

## CHAPTER II

### THEORY AND LITERATURE REVIEW

#### 2.1 Natural Rubber

The birth of natural rubber dates back to the fifteenth century when Columbus first reported that he had been intrigued on his journey through the New World to see natives playing with a ball that actually bounced.

The *Hevea brasiliensis* tree is the main source of natural rubber and its existence in the Amazon basin was first reported by Charles de la Condamine to the French Academy in 1736. He described to them the native methods of obtaining rubber from this tree and also methods that were used to convert it into useful products[6].

Natural latex concentrates have been commercially available since about 1930 and subsequently have been thoroughly exploited for the manufacture of a great variety of products. Despite their widespread use however, there is no complete understanding of the relation between composition and properties. This is especially true of the nature and non-rubber materials, and the causes of variability in processing behaviour. Much work has been done in the past on the non-rubber materials of the field latex from which the concentrate is derived, but little has been done on the concentrate itself. The reason for this is that the composition of latex is exceedingly complex, rendering chemical analysis very difficult to study[7].

### 2.1.1 Natural Rubber in Thailand

The data from Rubber Research Institute of Thailand shown that in 1995, Thailand produced 1,784,400 tons of natural rubber and exported 1,635,500 tons or 91.59 % of total production. The remaining 8.41 % was used in the country. Since 1991, Thailand was the biggest producer in world production of natural rubber, followed by Indonesia and Malaysia. The world production of natural rubber is shown in Table 2.1. The area of Thailand was about 12 million hectares employed for rubber cultivation. In 1995 Thailand produces 1.7 million tons of natural rubber. It is uneconomical to transport preserved field latex form before shipment. Therefore, after the natural rubber latex has been collected from the field, it is changed into many of rubber, which are showed in Table 2.2. Natural rubber latex was 60 % dry rubber content by concentration method. In 1995, it exported 168,200 tons to USA, Taiwan, German, Japan, China and Singapore.

**Table 2.1** World production of natural rubber in 1995

Country	Ton( $10^3$ )
Thailand	1,635.5
Indonesia	1,323.8
Malaysia	777.5
Sri Lanka	68.2
Vietnam	63.0
Others	362
Total	4,230

Source : Rubber Research Institute of Thailand

**Table 2.2** The different types of rubber in Thailand in 1995

Types of Rubber	Content of Rubber (%)
Smoked sheet	66.42
Block rubber	17.06
Crepe rubber	0.18
Concentrated latex	10.35
Air Dried Sheet	0.82
Others rubber	5.17

Source : Rubber Research Institute of Thailand

### 2.1.2 Properties of Raw Natural Rubber [8]

Natural rubber latex consists of particles of rubber hydrocarbon and nonrubbers suspended in an aqueous serum phase. The average dry-rubber content of latex may range between 30% and 45%. A typical composition of fresh latex is shown in Table 2.3. The rubber hydrocarbon in freshly tapped latex is almost completely soluble (more than 95%) in common solvents such as toluene and tetrahydrofuran. It has a chemical structure of almost 100% cis-1,4-polyisoprene units.

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**Table 2.3** Typical Composition of Fresh Latex and Dry Rubber [8]

Composition	Latex,%	Dry rubber,%
Rubber hydrocarbon	36	93.7
Protein	1.4	2.2
Carbohydrates	1.6	0.4
Neutral lipids	1.0	2.4
Glycolipids +	0.6	1.0
Phospholipids	0.5	0.2
Inorganic constituents	0.4	0.1
Others	58.5	-
Water		

### 2.1.3 Composition of Natural Rubber

Freshly tapped latex, before preservation or concentration, is known as field latex. In addition to the suspended rubber particles, which range in diameter from less than  $0.05 \mu$  to about  $3 \mu$ , it contains a smaller number of easily deformable bodies named "lutoids". These lutoids, which consist essentially of a viscous aqueous solution or gel of non-rubber materials break down on addition of ammonia. The non-rubber constituents occurring in greatest quantity in field latex are proteins, lipids, quebrachitol and inorganic salts. The last two components occur entirely in the aqueous phase or serum the lipids are nearly all on the surface or in the interior of the rubber particles, and the proteins are distributed between the serum and the rubber-serum interface.

