint pebbles, and stainless steel balls. An internal cascading effect reduces the material to a fine powder.

2.10.2 The Two-Roll Mill

The two-roll mill is similar in operation to the cracker, but it is smaller and requires less horsepower. In earlier days, several of these mills were lined up with one common drive. Until recently, two two-roll mills in tandem had a common gearbox and motor or one two-roll mill had a gearbox and motor built on a unitized stand or foundation. Figure 2.4 shows this concept and how the torque can be held constant at a given roll-to-roll speed ratio without sacrificing efficiency. It is reported that greater output can be achieved by increasing the speed of one of the rolls while holding the other constant; a fine degradation is also obtained. These mills are rebuilt and are very rugged. The energy requirements can range from 150 to 1,000 horsepower, depending on the size of the unit or the number of units operated in unison.
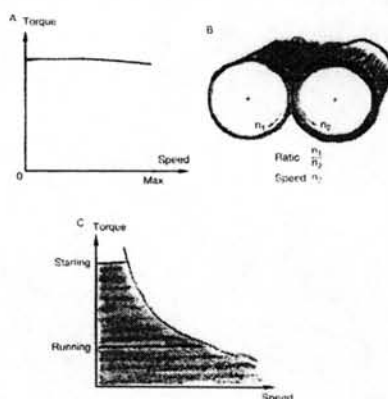

Figure 2.4 The dynamics of hydraulics A and B over a gear-driven mill C. (A) constant torque curve, (B) speed ratios varied between rolls n1 and n2, (C) lost torque of a gear-driven unit.

2.10.3 The Twin-Screw Extruder

The extruder has been found to be another excellent way to commute rubber chips. Extrusion technology has been around a long time in the plastics and rubber industries. Rubber chip are fed into the feed hopper and a screw transports the tire chips down a long

barrel. Depending on the screw design, the rubber chips intermesh with each other in a shearing action. Heat is generated and must be removed so that the produced crumb rubber material is not damage.

As rubber chunks are fed to the entrance of the Berstorff Maschinenabau extruder, the screw pulverizes the rubber as it passes through the chamber. It is claimed that the rubber is chemically altered or activated. More work needs to be done to verify this change. The extruder has a set of twin screws to pulverize the scrap rubber. Figure 2.5 illustrate the extruder concept. These units operate quietly and horsepower is a direct function of output. The uniqueness of these extruder units is that they seem to perform more efficiently with time. As the clearances between the barrel and the screw wear, production and efficiency improve. After a while, however, this does become a diminishing return and the unit needs to be serviced as with all machines.
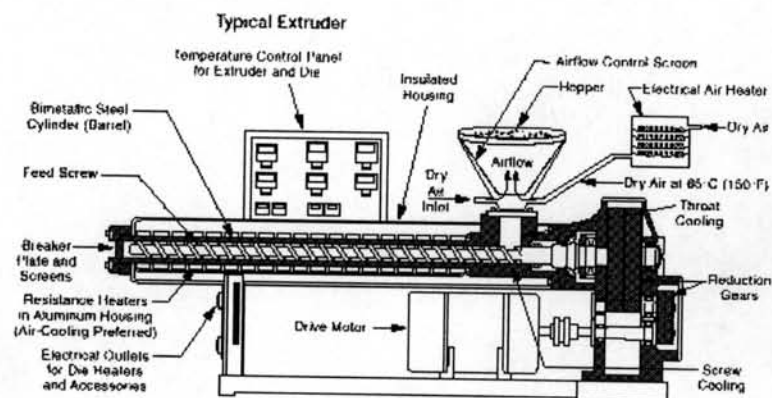
Figure 2.5 Typical extruder set-up.

2.10.4 Compression Molding

Compression molding is a process of applying heat and pressure to a plastic resin in matched dies. The resin melts due to the heat and then the pressure causes it to form into a desired shape. This is done in a compression molding press. Mainly application of compression moulding is used for molding thermoset materials; however, thermoplastic materials can also be used in the compression molding process.