

## CHAPTER II

### THEORY AND LITERATURE REVIEW

#### 2.1 Natural Rubber [3,6,8]

Natural rubber has been used for centuries by the South American Indians. Many years before anyone knew about it in Europe, the Indians collected latex from the rubber tree of their native jungles and made simple articles in molds, or dipped shapes into the rubber and allowed them to set. The first European to learn about rubber was Christopher Columbus, the famous explorer. In 1493-6, he returned from his second voyage to the new world with many strange tales. One was that the native of the island of Haiti played with a ball made from the gum of the tree. European explorers brought some of this magical stuff back with them. But, by the time it arrived in Europe, the rubber was hard and different to use, so it was through to be of little use. It came to be known as rubber in 1770 when Joseph Priestley, discovered that it would rub out pencil marks.

In 1820, Thomas Hancock, invented a machine called a masticator (a mixing mill). This machine shredded the rubber and made it soft, warm and pliable.

The cure for this was found in 1839, Charles Goodyear heated raw rubber with a chemical called sulfur. This process became known as vulcanization. It was discovered that rubber was vulcanized in a mold, the rubber article would stay in that shape when it cooled. This was a very important discovery. It opened the way for the manufacture of hundreds of different rubber goods and caused a great demand for raw rubber.

Natural rubber has been cultivated principally in Southeast Asia, especially the countries of Malaysia, Thailand and Indonesia. Where once only dense jungles and rain forests stood, natural rubber can be isolated from more than 200 different species of plants. However, only one tree source, *Hevea Brasiliensis*, is commercially significant.

Prior to World War II, natural rubber accounted for practically 100% of the total rubber usage in all products. Since then, SBR has become the largest volume general purpose rubber in use.

Commercially all natural rubber is derived from the species *Hevea brasiliensis*. The milky, rubber-bearing fluid in the tree is called latex and is obtained by a process called tapping. The latex is prevented from autocoagulation by a small amount of liquid ammonia. Latex fresh from the tree is called whole-field latex and will have 30-40 % total solids by weight.

The essence of dry natural rubber production is that whole-field latex, stabilized against coagulation by ammonia or other materials, is collected in bulk, screened to remove foreign matter, diluted, and the rubber coagulation with acid. The coagulum, a white spongy mass, is then squeezed between contrarotating rollers to remove much of the water and serum and then dried to a moisture content of less than 1 % by heat.

### 2.1.1 Natural Rubber in Thailand

The data from the Rubber Research Institute Department of Agriculture showed that in 1994 [1], Thailand produced 1,717,859 tons of natural rubber and exported 1,604,964 tons or 92.1% of total production. The remaining 132,195 tons or 7.9% was used in the country. Since it is uneconomical to transport preserved field latex over long distances to consumer countries, the normal procedure is to

change the latex form before shipment. Therefore, after the natural rubber latex has been collected from the field, it is changed into many forms of rubber, i.e. raw sheet, block rubber, crepe rubber and concentrated latex. There are various products made from different type of rubber and domestic consumption of Natural Rubber in Thailand, 1994 as shown in Table 2.1.

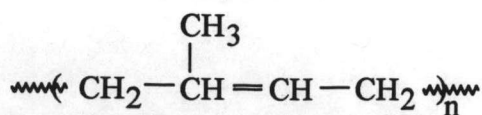
**Table 2.1** Domestic Consumption of Natural Rubber in Thailand, 1994 [1].

Type of Product	Quantities, tons
Tyre & tube for motorcars and airplanes	55,438
Tyre & tube for motorcycles and bicycles	10,308
Shoe layer	3,670
Rubber band	10,925
Glove	18,057
Elastic thread	12,002
Belt	908
Hose	1,414

Source : Thailand Rubber Statistic, Rubber Research Institute, Department of Agriculture .

### 2.1.2 Properties [9,10]

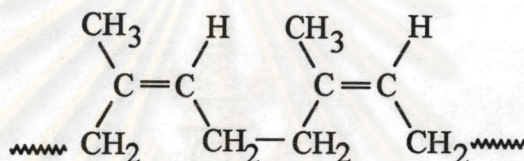
Chemically, natural rubber is cis-1,4-polyisoprene with a molecular weight in the region of one million. The molecular weight cannot be known precisely because there is always a proportion of the rubber which is insoluble. A linear, long-chain polymer with repeating isoprenic units ( $C_5H_8$ ), it has a density of 0.93 g/cm<sup>3</sup> at 20°C. Natural rubber has the following basic structure:



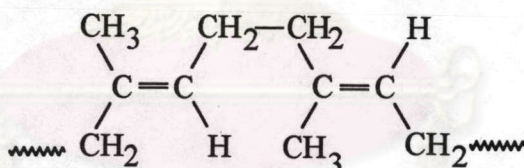
Structure of cis-1,4-polyisoprene

The naturally occurring polyisoprene are in the predominantly *cis* form of natural rubber or the *trans* form of gutta percha. The geometric isomers are as follows:

(a) *cis*-isomer (natural rubber)



(b) *trans*-isomer (gutta percha, balata and chicle)



Intensive plant breeding has produced a wide range of clonal types whose Mooney viscosity (when freshly coagulated) can vary from slightly below 50 to over 90. Mooney viscosity is a common test for toughness of a rubber; the higher value has more resistant to deformation. Paralleling this Mooney range is a very wide range of molecular weights. However, rubber in commerce is a blend of rubbers from various clones so the spread is less. It has been estimated that a random blend would have a weight average molecular weight of perhaps 2 million and a number average of 0.5 million.

Due to the blending mentioned above the Mooney viscosity for commercial rubber is approximately 60 when first made. However, due to crosslinking of aldehyde groups on the rubber molecule the Mooney viscosity rises in storage.

Because of its regularity of structure, natural rubber crystallizes when stretched or stored at low temperature below 20°C. The rate of crystallization varies with the temperature and also with the type of rubber.

The non-rubber materials in the serum from latex concentrates comprise a wide variety of chemical species. The major constituents are known to be protein and their decomposition products, fatty acid soaps, and a range of organic and inorganic salts.

A typical analysis of a natural rubber sample is given in Table 2.2. It is the acetone extract which contains various sterols, esters, and fatty acids. Certain natural rubber antioxidants are also found in the acetone extract. The protein and fatty acids are highly useful as vulcanizing activators.

**Table 2.2** Typical analysis of natural rubber [10].

Component	%
Moisture	0.6
Acetone extract	2.9
Protein ( calculated from nitrogen )	2.8
Ash	0.4
Rubber hydrocarbon	93.3
Total	100.0

Table 2.3 outlines in detail the complex variety of chemical substances present in the dry rubber and latex.

**Table 2.3** Approximate concentrations of non-rubber constituents in centrifuged latex concentrations. [3]

Constituent	% by weight of latex
Fatty acid soaps ( ammonium oleate )	0.5
Sterols and sterol esters	0.5
Proteins	0.8
Quebrachitol	0.3
Chroline	0.1
Glycerophosphate	0.1
Water-soluble carboxylic acid salts ( acetate, citrate, etc.)	0.3
Amino acids and polypeptides	0.2
Inorganic salts ( ammonium and potassium carbonate and phosphate )	0.2

### 2.1.3 Natural Rubber Latex [11]

Natural rubber latex as it emerges from the tree (field latex) has a dry rubber content of only about 30 percent. It can be preserved by the addition of ammonia or caustic alkali, but its low rubber content and high non-rubber solids content severely limits the usefulness of preserved field latex.

Latex concentration processes were developed for increasing the dry rubber content of natural latex to 60 percent or more. Of the surviving types of concentrated natural latex, nearly 90 percent is of the centrifuge latex.

Centrifuged natural latex are available commercially as high-ammonia (0.6-0.8% ammonia) and low-ammonia (0.2% ammonia) types. The former is preserved solely, or principally, with ammonia whereas the latter contains at least one other preservative in addition to ammonia.

High-ammonia latex was the original type but it is being replaced steadily by the low-ammonia varieties, a trend that is likely to continue. The reason for this trend are the increasing resistance of latex bacteria to ammonia alone, the fact that a number of latex manufacturing process require a low alkalinity and the recent introducing of stringent regulations governing ammonia concentrations in factory atmospheres. A typical properties of high-ammonia type of centrifuged NR latex is shown in Table 2.4

Natural latex dominates the production of dipped good and extruded thread and is widely used in water-based adhesives. It is also employed in the manufacture of molded and cast articles, rubberised hair and various other applications where its high strength is necessary.