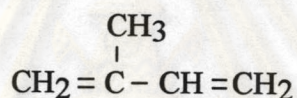
### 2.1.4 Chemical Formula of Natural Rubber [9]

The empirical formula for the natural rubber (NR) molecule appears to have been first determined by Faraday who reported his findings in 1826. He concluded that carbon and hydrogen were the only elements present and his results correspond to the

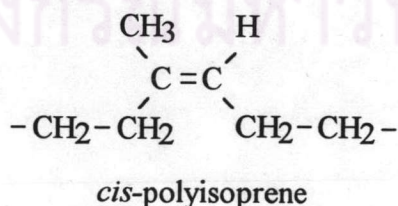
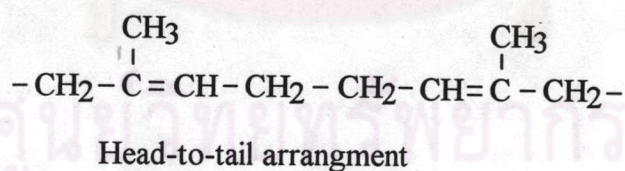
formula  $C_5H_8$ . Many years later Weber indicated that the natural rubber molecule was unsaturated since it reacted with bromine to give a material of empirical formula  $C_5H_8Br_2$ .

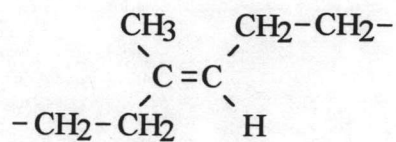
Having established the empirical formula, the next step was to determine the arrangement of carbon and hydrogen atoms within the rubber molecule. One approach was to study the products of destructive distillation and this was done by such workers as Gregory, Bouchardat and Greville Williams. Such reactions gave rise to a variety of products but fractional distillation was found to lead to two main fractions of fairly uniform composition, one with a boiling range of 34-37 °C and the second with a boiling range of 175-176 °C.

The first, isoprene, was found to have the formula  $C_5H_8$  which structure is as follows



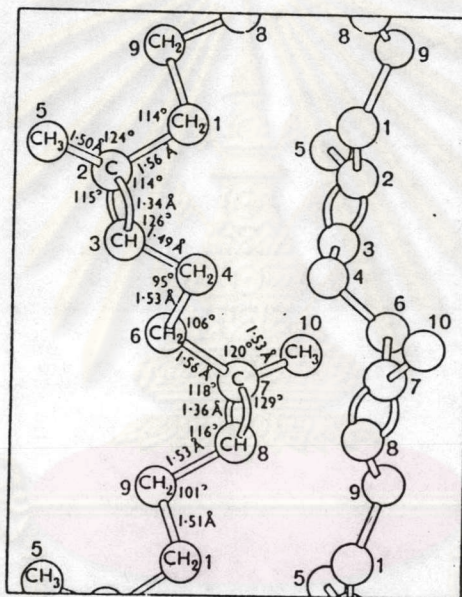
Natural rubber is a polymer of isoprene, in which essentially all the isoprene units are linked together at carbon atom 1 and 4 in a head-to-tail arrangement, and in which all or nearly all the repeating units possess the "cis" configuration.





*trans*-polyisoprene

Natural rubber is the *cis*-polymer which the structure and unit cell of the crystalline stretched rubber molecule is shown in Figure 2.1



**Figure 2.1** Unit cell structure of the natural rubber molecule [9].

### 2.1.5 Concentrated Natural Latex [27]

Apart from the fact that natural latex concentrates are more uniform in composition than normal latex, their chief technical advantage is that in the many manufacturing processes involving gelation of the latex, their lower water content results in higher wet gel strength. Because of this, the use of concentrated latices is often essential. Four methods of concentration are used, viz. centrifuging, creaming, electrodecantation, and evaporation.

a) *Centrifuged latex*

Most of the latex exported from the Far East is of this type. As carried out commercially, centrifuging leaves most of smaller rubber particles, i.e. those of diameter less than  $0.15 \mu$ , in the skim. Although these particles account for only about 12 % of the rubber by weight, they contain a much higher percentage of the adsorbed non-rubbers because of their large surface area-to-volume ratio. As a result, the non-rubber content of centrifuged latex is low, and less than that of other types of concentrate at same DRC (dry rubber content).

b) *Creamed latex*

Commercial creamed latices contain many more of the smaller rubber particles than centrifuged latex, and the content of adsorbed non-rubbers is correspondingly higher. However, since creaming is usually carried to 62% DRC or higher, as compared with 60% DRC for centrifuged latex, the proportion of serum constitutes is somewhat smaller. Small amounts of added fatty acid soaps, which facilitate creaming, and the creaming agent itself (ammonium alginate) are present in creamed concentrates.

c) *Electrodecanted latex*

In concentrates of this type, the proportion of small rubber particles is higher than in centrifuged but slightly lower than in creamed latex. Concentration is carried to 60% DRC. Approximately 0.1% of fatty acid soap, added as a stabilizer during electrodecantation, is partly retained in the concentrate and contributes towards the relatively high mechanical stability of electrodecanted latex. The ammonia content of the latex is also a little higher than in the other types of concentrate.

#### d) *Evaporated latex*

Evaporated concentrates are produced under the trade-names T-Revertex and Standard Revertex, which contain approximately 62% and 73% total solids respectively. Such "whole" latices possess a smaller number-average and weight-average particle size, a wider particle size distribution, and a higher proportion of non-rubbers than the other types of concentrate. Standard Revertex is preserved with fixed alkali (KOH) and T-Revertex due to the high total solids content and small particle size; it also has a very high mechanical stability.

### **2.2 Rubber-Toughened Plastic [3]**

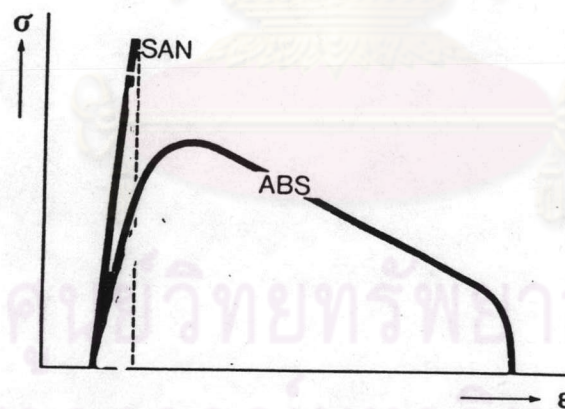
The use of brittle polymers, such as poly(vinyl chloride) (PVC) and polystyrene (PS), was limited prior to the development of rubber-toughened polymers in the 1930s and 1940s. PVC has been toughened by the addition of small amounts of acrylonitrile rubber (NBR) and other elastomeric materials. Over 1.5 million tons of rubber-toughened PVC is produced annually in the United States. The preferred toughening additive for PS is a styrene-butadiene rubber (SBR). Copolymers of styrene, such as styrene-acrylonitrile and styrene-maleic anhydride, have been toughened by the addition of NBR. The low -temperature resistance of these composites has been improved by grafting the polymers onto the elastomer. Polystyrene is also toughened by the addition of styrene-butadiene block copolymers. The art of toughening plastics by the addition of elastomers has been extended to include acrylics, polyolefins, polyesters, acetals, and thermoset. The impact resistance of epoxy resins has been enhanced by the addition of acrylonitrile-butadiene elastomeric copolymers.



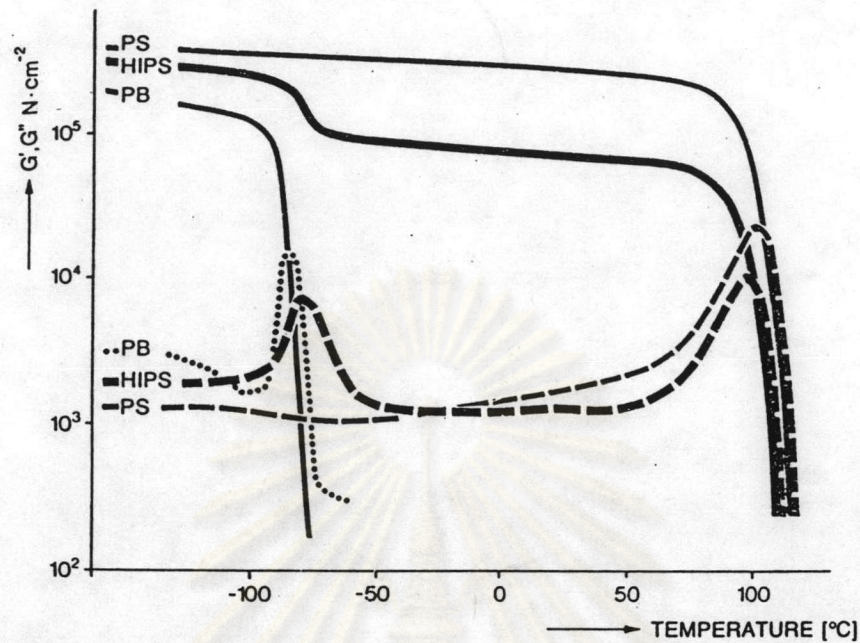
### 2.2.1 Acrylonitrile-Butadiene-Styrene

Styrene-Acrylonitrile copolymer (SAN) are transparent and brittle thermoplastic materials. The addition of rubber increases impact strength considerably, as can be seen from the stress-strain curves determined by an instrument impact pendulum (Figure 2.2)

Styrene-butadiene rubber was replaced long ago by polybutadiene as a toughening agent in HIPS and ABS. Polybutadiene has much lower glass-transition temperature ( $-85\text{ }^{\circ}\text{C}$ ) than SBR ( $-50\text{ }^{\circ}\text{C}$ ) (Figure 2.3) and therefore gives a much better low-temperature impact strength. This strength is required mainly in refrigerators, and to lesser extent in automotive and some other applications.