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**Table 2.4** Show typical properties of high-ammonia type of centrifuged natural latex.

Properties	Tested results
Total solid content, %	61.45
Dry rubber content, %	60.04
Non-rubber solids, %	1.41
Ammonia content (on total weight), %	0.72
Ammonia content (on water phase), %	1.87
pH value	10.48
KOH number	0.51
Volatile fatty acid number (VFA)	0.0205
Mechanical stability time @ 55% TSC, sec	1040
Specific gravity at 25°C	0.9450
Magnesium content (on solids), ppm	37

Source: Thai Rubber Latex Corporation (Thailand) Public Co., Ltd. Bangplee Samutprakarn.

#### 2.1.4 Modified Natural Rubber [5,6,12]

Natural rubber has been modified in many ways. The term modified rubber can be referred to any degree of chemical modification from a very small mole percent for the purposes of introducing bound antioxidant functions, crosslinking, bonding, etc., without introducing any changes to the basic physical properties, through to the reaction of significant number of the repeat units, say 20 - 50 mol %, which does result in changes in the physical properties of rubber. Higher levels



of modification tend to alter the nature of the polymer from a rubber to more plasticlike or resinous materials.

#### Depolymerized Rubber

When raw rubber is exposed for several hours at 140°C or higher, degradation of the polymer occurs, as liquefaction of the rubber to a pourable state, and considerable reduction of molecular weight. There are commercial grades which are used for casting articles and can be vulcanized to a soft or hard rubber state. Potting compounds, binders for abrasive wheel, casting mold, etc., are examples.

#### Cyclized Rubber

In the presence of heat and acidic catalysts, rubber is transformed into a resinous material of greatly reduced unsaturation. The substances increase in density to 0.99, and exhibit a softening point of 90-120°F.

#### Chlorinated Rubber

Natural rubber readily undergoes both substitutive and addition reaction with chlorine. Although it is possible to chlorinate in the rubber latex system, the best process is the direct chlorination of a rubber solution in an inert solvent, such as carbon tetrachloride at about 80°C. The fine, white powder of chlorinated rubber is obtained by steam distillation to remove the solvent.

Fully chlorinated rubber (65 % chlorine) has a specific gravity of 1.63-1.66, and is readily soluble in aromatic hydrocarbons and chlorinated solvents. Since it is inert, chlorinated rubber is used as a base in chemically resistant paints. It is also useful as an adhesive for rubber to metal bondings.

#### AC Rubber

Better known as "anticrystallizing" natural rubber, AC rubber is an equilibrium mixture of *cis* and *trans* isomers, which interfere with the orientation, and hence crystallization of the rubber when exposed to low temperatures. It is obtained most readily in two ways: (1) addition of thiols or thiol acids to the rubber

latex at room temperature, overnight; or (2) treatment of dry rubber with sulfur dioxide for 10-15 minutes at 170-180°C.

#### Isomerized Rubber [13]

When rubber is heated with acids such as sulfuric, benzenesulfonic, or p-toluene sulfonic, a rearrangement occurs in the molecule, producing "thermoprene," used in a cement for bonding rubber to metal and in chemically resistant paints. A similar compound is produced by reacting rubber with certain metallic chlorides, such as stannic or titanium chlorides. It is used as a chemically resistant tank lining, in paints, and as a thermoplastic molding compound.

#### Deproteinized Rubber

Deproteinized rubber, called DPNR, is a useful rubber where low water absorption is wanted, vulcanizates with low creep are needed, or when more than ordinary reproducibility is required. Normally natural rubber has between 0.25 and 0.50% nitrogen as protein; deproteinized rubber only about 0.07%. One trade-off occurs here; protein matter in the rubber accelerates cure so that deproteinized rubber requires more acceleration.

Deproteinized rubber is made by treating natural rubber latex with a bioenzyme which hydrolyzes the proteins present into water-soluble forms.

#### Epoxidized Natural Rubber (ENR) [14]

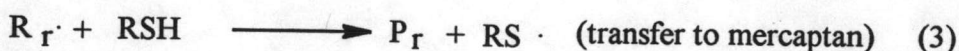
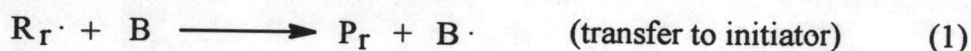
This is perhaps the most important modification of natural rubber ever made. It is produced by epoxidizing natural rubber in the latex stage by reaction with formic acid and hydrogen peroxide. ENR10, ENR25 and ENR50 contain 10 mole %, 25 mole % and 50 mole %, respectively, of epoxide groups. The introduction of epoxide groups progressively increases the glass-transition temperature of natural rubber and changes some of its properties markedly. For example, ENR50 has low air permeability, comparable to butyl rubber and good oil resistance at room temperature, comparable to medium nitrile rubber.

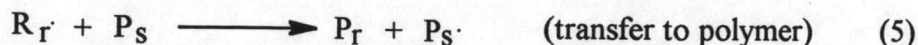
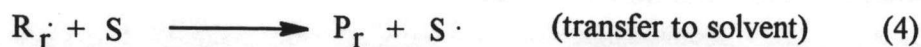
## 2.2 Synthesis of Natural Rubber Block and Graft Copolymers [5,15]

Natural rubber (NR) can be transformed into thermoplastic rubbers which are in many ways similar to some of the synthetic block copolymer thermoplastic rubbers of commercial importance. The process makes use of specialized chemistry to attach preformed chains of glassy polymer to the NR backbone and requires some degree of control over the molecular weight of the glassy polymer and the frequency of attachment to the NR backbone. The synthesis of block and graft copolymers has been extensively reviewed in recent years and there have been several reviews that are specifically directed to block and graft copolymers of natural rubber. As a polymeric chemical intermediary, natural rubber is a very versatile material and practically all of the methods that have been adopted for the synthesis of block and graft copolymers of natural *cis*-polyisoprene. The use of the following basic methods of synthesis have been reported: (i) polymer transfer; (ii) copolymerization via unsaturated groups; (iii) redox polymerizations; (iv) photochemical syntheses; (v) mechanico-chemical reactions; and (vi) high energy irradiation techniques.

### (i) Grafting of Polymers to Natural Rubber by Transfer Mechanisms

In general, during free-radical initiated polymerizations of ethylenic or vinyl monomers, e.g. methyl methacrylate, transfer reactions may take place between the growing polymer radical and initiator, monomer, 'short stop', solvent, dead polymer, or to a growing polymer radical, equations (1)-(6).

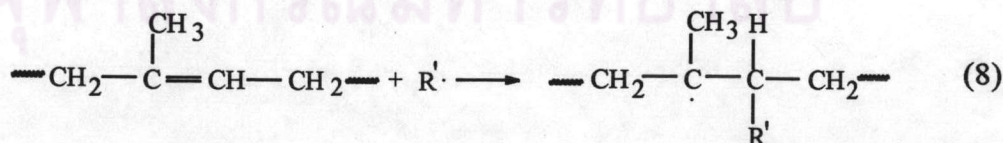
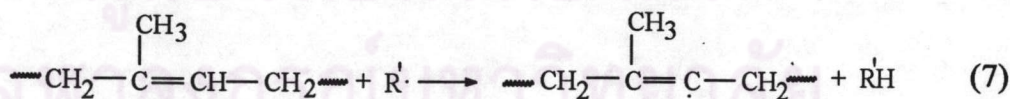




In each of these generalized mechanisms the reaction proceeds by transfer of a hydrogen or halogen atom of the transfer molecule to the growing polymer chain. The growing chain is therefore terminated but the free-radical activity is transferred to the molecule donating the hydrogen or halogen atom. In this way a number of polymer chains are formed from each initiator fragment and each chain so formed has a reduced chain length compared to that which would have been formed in the absence of the chain-transfer reaction. Although each of these reactions may take place to some extent, during block and graft copolymerization with natural rubber, it is equation (5) which is of particular importance in the synthesis of graft copolymer by transfer reactions.

### (ii) Graft Copolymerization via the Unsaturation in Natural Rubber

The addition of a growing polymer chain to unsaturated groups in natural rubber hydrocarbon has already been referred to as part of the normal grafting process, equation (8), accompanying the transfer reaction, equation (7).