**Figure 2.2** Impact resistance of styrene-acrylonitrile copolymer and acrylonitrile-butadiene-styrene[3].



**Figure 2.3** Storage modulus  $G'$  and loss modulus  $G''$  of Hips and its two components[3].

ABS are two phase materials which obtain from TEM images made from microtome cut films stained by osmium tetroxide . Figure 2.4 shows a two phase nature of ABS which polymerized in emulsion or bulk polymerization. The particles contain relatively large inclusions of matrix material. Because of the appearance in the images. The inclusions enlarge the share of the rubber phase far beyond the calculated rubber content. ABS, however, is produced either in bulk or in emulsion. Most producers prefer the emulsion process to the bulk, generally because the optimum rubber particle size is much smaller and can be adjusted more easily by emulsion polymerization.

In two phase polymer systems, the technical properties do not depend solely on the technical properties of the pure components. In a complex way, numerous parameters affect the technical properties of the final products. (Figure 2.5)

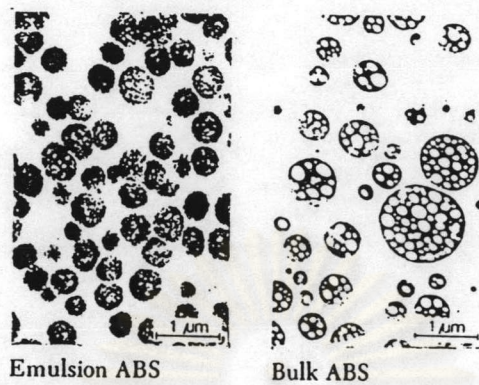


Figure 2.4 Morphology of ABS polymerized in emulsion or bulk [3].

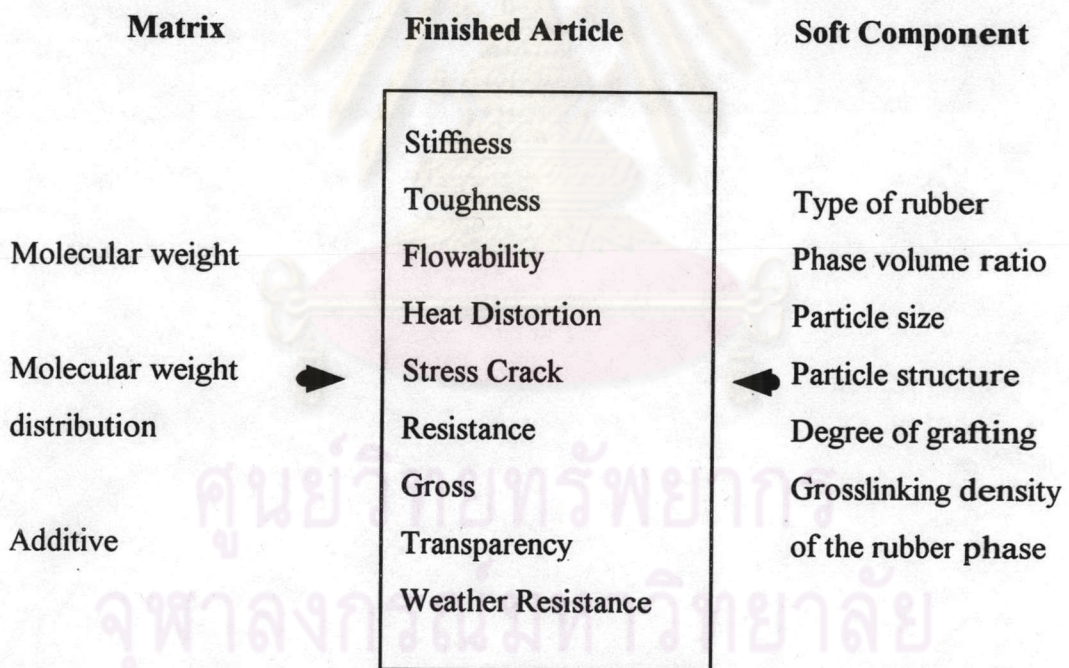


Figure 2.5. Molecular and morphological parameters that influence technical properties [3].

### 2.3 The Interpolymer [5,10,11,12]

The interpolymers (thermoplastic moulding composition) of both the matrix resin (such as SAN matrix) and the graft superstrates ("elastomer phase" or "grafted rubber") consist at least principally of a monovinylidene aromatic hydrocarbon and an ethylenically unsaturated nitrile, i.e., such monomers comprise at least 50.0 percent by weight and preferably at least 75.0 percent by weight of the interpolymers. Most desirably, such monomers comprise at least 90.0 percent by weight of the interpolymer and the usual commercial compositions are substantially completely comprised of such monomers although minor amounts, i.e., less than 5.0 percent by weight of other components such as chain transfer agents, modifiers, etc., may be included.

As will be readily appreciated, the interpolymers used for the graft superstrates should be compatible with the interpolymer of the matrix so as to obtain good properties which will require the presence of the similar monomers. Most desirably, the superstrate interpolymers closely approximate the chemical composition of the interpolymer of the matrix so as to obtain matching of the chemical properties, and accordingly, it is desirable that the superstrates of both graft copolymers closely approximate each other. In addition, it is believed that increased chemical bonding is thereby obtained with commensurate improvement in chemical properties. Moreover, by close matching of certain interpolymers used in the matrix and superstrate such as those containing acrylate, it is possible to obtain a high degree of translucency and substantial transparency. However, it will be appreciated that deviations in the composition of the interpolymers of the matrix and superstrates such as different monomers and/or ratios may be desirable for some applications and that some deviations may inherently occur as the result of process variables.

Exemplary of the monovinylidene aromatic hydrocarbons which may be used in the interpolymers are styrene; alpha-alkyl monovinylidene monoaromatic compounds,

e.g., alpha-methylstyrene, alpha-ethylstyrene, alpha-methylvinyl toluene, alpha-methyl dialkylstyrene, etc.; ring substituted alkylstyrene, e.g., vinyltoluene, o-ethylstyrene, p-ethylstyrene, 2,4-dimethylstyrene, etc.; ring-substituted halostyrene, e.g., o-chlorostyrene, p-chlorostyrene, o-bromostyrene, 2,4-dichlorostyrene, etc.; ring-alkyl, ring-halosubstituted styrenes, e.g., 2-chloro-4-methylstyrene, 2,6-dichloro-4-methylstyrene, etc.; vinyl naphthalene; vinyl anthracene, etc. The alkyl substitutions generally have 1 to 4 carbon atoms and may include isopropyl and isobutyl groups. If so desired, mixture of such monovinylidene aromatic monomers may be employed.

Exemplary of the ethylenically unsaturated nitriles which may be used in the interpolymers are acrylonitrile, methacrylonitrile, ethacrylonitrile, and mixture thereof.

Exemplary of the monomers which may be interpolymerized with the monovinylidene aromatic hydrocarbons and unsaturated nitrile are conjugated 1,3-dienes, e.g. butadiene, isoprene, etc.; alpha- or beta-unsaturated monobasic acids or derivatives thereof, e.g., acrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethyl-hexyl acrylate, methacrylic acid and the corresponding esters thereof; acrylamide, methacrylamide; vinylidene chloride, vinylidene bromide, etc.; vinyl esters such as vinyl acetate, vinyl propionate, etc. dialkyl maleates or fumarates such as dimethyl maleate, diethyl maleate, dibutyl maleate, the corresponding fumarates, etc. As is known in the art, the amount of these comonomers which may be included in the interpolymer will vary as the result of various factors.

In addition, the monomer formulation at the time of polymerization may include a performed polymer of a partially polymerized material such as partially polymerized monovinylidene aromatic hydrocarbon or inter-polymer thereof.

The polymerizable monomer mixtures contain at least 20 percent by weight of the monovinylidene aromatic monomer and preferably at least 50 percent by weight thereof. They also contain at least 5 percent by weight of the unsaturated nitrile and preferably at least 10 percent by weight thereof. From the standpoint of highly

advantageous commercial practice, the monomer formulations contain 20 to 95 percent, and preferably 60 to 85 percent, by weight of the vinylidene aromatic hydrocarbon and 80 to 5 percent, and preferably 40 to 15 percent, by weight of the unsaturated nitrile.

### 2.3.1 The Matrix [5]

As is wellknown in the art, the polyblend is produced by polymerizing the monomers in the presence of the performed rubber. It is generally believed that a portion of the polymer formed grafts onto the performed rubber since it is generally not possible to extract the rubber from the polymerized mass with the usual rubber solvents although some of the rubber polymer may not be in actual chemical combination with the polymer.

Since 100 percent grafting efficiency normally is approached only at ratios of monomers to substrate of below about 0.3:1, at least a portion of the monomers polymerized in the presence of the performed rubber will not chemically combine therewith so as to provide a matrix for the graft copolymers. This portion may be increased or decreased depending upon the ratio of monomers to rubber, the particular monomer formulation, the nature of the rubber, and the condition of polymerization. Generally, interpolymers prepared without the inclusion of rubber will be compounded with material from the graft polymerization reactions to obtain the desired composition.

Any of the usual polymerization processes may be used to affect the polymerization of the ungrafted superstrate, i.e., mass, suspension and emulsion, or combinations. Such techniques are wellknown and are also described herein with respect to the graft copolymerization reactions.