### (iii) Redox polymerization

Redox polymerization are among the most popular techniques for grafting reaction and, of the possible initiator systems, ferrous ion oxidation and these based

on ceric ion reduction are widely used. In redox polymerization, a hydroperoxide or similar group is reduced to a free radical plus an anion, which the metal ion is oxidized to higher valency state, and at the same time a monomer is added. When the reducible group is attached to a polymeric chain, the free radical grafting sites thus formed on the macromolecular backbone act as initiators for graft copolymerization. This method has been used to graft methyl methacrylate to natural rubber latex. (Actually, fresh latex contain a few hydroperoxide groups per macromolecule, which can take part in grafting reactions.) Recentrifuged latex concentrate is mixed with methyl methacrylate and a solution of tetraethylene pentamine is added, followed by a small quantity of ferrous sulfate solution. The homogenized blend is allowed to stand, often overnight. The graft copolymer is isolated by coagulation. Since practically all free radical sites are formed on the rubber backbone, There is very little free poly(methyl methacrylate) in the graft system, on the other hand, some rubber chain are without grafts, since not all chain have hydroperoxy groups. Higher yields of graft copolymer are obtained by allowing the monomer to dissolve in, and equilibrate with, the latex particles before adding the amine and ferrous ion initiator. Passing oxygen (air) through the latex for several hours has been claimed to reduce the free rubber content of the polymerization product, but nitrogen purging is then necessary to prevent dissolved oxygen from acting as a polymerization inhibitor.

#### (iv) Photochemical Synthesis

Organic molecules with appropriate structure can absorb energy during irradiation by visible or ultraviolet light to be raised to so-called 'excited state'. This applies equally well to macromolecules containing photosensitive groups although there only a few common polymers capable of direct photo-excitation. In the presence of photosensitizers, however, the energy of the excited molecules may be transferred to groups attached to polymer chain which in turn degrade, as a result

of the excess energy, into polymeric free radicals which can initiate block or graft copolymerization in the presence of vinyl monomers. When the degradative process involves main-chain scission, block copolymers are formed, and when side groups are activated by the photosensitization, the process leads to graft copolymerization. Graft copolymerization by photochemical initiation has been extended to emulsion systems for grafting by both methyl methacrylate and styrene. In spite of the fact that natural rubber latex is practically opaque to ultraviolet light, good yields of graft copolymer were obtained using 1-chloranthraquinone as the sensitizer.

(v) Mechanico-Chemical Reactions

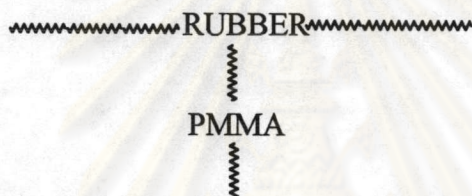
The physical scission of carbon-carbon bonds linking the atoms of the macromolecular rubber chains under the influence of an applied stress is the underlying principle which is utilized in the mechanico-chemical synthesis as block copolymers. For the mechanical scission of natural or synthetic polyisoprene the weakest bond is the  $\text{CH}_2\text{-CH}_2$  linkage and the bond energy is reduced by the contribution from the resonance energy of the stabilized polyisoprene radicals formed by mechanico-chemical scission.

(vi) High Energy Irradiation Techniques

When polymers are subjected to high energy irradiation there are two primary effects of the irradiation that may be exhibited, (i) the random loss of side groups, such as hydrogen atoms, from the polymer chains, and (ii) main chain scission. In both cases polymeric free radicals are formed which can be used directly or indirectly to synthesize graft copolymers, in the former case, and block copolymers in the latter case. The natural cis-1,4-poly(isoprene-g-methyl methacrylate) synthesized by irradiating natural rubber latex homogenized with methyl methacrylate monomer using a  $\text{Co}^{60}$  source with a field intensity of 6,000-400,000 r/hour. High grafting efficiencies were obtained and the system was practically free from homopolymeric poly(methyl methacrylate).

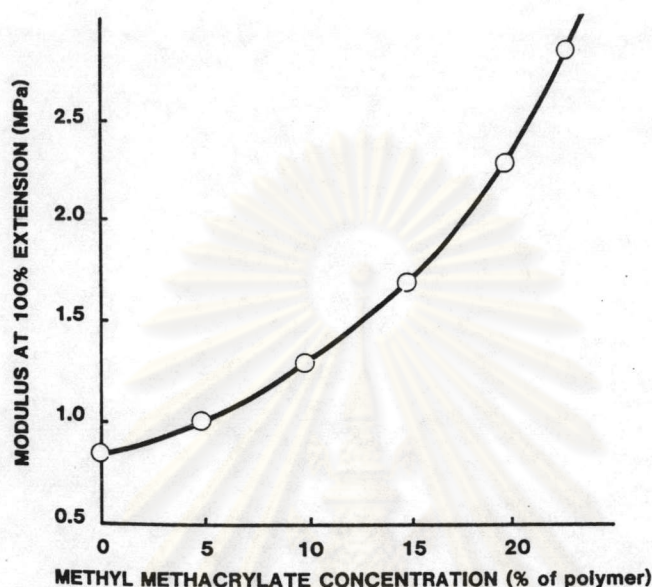
### 2.3 Poly(methyl methacrylate)-grafted Natural Rubber [12,16]

Polymer-modified forms of natural rubber can be made by the polymerization of vinyl monomers either in rubber solution or in latex. The only product of commercial significance is the 'MG' rubber in which the grafted side chains are poly(methyl methacrylate). The general structure of final rubber copolymer graft can be indicated as follows:



Poly(methyl methacrylate)-modified natural rubber has been marketed since the mid-1950s under the trade name Heveaplus. Heveaplus MM, which was a simple mixture of poly(methyl methacrylate) and natural rubber prepared by combining NR latex concentrate with the appropriate amount of poly(methyl methacrylate) dispersion to give the required rubber/polymer ratio, followed by coagulation, washing, and drying; and Heveaplus MG, which was the grafted form prepared by reacting NR latex with the required amount of methyl methacrylate monomer with *t*-butyl hydroperoxide as the polymerization initiator. After stirring in tetraethylene pentamine (as the other half of the redox system), the reaction is essentially complete in 2 hr. The product is coagulated by adding boiling water containing 0.1% calcium chloride and then sheeted out and dried. The first of these types never appeared to be of commercial interest, but the grafted type has proved useful on several counts and indeed is still in production in Malaysia. Various levels of modification can be achieved according to the proportion of grafted poly

(methyl methacrylate), and this alters the modulus of the rubber as indicated in Figure 2.1.



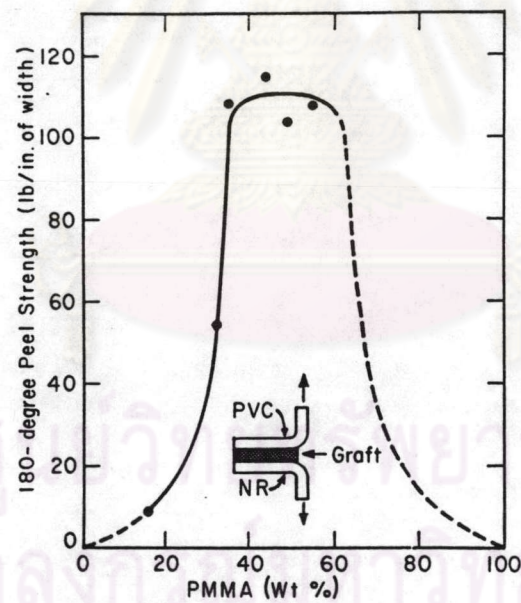
**Figure 2.1** Increase of modulus with methyl methacrylate concentration. [12]

The film forming ability of MG latex decreases as the poly(methyl methacrylate) content increases, due to the tendency for the poly(methyl methacrylate) side-chain to form a shell around the latex particles [6]. Thus the maximum poly(methyl methacrylate) content for coherent film formation at a thickness of 0.5 mm is about 15 percent (MG15), and above this level there is an increasing tendency to cracking on drying. The film forming characteristic is improved if the methyl methacrylate is partially replaced by butyl methacrylate in the grafting reaction.