### 2.3.2 The Rubber Substrate [5,10,11,12]

Various rubbers onto which the interpolymer may be grafted during the polymerization in the presence thereof are utilizable as the substrate of the graft copolymer including conjugated 1,3-diene rubber, ethylene-propylene-diene terpolymer rubbers, acrylate-diene interpolymer rubbers, and mixtures. Although saturated rubbers may be grafted, it has been found desirable to include at least a small amount (at least 1.0 percent by weight) of a diene monomer component such as butadiene or hexadiene to facilitate grafting in ethylene/propylene and acrylate rubbers. This diene monomer component will normally comprise 1 to 20 percent by weight and preferably 2 to 8 percent by weight of the ethylenepropylene-diene terpolymer or acrylate copolymer rubber.

The preferred rubbers are diene rubbers or mixture of diene rubbers, i.e., any rubbery polymers (a polymer having a second order transition temperature not higher than 0 °C, preferably not higher than -21 °C, as determined by ASTM Test D-746-52T) of one or more conjugated 1,3-dienes, e.g., butadiene, isoprene, chloroprene, etc. Such rubbers include homopolymers of conjugated 1,3-dienes and interpolymers of such 1,3-dienes with up to equal amount by weight of one or more copolymerizable monoethylenically unsaturated monomers, such as monovinylidene aromatic hydrocarbons (e.g., styrene; an alkyl styrene, such as the o-, m-, and p-methylstyrene, 2,4-dimethyl styrene, the ethylstyrene, p-*tert*-butylstyrene, etc.; an alpha-alkylstyrene, such as alpha-methylstyrene, alpha-ethylstyrene, alpha-methyl-p-methylstyrene, etc.; vinyl naphthalene, etc.); halomonovinylidene aromatic hydrocarbons (e.g., the o-, m-, and p-chloro styrenes, 2,4-dibromostyrene, 2-methyl-4-chlorostyrene, etc.); acrylonitrile; methacrylonitrile; alkyl acrylate (e.g., methyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, etc.), the corresponding alkyl methacrylates; acrylamides (e.g., acrylamide, methacrylamide, n-butyl acrylamide, etc.); unsaturated ketones (e.g., vinyl

methyl ketone, methyl isopropene ketone, etc.); alpha-olefins (e.g., ethylene, propylene, etc.); pyridines; vinyl esters (e.g., vinyl acetate, vinyl stearate, etc.); vinyl; and vinylidene halides (e.g., the vinyl and vinylidene chlorides and bromides, etc.); and the like.

Although the rubber may contain upto about 2 percent of a cross-linking agent, based on the weight of the rubberforming monomer or monomers, cross-linking may present problems in dissolving the rubber in the monomers for the graft polymerization reaction. In addition, excessive cross-linking can result in loss of the rubbery characteristics. The cross-linking agent can be any of the agents conventionally employed for cross-linking diene rubbers, e.g., divinylbenzene, diallyl maleate, diallyl fumarate; diallyl adipate, allyl acrylate, allyl methacrylate, diacrylates and dimethacrylates of polyhydric alcohols, e.g., ethylene glycol dimethacrylate, etc.

A preferred group of rubbers are those consisting essentially of 75 to 100 percent by weight of butadiene and/or isoprene up to 25 percent by weight of a monomer selected from the group consisting of monovinylidene aromatic hydrocarbons (e.g., styrene) and unsaturated nitriles (e.g., acrylonitrile), or mixtures. Particularly advantageous substrates are butadiene homopolymer or an interpolymer of 90 to 95 percent by weight butadiene and 5 to 10 percent by weight of acrylonitrile or styrene.

Of the various techniques customarily employed for polymerizing rubber monomers including mass, suspension and emulsion polymerization, emulsion polymerization is preferred since it will provide the particle size for which the present invention is most beneficially employed and may be used to produce a latex which is useful as the base for emulsion polymerization of the graft copolymer. In this techniques the rubber particle size is determined by a suitable choice of emulsifier concentration and mode of operation (monomer-to-water ratio, temperature). In



principle, big rubber particles are made by reduced emulsifier concentration, by monomer feed, or by seeded polymerization.

#### **2.4 Graft Copolymerization Processes [5,10,11,12]**

The graft copolymers are prepared by polymerizing monomers of the interpolymer in the presence of the performed rubber substrate, generally in accordance with conventional graft polymerization techniques. Although suspension and mass polymerization techniques may be employed, the preferred processes use an emulsion technique to obtain the particle size of not more than about 0.6 micron for the graft copolymer with which the present invention is most beneficially employed. In such graft polymerization, the performed rubber substrate generally is dissolved or dispersed in the monomers and this admixture is polymerized to combine chemically or graft at least a portion of the interpolymer upon the rubber substrate. Depending upon the ratio of monomers to rubber substrate and polymerization condition, it is possible to produce both the desired grafting of the interpolymer onto the rubber substrate and the polymerization of ungrafted interpolymer to provide a portion of the matrix at the same time.

As will be pointed out, more in detail hereinafter, the ratio of monomers to rubber charged to the graft polymerization reaction is the primary determinant of the superstrate : substrate ratio of the resultant graft copolymer. However, conditions of polymerization, rubber chemistry and particle size, rates of monomer addition, chain transfer agents, etc., may also exert an effect.