PVC does not adhere well to natural rubber [17]. An effective and commercially used adhesive for these two is a graft copolymer of methyl methacrylate (MMA) onto NR. The NR backbone of this material adhere well to



NR, while PMMA graft chains will adhere to PVC because of the partial miscibility of PMMA with PVC. Figure 2.2 shows the results of a 180-degree peel strength test on laminates of PVC and NR bonded together by a layer of the above mentioned grafts the PMMA content of which was varied. The dashed lines schematically extended these data to show the expected behavior for the extreme cases. When there is no PMMA, the adhesive is simply NR, which adheres well to the NR sheet but not to the PVC sheet, and the peel strength would be zero. When a pure PMMA adhesive is used, it sticks to the PVC sheet but not to the NR sheet, and peel strength is again zero. It is reasonable that the peel strength would be highest when PMMA and NR are present in nearly equal proportions in the graft.



**Figure 2.2** Effect of the PMMA content of graft on peel strength. Dotted lines drawn to illustrate expected response. Use of NR-g-PMMA as an adhesive for natural rubber and poly(vinyl chloride) laminates. [17]

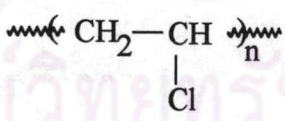
The graft can adhere to both NR, and PVC because its surface can present two different kinds of segments to promote wetting and/or interpenetration of chain segment between the two phases.

The main advantage of the poly(methyl methacrylate)-grafted NR lie in an ability to produce self-reinforced vulcanizates and in adhesives applications. Heveaplus MG was thought to have potential in tire treads as a means of producing a hard rubber that should be more easily processable than vulcanizates filled with carbon black to the equivalent hardness. Unfortunately, the abrasion resistance was found to be inadequate, and hence this use never developed.

## 2.4 Poly(vinyl chloride)

### 2.4.1 Chemical Structure and Molecular Weight [18,19]

Poly(vinyl chloride) or PVC is produced by the free radical polymerization of vinyl chloride. The basic repeat unit of the PVC polymer chain has the following structure:



The units are linked essentially 'head-to-tail', with very few head-to-head junctions. In commercial PVC polymers the average number of repeat units in the molecular chain (i.e. the degree of polymerization) can range between about 500 and 1,500; this corresponds to a theoretical molecular weight range of about 31,000-94,000.

In industrial practice, dilute-solution viscosity of PVC polymers is normally determined (by direct measurement of solution and solvent flow times) as an index of the molecular weight. The results are commonly expressed in terms of the *K value* or *viscosity number*, but sometimes also as *specific viscosity* or *inherent viscosity* (logarithmic viscosity number). Where the actual value of  $M_v$  is required, it can be calculated, under certain assumptions, from the Mark-Houwink equation (also known as the Staudinger-Kuhn equation):

$$[\eta] = K(M_v)^\alpha \quad (9)$$

where  $K$  and  $\alpha$  are constants for a given polymer/solvent system at a given temperature, and  $[\eta]$  is the limiting viscosity number (intrinsic viscosity) determined by extrapolation to zero-concentration of a plot of the inherent viscosity versus dissolved polymer concentration.

The version of the  $K$  value in widest use is the Fikentscher  $K$  value. It was first introduced as an index of the molecular weight of cellulose polymers. It is dependent on the nature of the solvent, but little influenced by the concentration (in generally dilute solutions) and the temperature of determination. For PVC polymers it is related to the viscosity ratio ( $\eta/\eta_0$ ) by the expression:

$$\ln(\eta/\eta_0) = \frac{cK}{1000} \left( \frac{75K+1}{1.5cK+1000} \right) \quad (10)$$

Most commercial PVC polymers have Fikentscher  $K$  values within the range 50-80. Polymers with much higher values have also been made.

Like those of other thermoplastics, the properties of PVC polymers are influenced by the average molecular weight and also by the molecular weight

distribution. The ratio  $M_w/M_n$  ( known as the 'dispersion of distribution') is a function of the latter (giving an indication of the width of the distribution curve but not greatly influenced by its shape). Commercial PVC polymers usually have a relatively narrow molecular weight distribution, with  $M_w/M_n$  values of suspension polymers typically within the range 2-2.5 (reducing with increasing polymerization temperature).

The chemical structure of the molecules of commercial PVC polymers deviates from the theoretical ideality of linear chains of vinyl chloride units joined head-to-tail and terminating in  $-CH_2-CH_2Cl$  and  $-CHCl-CH_3$  end groups. Two of these irregularities, viz. chain-branch junctions containing a tertiary chlorine atom, and mid-chain chloroalkyl groups, are thought to be largely responsible for the low thermal stability of PVC.

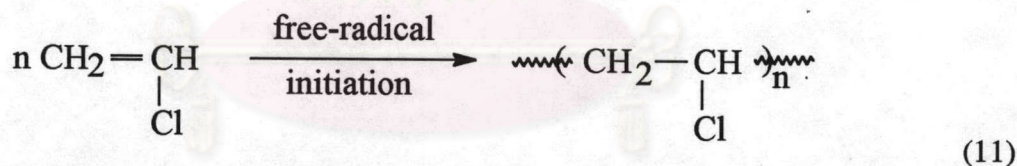
It is well-known that PVC, like other polymers, does not have wide processing latitude without being compounded with other ingredients. The mechanical properties and processing methods can be optimized only by proper choice of additives, which in turn must be matched to the final application. Typical PVC compounds can contain plasticizers, thermal stabilizers, lubricants, pigments, flow modifiers, impact modifiers, UV stabilizers, and so forth.

Plasticizers are chemicals employed to enhance the flexibility of compounds by lowering the glass-transition temperature of the matrix polymer. These materials are most commonly liquids of high boiling point, such as phthalate ester, but can also be polymeric. The physical properties and chemical resistance of PVC compounds are affected by the type and amount of plasticizer employed. Plasticizers, in general, reduce the modulus of a PVC compound, decrease hardness, decrease mechanical strength, but increase elongation, creep, and friction.

Nitrile rubber, actually a copolymer of butadiene and a designed amount of acrylonitrile, has been used as a polymeric plasticizer/impact modifier because of its high molecular weight, but is difficult to process and thoroughly mix because of its high-melt viscosity compared to liquids.

#### 2.4.2 Production of PVC Polymers [18]

Commercial PVC polymers are the products of polymerization of vinyl chloride (monochloroethane; chloroethylene),  $\text{CH}_2=\text{CHCl}$ . Vinyl chloride is a colourless gas, slightly sweet-smelling gas at room temperature and normal pressure (boiling point,  $-13.4^\circ\text{C}$ ), with explosive limits of about 4-20% by volume in air. Because of its carcinogenic effects, vinyl chloride monomer is regarded as a health hazard and precautions must be observed in its handling and processing to prevent direct body contact and to keep the concentration in the factory air within the permitted maximum limits laid down by the relevant national authorities.



The polymerization techniques used to produce PVC polymers are, three major methods; namely, suspension polymerization (about 80% of total commercial polymer production), emulsion polymerization (about 10-15%), bulk (mass) polymerization, also called mass polymerization (about 10%), and solution polymerization.

The commercial application of the solution process is almost entirely confined to the manufacture of PVC copolymers for use in surface coatings. Polymerization is carried out in a liquid which may be a solvent for both the monomer(s) and the polymer, or only for the monomer(s) so that the forming

polymer precipitates out of the system ('precipitation polymerization'). This can also happen in initially homogeneous systems above a certain degree of conversion. Initiator and selected chain-transfer agents are included in a typical solution polymerization system. The resulting polymers can be of high purity, and the method affords good control over molecular weight.

### 2.4.3 Polymer Morphology and some Related Properties [18]

Commercial PVC polymers may be regarded as essentially amorphous in nature, although they do contain small crystallites in proportions amounting to about 8-10% crystallinity as determined by X-ray diffraction.

The glass transition temperature ( $T_g$ ) of commercial homopolymers lie in the range 80-84°C (as determined by DMA, DSC, and TMA). Annealing above the  $T_g$  increases crystallinity and also the crystalline melting temperature. As would be expected, annealing below the  $T_g$  has no effect on crystallinity.

PVC plastics exhibit good mechanical toughness, resistance to weathering, and electrical insulating properties. Although they have a high-melt viscosity and require heat stabilizers, they are fairly easily processed by extrusion, calendaring, milling, or injection-molding techniques. PVC materials have excellent resistance to inorganic acids, alkalis, water, and very good resistance to oxygen and ozone degradation, an important attribute of poly(vinyl chloride) is its low flammability. This also is a consequence of its high chlorine content.

If poly(vinyl chloride) is compounded with sufficient plasticizer, the glass transition temperature is reduced to below room temperature and the product is rubber-like at normal temperature. It is customary to regard this material as a kind of synthetic rubber, partly because it does exhibit something of the reversible long-range elasticity which is conventionally associated with a rubber, and partly because

it competes with other synthetic rubbers, such as chloroprene rubber, in certain applications such as belting and cable sheathing. Considered as a synthetic rubber, poly(vinyl chloride) presents at least three unusual features:

- 1) plasticization is essential;
- 2) it is not normally crosslinked; and
- 3) stabilization against dehydrochlorination is necessary.

Poly(vinyl chloride) (PVC) homopolymer [20] is a stiff, rather brittle plastic with a glass temperature of about  $80^{\circ}\text{C}$ . While somewhat more ductile than polystyrene homopolymer, it is still important to blend PVC with elastomer system to improve toughness. PVC when processed is almost always used mixed with other materials to improve its heat stability or its processibility or to modify its properties. A large number of butadiene based rubbers are available for blending with PVC. These are either based on a butadiene/styrene or polybutadiene rubber grafted with poly(methyl methacrylate) or styrene/acrylonitrile and these products are then blended, usually at the 5-15% concentration with suspension PVC and the usual other additives. For example, methyl methacrylate-butadiene-styrene (MBS) elastomers can impart impact resistance and also optical clarity. ABS resins are also frequently employed for this purpose. On incorporation of this elastomeric phase, PVC, which is ordinarily a stiff, brittle plastic, can be toughed greatly. A nonpolar homopolymer rubber such as polybutadiene (PB) is incompatible with the polar PVC. However, the introduction of a small amount of AN as a comonomer in the PB component results in the more polar, and more compatible, acrylonitrile-butadiene rubber (NBR). Fabricated articles made from these blends, when examined optically, are seen to consist of a continuous PVC phase in which are suspended discrete rubbery particles. The product consequently retains most of the properties (rigidity, softening point) of rigid PVC with enhanced impact strength.

By correct choice of the composition and particle size of the rubber phase it is possible to produce transparent blends with these materials.

## 2.5 Polymer Blends [20]

Polymer mixture containing of two distinguishable kinds of polymer molecules, such mixture, known as polymer blends, polyblends, or simply blends, include mechanical blends, graft copolymers, block copolymers and interpenetrating polymer networks. Polymer blends may be defined as intimate mixtures of two kinds of polymers, with no covalent bonds between them. Polymer blends containing one plastic phase and one rubbery phase, depending on which phase predominates, such combinations yield impact-resistant plastics or reinforced elastomers.

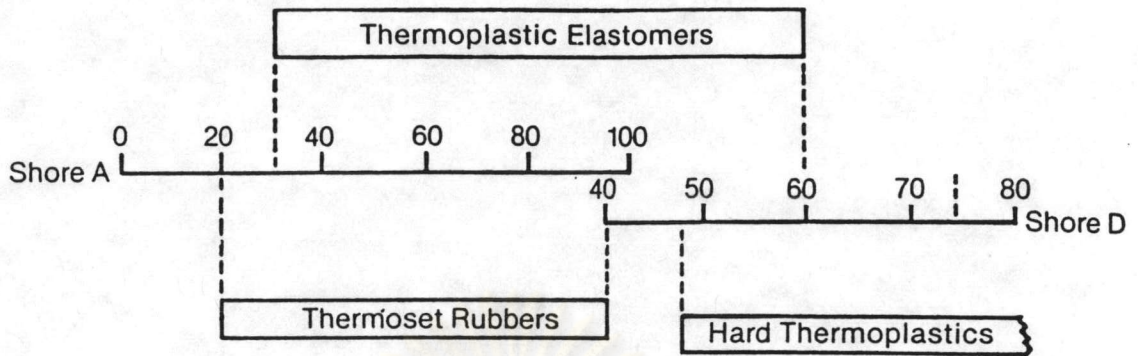
The principal methods of mixing two kinds of polymer molecules include mechanical blending, graft copolymerization, block copolymerization, and interpenetrating of two networks. Historically, the oldest and simplest method involves mechanical blends, where a plastic and a noncrosslinked elastomer are blended either on open rolls or through extruders. In simple mechanical blends the plastic component usually predominates, with the dispersed elastomer having dimension of the order of several micrometers. The shear action of mechanical blend also generates free radicals through polymer degradation reactions. The free radicals thus induced by mechano-chemical action subsequently react to form a small number of true chemical grafts between the two components. The quantity and importance of such grafted material obviously depend on the exact mode of blending.



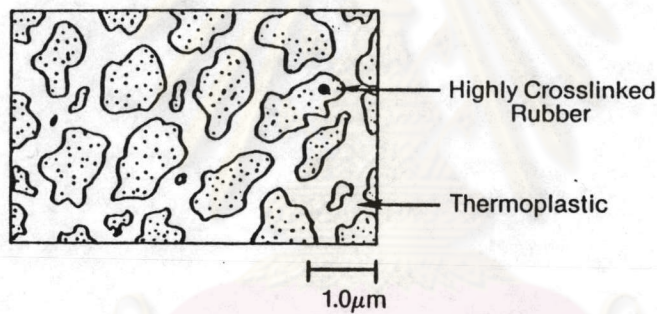
## 2.6 Thermoplastic Elastomer [17,21]

Thermoplastic elastomer (TPE) prepared by block copolymerization and blend polymer having a hard segment and a soft segment have been widely used in some industries. The TPE could be synthesized by graft copolymerization of monomer on rubber material. A TPE is a rubbery material which can be processed in the molten state as a thermoplastic and which has many of the performance characteristics of a thermoset rubber. By definition, a TPE is an elastomer because of its elastic properties, such as its flexibility, its ease of distortion under an applied load, and its recovery of most of its original shape after removal of an externally applied stress. A TPE is also a thermoplastic because it is fluid at temperatures above its melting point and can be processed on thermoplastic extrusion and molding equipment. Unlike a thermoset rubber, a TPE can be recycled to recover scrap from processing operations.

Figure 2.3 indicates how TPEs bridge the range of materials available to the rubber and plastics industries, with greater overlap with thermoset rubbers. With the exception of melt-processible rubbers, which are single phase materials, TPEs consist of at least two polymeric phases. A hard thermoplastic phase is combined with a soft elastomer phase, and the properties of the resulting TPE will be derived from the properties of each of the two phases and from the interaction between these phases. The two phases may result from simply mixing two different polymers, as in a blend of a hard thermoplastic with a soft elastomer.



**Figure 2.3** Thermoplastic elastomers bridge the hardness ranges of rubbers and plastics. [21]



**Figure 2.4** Morphology of elastomeric alloys. [21]

The performance characteristic of a TPE depend on the melting point ( $T_m$ ) of the hard thermoplastic phase and the glass-transition temperature ( $T_g$ ) of the soft elastomeric phase. The useful temperature range for a TPE is between  $T_m$  and  $T_g$ . Within this range, the TPE displays its desirable elastomeric properties. At temperature above  $T_m$ , the hard thermoplastic phase melt and the TPE becomes fluid and can be processed by usual thermoplastic techniques. Below  $T_g$  the TPE becomes brittle and loses all of its useful elastomeric characteristics.

Passage of a TPE through  $T_g$  and through  $T_m$  is reversible and can take place many times, since both are physical (and not chemical) transformations. On the other hand, the passage of cross-linked thermoset rubber through  $T_g$  is reversible, but that through  $T_m$  does not exist due to the thermoset nature of the material. Thus on heating a cross-linked thermoset rubber to progressively higher temperatures, nothing will happen until the onset of chemical attack from either the environmental or internal decomposition. This chemical attack is irreversible since it entails the destruction of the cross-links between the elastomer chains and, to a lesser extent, the chain backbones themselves.

The simplest type of TPE is the polymer blend, a simple mixture of a thermoplastic polymer with a compatible elastomeric polymer. Each of the polymeric components has its own phase, but the interaction between the phases is quite weak, if it exists at all. The properties of the blend are approximately those predicted directly from the properties of the components, and a knowledge of the  $T_m$  and  $T_g$  for the hard and soft phases, respectively. The hard phase must be continuous, or at least cocontinuous, in order for the blend to be thermoplastic and melt at  $T_m$ .