The catalyst is generally included within the range of 0.001 to 3.0 percent by weight, and preferably on the order of 0.005 to 0.5 percent by weight of the polymerizable material, depending upon the monomers and the desired polymerization cycle [10,12].

As is well known, it is often desirable to incorporate molecular weight regulators such as mercaptans, halides and terpenes in relatively small percentages by weight, on the order of 0.001 to 2.5 percent by weight of the polymerizable material. In addition, it may be desirable to include relatively small amounts of antioxidants or stabilizers such as the conventional alkylated phenols, although these may be added during or after polymerization.

In the emulsion polymerization process, the monomers and rubber substrate are emulsified in water by use of suitable emulsifying agents such as fatty acid soaps, alkali metal or ammonium soaps of high molecular weight alkyl or dialkyl sulfates and sulfonates, mineral acid salts of long chain aliphatic amines, etc. Emulsifying agents which have proven particularly advantageous are sodium oleate, sodium palmitate, sodium stearate and other sodium soaps. Generally, the emulsifying agent is provided in amounts of about 0.1 to 15 parts by weight per 100 parts by weight of the monomers, and water is provided in an amount of about 1 to 4 parts per part of monomers, and even in larger ratios where greater dilution is desirable [10,11].

If so desired, an aqueous latex formed in the emulsion polymerization of the rubber substrate may provide the aqueous medium into which the monomers are incorporated with or without additional emulsifying agents, water, etc. However, the rubber may be dissolved in the monomers and the mixture emulsified, or a latex thereof may be separately prepared [3].

Various water-soluble free radical polymerization initiators are conventionally used for emulsion polymerization of the rubber monomer including conventional peroxy and azo catalysts, and the resultant latex may be used as the aqueous medium with which the interpolymer monomers are admixed. In this manner, the catalyst for the rubber polymerization may function in whole or in part as the catalyst for the graft polymerization. However, additional catalyst may be added at the time of graft polymerization. Exemplary of suitable peroxy catalysts are the alkali metal peroxides,

persulfates, perborates, peracetates and percarbonates, and hydrogen peroxide. If so desired, the catalysts may be activated to form redox systems. In addition, it may be advantageous to include an oil-soluble catalyst such as di-tert-butyl peroxide, benzyl peroxide, lauryl peroxide, oleyl peroxide, toluyl peroxide, di-tert-butyl diperphthalate, tert-butyl peracetate, tert-butyl perbenzoate, dicumyl peroxide, tert-butyl peroxide, isopropyl peroxy dicarbonate, 2,5-dimethyl-2,5-di-(tert-butylperoxy)hexane, 2,5-dimethyl-2,5-di-(tert-butylperoxy)hexyne-3-tert-butyl hydroperoxide, cumene hydroperoxide, p-methane hydroperoxide, cyclopentane hydroperoxide, diisopropylbenzene hydroperoxide, p-tert-butyl-cumene hydroperoxide, pinane hydroperoxide, 2,5-dimethylhexane-2,5-di-hydroperoxide, etc., and mixtures thereof. However, other free-radical generating catalysts may be employed such as actinism radiation.

Chain transfer agents and other polymerization modifiers may be desirably included and it is generally advantageous to incorporate a higher alkyl mercaptan such as tert-dodecyl mercaptan [5,12], which acts both as a promoter and a regulator. In addition, antioxidants and stabilizers such as the alkylated phenols may be added.

The emulsion mixture is then polymerized in an inert atmosphere at temperatures in the range of 20 °C to 100 °C with agitation. Pressures of 1 to 100 pounds per square inch may be employed and the monomers and/or additional catalyst may be added incrementally or continuously over a portion of the reaction cycle. Polymerization is continued until substantially all, i.e., more than 90 percent, of the monomers have reacted. The remaining monomers and other volatile components are then distilled from the latex, which is then dewatered, washed and dried [5,11,12].

Particle size of the emulsion graft particles may be varied by seeding, emulsifying agent concentration, agitation, rubber size variation through agglomeration prior to grafting, coagulation techniques, etc. One of the most advantageous means

for achieving the desired particle size rubber substrate is by controlled agglomeration using acidulation or freeze-thaw techniques [3].

The particle structure of emulsion-polymerized ABS is of the core-shell type (Figure 2.6). Particles of polybutadiene must be tied in the surrounding matrix by a graft shell to provide good coupling of the two phases. The more closely covered the particle, the better the coupling and the more uniform the distribution in the matrix. Because the grafting is nearly complete (scarcely any free SAN polymer present after the graft reaction), the proportion of grafted SAN in the interface depends on the total amount of glassy monomer added and external grafts. The proportion of graft copolymer included rises with increasing particle size and decreases with its cross-link density.