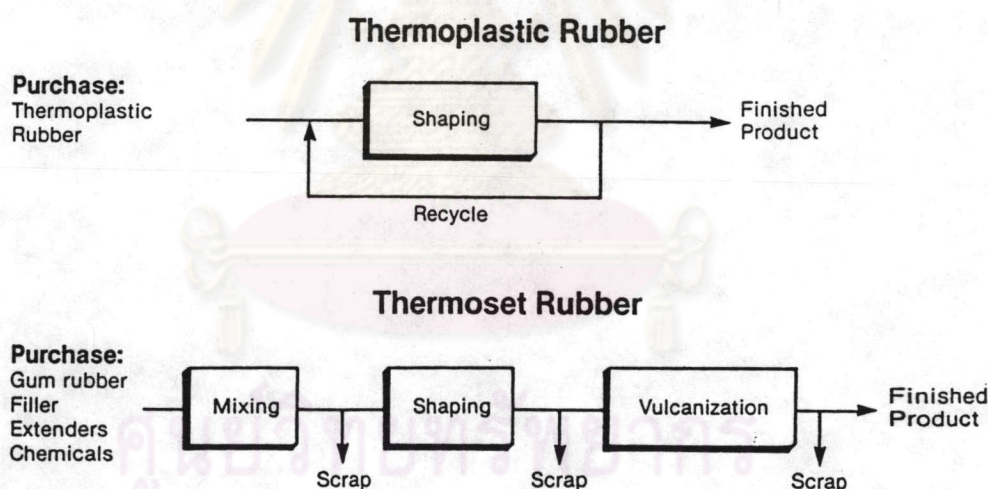
A Elastomeric Alloy (EA) is a two-phase material in which there is a synergistic interaction between the phases. This interaction gives the alloy properties different from those predicted by a simple blend of the polymers. Just as with blend, the hard phase must be continuous or cocontinuous (as shown in Figure 2.4) for the alloy to be thermoplastic and melt at  $T_m$ . These EAs consist of a finely divided dispersion of highly cross-linked rubber particles in a continuous matrix of thermoplastic. The interfacial surface area between the two phases is sufficiently large to generate significant thermoplastic-elastomer interaction. The cross-linking of the elastomer continuous phase becomes molten. Commercial EAs include

compositions containing EPDM, NBR, or natural rubber (NR) as the soft phase and a polyolefin, often PP, as the hard phase.

### 2.6.1 Comparison of TPEs and Thermoset Rubbers [21]

To understand how TPEs have succeeded in replacing thermoset rubber in a wide range of parts, the advantages and disadvantages of TPEs must be examined in comparison with thermoset rubbers. Among the practical advantages offered by TPEs over thermoset rubbers are the following:

1) Processing is simpler and requires fewer steps. Figure 2.5 shows the simple thermoplastic processing used to make TPE parts with the multistep process required for conventional thermoset rubber parts.



**Figure 2.5** Thermoplastic elastomer processing consists of a single step, compared to three or more for thermoset rubbers. [21]

2) Processing time cycles are much shorter for TPEs. Molding cycles need only be long enough for the TPE part to cool sufficiently to hold its shape when ejected from the mold. These times are on the order of seconds, compared to

several minutes for thermoset rubber parts, which must be held in the mold while the chemical-linking (vulcanization) reaction takes place.

3) TPE scrap (regrind) may be recycled. Most TPEs will tolerate several regrind-recycle steps without any significant change in properties

4) TPE part production consumes less energy, a result of the fewer and simpler processing steps. Like other thermoplastics, TPEs are melted, the parts are shaped from the melt, and then they are cooled to freeze them into the desired shape.

5) TPEs require little or no compounding with other materials. They are available fully compounded and ready for a wide range of uses. Their compositional consistency is higher than that of thermoset rubbers, which must be mixed with curatives, stabilizers, processing aids and specialty additives such as flame retardants.

6) Thermoplastic processing allows tighter control on part dimensions than thermoset rubber processing.

7) For the same application, a TPE is typically lower in specific gravity than a comparable thermoset rubber containing carbon black or inorganic fillers.

8) TPEs permit thermoplastic fabrication methods not feasible for thermoset rubbers. These methods include blow molding, coextrusion with rigid thermoplastics, thermoforming, heat welding, and film blowing.

It should not be surprising that there are off-setting disadvantages to the use of TPEs compared to thermoset rubbers:

1) Many TPEs require drying before processing. While this is familiar step to thermoplastic processors, it is not necessary for thermoset rubbers, and drying equipment is usually not available in a rubber shop.

2) TPEs have melting points at a specific elevated temperature, above which a part will not maintain its structural integrity.

3) For thermoset rubber processors, TPEs represent new technology requiring unfamiliar processing equipment and techniques. Thermoplastics processors are familiar with this technology and have the necessary equipment, though they are generally not familiar with the markets for rubber articles.

4) TPEs require moderately high production volume for good processing economics. Thermoplastics tooling costs are generally higher than those for thermoset rubber parts.

### **2.6.2 Thermoplastic Rubber-Plastic Blends [12,22]**

In recent years, elastomeric rubber-plastic blends have become technologically interesting for use as thermoplastic elastomers. They can have many of the properties of rubbers. They do not need to be vulcanized during fabrication into end-use parts. Thus, they offer a substantial economic advantage in respect to the fabrication of finished-parts. Due to their unique fabricability, such materials have added value as raw materials, provided that they also have good properties as elastomers.

Although there are many possible elastomeric blend compositions, relatively few of them have been of technological importance. This is largely because of the fact that most polymer have been incompatible with one another, at least in the thermodynamic sence. If the polymers of a blend are thermodynamically compatible, then their blend could exist as a single phase, with mixing having been accomplished on the molecular-scale level. In such a case, the properties of the resulting blend would tend to be the average of the properties of the two pure phase. For example, blending a rubber with a thermodynamically compatible plastic would give a composition with a glass transition temperature between those of the rubber and plastic. Frequently, such an average glass transition temperature is near

room temperature. Thus, a rubber and a plastic might be blended to give a highly damped, almost "leathery" material. This, of course, would not be a desirable result.

On the other hand, if the rubber and plastic are not thermodynamically compatible, then the blend would contain two phases, with two glass transition temperatures. However, such blends frequently contain large particles of one of the polymers only loosely bonded to the other (matrix) polymer. The large, essentially unbonded particles generally act as stress-concentrating flaws. In some cases it is possible to obtain very small droplets of one polymer dispersed in the other during mixing; however, later, after mixing, coarsening of the droplets can occur by coalescence during some phase of processing a blend into a fabricated part.

For many technological end-use applications, the ideal elastomeric rubber-plastic blend would comprise finely divided rubber particles dispersed in a relatively small amount of plastic. The rubber particles should be crosslinked to promote elasticity (the ability of the blend composition to retract forcibly from a large deformation). The favorable morphology should remain during the fabrication of the material into parts.

It should be pointed out that, in the ideal case proposed above, many of the desired properties could arise as a result of the polymers being thermodynamically incompatible. The low glass transition temperature of the rubber phase (not "average up" by the hard-phase material) would be maintained because of the relative purity of the rubber phase; yet the high crystallinity or high glass transition temperature of the hard plastic phase could be retained for structural integrity.

### 2.6.3 Rubbers and Plastics Used in Blends [12]

Before examining the properties of rubber-plastic blends, it is appropriate to consider the characteristics of the rubber and plastic blend components. This is, of course, because the properties of a blend depend on the characteristics of the component parts.

The great difference between the mechanical properties of the rubbers and plastics is shown by Figure 2.6, which gives stress-strain curves of typical plastics and rubbers. The curve for polypropylene and high density polyethylene are typical of crystalline plastics, the curve for polystyrene illustrates glassy materials, while the curve for natural rubber and BR are typical of crystallizable and noncrystallizable unvulcanized rubbers. The stress-strain curve for a melt-mixed blend of polypropylene with BR is also shown.

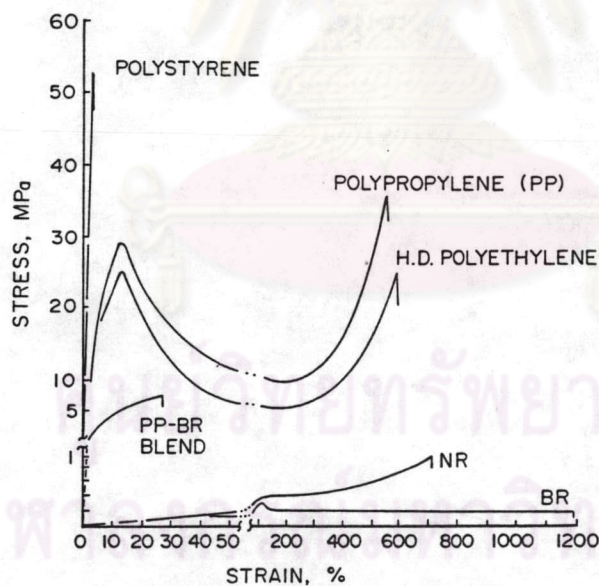


Figure 2.6 Stress-strain curves for various polymeric materials. [12]

Elastic properties of a blend, such as Young modulus or shear modulus, are a function of the elastic properties of the blend components and the phase



morphology of the blend. The strength-related or ultimate mechanical properties of blends (such as tensile strength, ultimate elongation, and fatigue life), however, are only partly determined by the mechanical properties of the components. Also the importance is the interaction between the polymers at their interfaces. The interfaces between phases of polymer blends are sometimes called "interphases," since some localized intermolecular mixing or interdiffusion can occur, in the case of polymer blends, which approach thermodynamic compatibility. In other words, a small domain of a mixed phase (interphase) can exist between the "pure" phases. This molecular interdiffusion can increase the wetting of one polymer by the other, increase the adhesion between the phase, or reduce the effective interfacial tension. Increase adhesion or interdiffusion between the phases would be expected to confer improved ultimate properties upon the blends. The decrease interfacial tension would be expected to give more extensive subdivision of particles (by the formation of smaller droplets) during melt mixing. The smaller particles can also give rise to improve blend properties.

#### **2.6.4 Preparation of Rubber-Plastic Blends [12]**

Polymer blends, in general, have been prepared commercially by melt mixing, solution blending, and latex mixing. Rubber-plastic blends have generally been prepared by melt-mixing techniques. Melt mixing avoids problems of contamination, solvent or water removal, etc. Mixing has been accomplished on heated (above the melting point of the plastic) on roll mills. However, in most of the cases considered here, this is not very practical since the plastic have high melting points. Mixing on an open-roll mill in air at elevated temperatures induces oxidative degradation in many cases. Banbury and other internal mixers are more efficient, and their use gives less oxidative degradation. In general, banbury mixers,

mixing extruders, and the newer twin-screw mixers are suitable for melt mixing rubbers with plastics. Several techniques for the preparing rubber-plastic blends will be considered. First, prepared by merely mixing molten thermoplastic resin (the plastic phase) with unvulcanized or slightly vulcanized rubber at temperature above the melting point of the plastic resin. The other technique, prepared by dynamic vulcanization, the process of vulcanizing the rubber during its melt mixing with rubber. The dynamic vulcanizates wherein the rubber and plastic phases had been compatibilized by the incorporation or in situ formation of small amounts of rubber-plastic block copolymer.

#### **2.6.5 Rubber-Toughened Plastics [20]**

One of the oldest, and certainly one of the most important methods of preparing polymer mixtures involves blending techniques. There are three principal ways of preparing blends with toughness or high impact resistance. The original method involved blending by mechanical techniques (method 1). Blends of poly(vinyl chloride) with poly(butadiene-co-acrylonitrile) are presently manufactured by a variation of this technique. While high-impact polystyrene is also produced by means of mechanical blending with linear polybutadiene, currently a solution-graft copolymer technique (method 2) is more often employed, in which the elastomer component is first dissolved in the styrene monomer and then the latter is polymerized with agitation. The technologically important ABS (acrylonitrile-butadiene-styrene) polymers are produced by emulsion polymerization (method 3), a variation of the solution graft copolymer technique in which the plastic component is polymerized onto a seed-latex particle of the elastomer component.

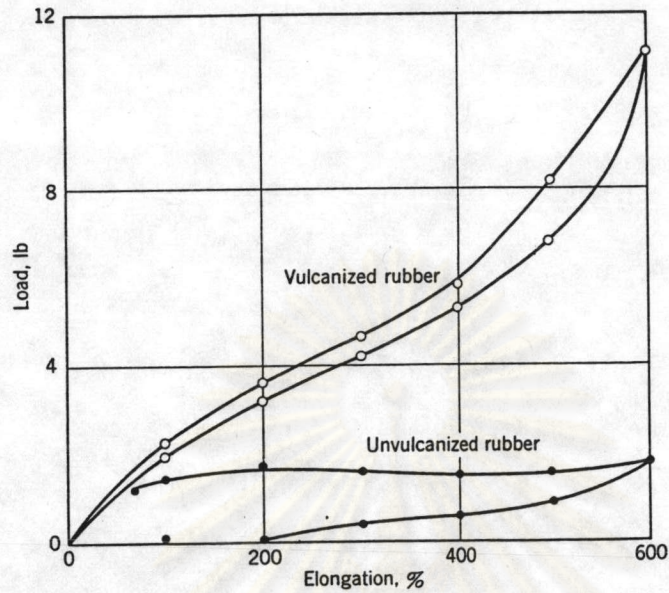
The properties of heterogeneous rubber-plastic blends are determined by a number of factors. The main factors are (1) the material properties of the rubber and

plastic phases, (2) the rubber/plastic proportions, (3) the phase morphology, and (4) the interactions and properties at the interface (or interphases).

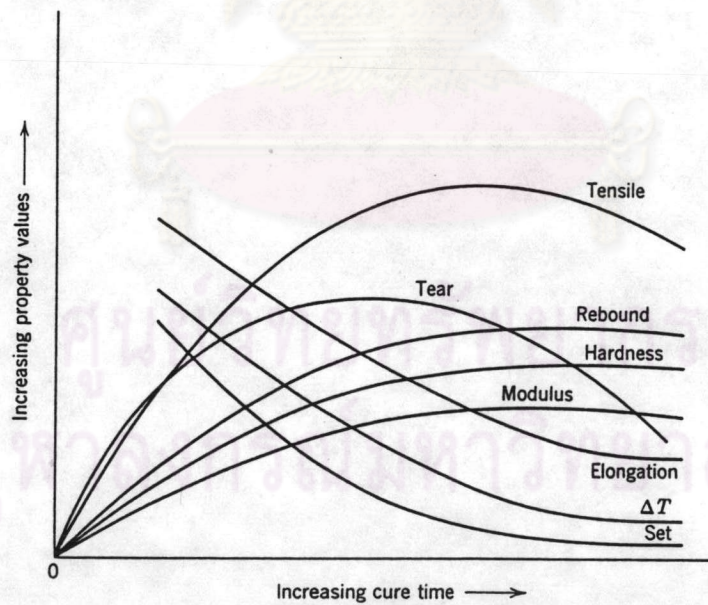
## 2.7 Vulcanization [23,24]

Vulcanization is a process of chemically producing network junctures by the insertion of cross-links between polymer chains. The term vulcanization is generally applied to rubbery or elastomeric materials. The cross-link may be a group of sulfur atoms in a short chain, a single sulfur atom, a carbon-to-carbon bond, a polyvalent organic radical, an ionic cluster, or a polyvalent metal ion. The process is usually carried out by heating the rubber (mixed with vulcanizing agents) in a mold under pressure. The profound effects of vulcanization, it transforms an elastomer from a weak thermoplastic mass without useful mechanical properties into a strong, elastic, tough rubber and reduces its sensitivity to changes of temperature. The tensile strength, stiffness, and hysteresis (representing loss energy as heat) of natural rubber before and after vulcanization are shown in Figure 2.7 and the effect of extent of vulcanization on these and other properties of elastomers are shown schematically in Figure 2.8. Thus, vulcanization increases elasticity while it decreases plasticity. It is generally accomplished by the formation of a cross-linked molecular network (Figure 2.9).

It has been found that neither heat nor sulfur is essential to the vulcanization process. Rubber can be vulcanized or *cured* without heat by the action of sulfur chloride, for example. A number of compounds that do not contain sulfur can vulcanize rubber; these fall generally into three groups: oxidizing agents, generators of free radicals, and phenolic resins. Vulcanization may be defined as any treatment that decreases the flow of an elastomer, increases its tensile strength and modulus,

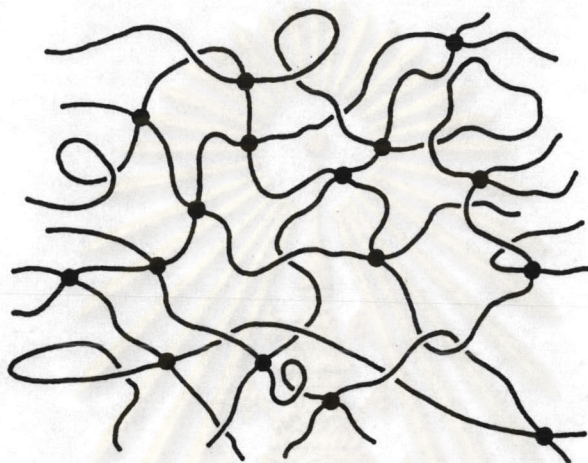


**Figure 2.7** Stress-strain curves to 600% elongation at break, typical of unvulcanized and vulcanized natural rubber. [24]



**Figure 2.8** Schematic representation of the effect of extent of vulcanization (cure time) on various physical properties of elastomers.  $\Delta T$  is heat build up in a compression flex test. [24]

but preserves its extensibility. As might be expected, such properties as tensile strength are relatively insensitive to the onset of these crosslinking reactions; tensile strength does indeed change tenfold during curing, but this is evidence of the profound alteration of polymer properties by the process.



**Figure 2.9** Idealized representation of a crosslinked elastomeric network.

Filled circles indicate crosslink points (e.g., polysulfide bridges). [23]

The most popular and widely used vulcanizing agent is sulfur, although vulcanization takes place by heat in the presence of sulfur alone, the process is relatively slow and no longer commercially practice. It can be speeded many fold by the addition of small amounts of organic or inorganic compounds known as *accelarators*. Many accelerators require the presence of other chemicals known as *activator* or *promotors* before their full effects are realized. These activators are usually metallic oxides, such as zinc oxide. They function best in the presence of a rubber-soluble metallic soap, which may be formed during the curing reaction from the activator and a fatty acid. The most efficient combination of chemicals for sulfur vulcanization include sulfur, an organic accelerator, a metallic oxide, and a

soap. A typical formulation for the vulcanization of a diene elastomer includes the following [23]:

<u>Component</u>	<u>phr</u>
Sulfur	0.5-4
Fatty acid	1-4
Zinc oxide	2-10
Accelerator	0.5-2

Useful rubber articles, such as tires and mechanical goods, cannot be made without vulcanization. Unvulcanized rubber is generally not very strong, does not maintain its shape after a large deformation, and can be very sticky; it has about the same consistency as chewing gum.

These materials forcible retract approximately to their original shape after a large mechanically imposed deformation. Vulcanization can be defined as a process that increases the retractive force and reduces the amount of permanent deformation remaining after removal of the deformation force.

## 2.8 Recent Literature Review

Blending is widely employed as a simple and practical means of obtaining new materials with novel properties. In the development of blend-type thermoplastic elastomers, Coran and coworkers [25,26,27] introduced the concept of dynamic vulcanization, in which the rubber component is chemically crosslinked during the process of blending.

Chuan Qin, Jinghua Yin and Baotong Huang [28] studied the NR/LDPE blends as a model, a comparison of the mechanical properties and structure and

morphology was made between blends in varying compositions. Blends were prepared by unvulcanized and static or dynamic vulcanizations of the NR component in the blends. From morphological studies in unvulcanized NR/LDPE blends, phase inversion occurred between NR/LDPE = 40/60 to 60/40; for dynamically vulcanized blends, LDPE remained as a continuous phase even at NR/LDPE = 70/30. From the suggested model and the experimental results, it was shown that the mechanical properties of dynamically vulcanized blends were higher than those of unvulcanized blends but lower than those of statically vulcanized blends.

K.E. George, Rani Joseph and D. Joseph Francis [29] studied the modification PVC/NBR blends by using of natural rubber, styrene-butadiene rubber to replace part of the NBR in a 70/30 NBR/PVC. Such replacement up to 15% of the total weight of the blend improved the mechanical properties, while decreasing the cost of the blend. Styrene-butadiene rubber could replace NBR up to 30% of the total weight of the blend without deterioration in the mechanical properties.

M.D. Salleh Nordin [30] studied the modification of natural rubber by epoxidation. This improved the oil resistance of NR, and increasing the level of epoxidation also improved the oil resistance of the rubber. The significant change in the characteristics of NR was brought about by the presence of epoxy group in the main chain of the elastomer.

Zainal A. Nasir and Chantera T. Ratnam [31] studied the blending properties of poly(vinyl chloride)/epoxidized natural rubber (PVC/ENR). Their rheological properties were studied with a Brabender Plasticorder. It was found that the rheological properties of any PVC/ENR blends were governed by their blending conditions. To ensure homogenous PVC/ENR blends, adequate and suitable blending conditions must be utilized. PVC thermoplastics phase enhanced rigidity while ENR rubbery phases imparted flexibility and processability to the blends.

With premixing, Ba/Cd/Zn-based PVC stabilizer was effective in stabilizing the PVC/ENR blends. Their properties were further enhanced by the addition of curatives.

D. J. Hourston and J. Romaine [32] studied the composite latex particles based on natural rubber latex. It has been synthesized to yield materials which may be formally regarded as interpenetrating polymer networks and semi-interpenetrating polymer networks. Methyl methacrylate was added to a carefully stabilized natural rubber latex and polymerized in situ using an amine-activated initiator, tert-butyl hydroperoxide. The resulting materials were cast to yield solid sheets. The morphology of the materials was determined both by transmission electron microscopy and by dynamic mechanical analysis. In addition the stress-strain behavior was studied.

F. Sundardi and S. Kadariah [33] studied the method of radiation grafting of methyl methacrylate (MMA) monomer on natural rubber (NR). The irradiation dose in radiation emulsion polymerization of MMA monomer was lower compared to the irradiation dose for grafting of MMA monomer on NR latex, in order to obtain the same degree of conversion. This is due to the size of the rubber particles which are quite large and, hence, not sufficient to ensure an ideal emulsion polymerization. The irradiation dose for radiation grafting of MMA monomer on latex was around 300 krad to obtain a 75% degree of conversion. However, this irradiation dose was lower compared to the irradiation dose for bulk polymerization of MMA monomer, in order to obtain the same degree of conversion. This is due to the gel effect in the viscous media. Radiation grafting of MMA monomer on NR latex does not influence the pH of the latex, but influences the viscosity significantly. The viscosity of the NR latex increased with an increase in irradiation dose, due to the increase of the total solid content in the latex. The MMA monomer converted to PMMA in NR latex largely grafted on the NR, or at least insoluble in a solvent for



PMMA, such as acetone or toluene. The hardness of the pure gum vulcanized increased with an increase in the degree of grafting or PMMA content, but the other physical properties, such as tensile strength, modulus, elongation at break, and thermal stability, were not greatly influenced by the degree of grafting.

Mirzan T. Razzak, Fumio Yoshii, Keizo Makuuchi and Isao Ishigaki [34], studied the preparation of Thermoplastic Elastomer by radiation grafting. Processability of thermoplastic elastomer (TPE) prepared by radiation-induced grafting of methyl methacrylate (MMA) onto radiation vulcanized natural rubber latex (RVNRL) has been evaluated using a kneader and a hot mill at 150°C. It was found that mixing time and revolution rate (rpm) of the kneader have significantly affected the processability. The longer mixing time and the higher revolution rate result in better processability. In such processing conditions, however, the mechanical properties were found to be inferior because the molecular chain scissions occurred during the mixing. A considerable improvement of mechanical properties was obtained when the mixing was carried out without added processing oils. Blends of the grafted vulcanized natural rubber latex (RVNRL-g-PMMA) and MMA grafted on unvulcanized natural rubber latex (NRL-g-PMMA) improved processability where the better processability could be achieved at a shorter mixing time and a lower revolution rate. In addition, a comparable value of mechanical properties was obtained.

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