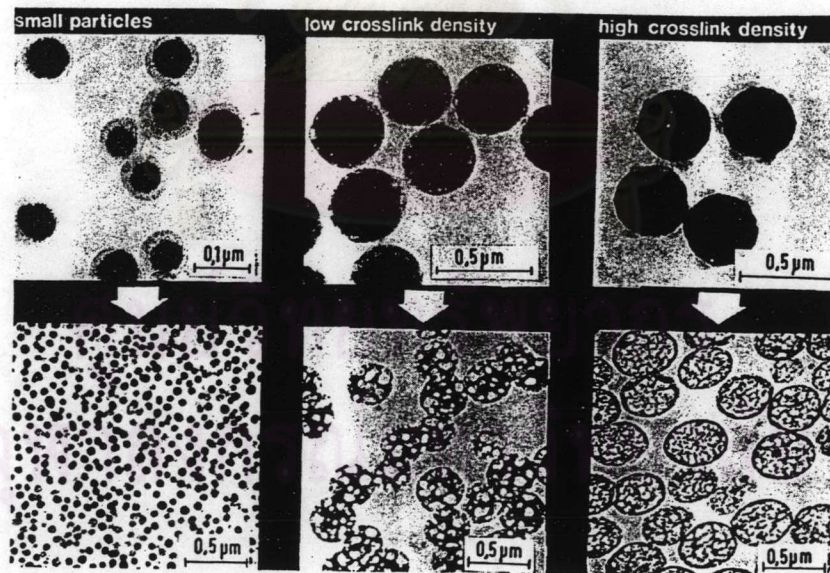


Figure 2.6. Structure of grafted particles in ABS [3].

Emulsion grafted small particles exhibit a closed shell of graft copolymer on their surface, and no inclusions are visible in the images either before or after the mixing process. Bigger particles with low cross-link density have hardly any detectable graft shell, and the mixture with matrix polymer shows that the particles contain many large inclusion. If the cross-link density is enhanced, the graft shell become more clearly marked, but a considerable part of matrix polymer is still located inside the particle [3].

If the size and cross-link density are constant grafting is of crucial importance for the mechanical properties (Figure 2.7). If the particles are not completely converted by the graft shell, they will tend to agglomerate to large and irregularly shaped clusters during the mixing process, and the impact strength of the final ABS will depend on the mixing conditions.

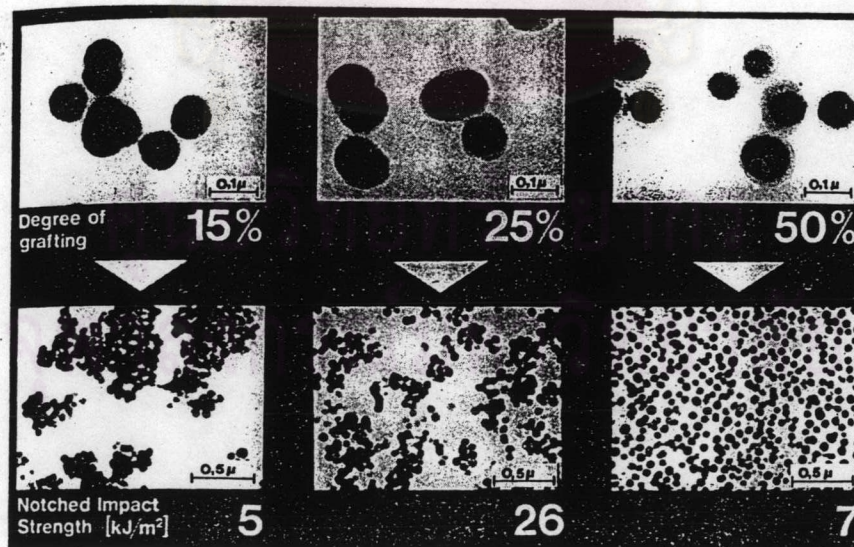


Figure 2.7. Influence of degree of grafting on ABS structure [3].

If the primary particles are small ( $0.1\ \mu\text{m}$  in diameter), an increase in grafting will first reduce the cluster dimensions to the optimum value. [3,4,5] Consequently, impact strength increases. If grafting is increased further, particles will be prevented from clustering and impact strength will drop again. With larger particles, less than 50% grafting is sufficient to obtain very tough materials, and products with bimodal particle-size distribution are even more advantageous. In contrast to HIPS, the internal structure of ABS is of minor influence on the mechanical properties. Most ABS types have more or less solid particles with few and small inclusions, depending on particle size and cross-link density.

### **2.5 Formation of the Blend [3,4,5]**

The graft copolymers may be blended in the ungrafted interpolymer matrix by various techniques. In the preferred techniques, the graft polymers are extrusion blended or mill rolled with or without the addition thereto of additional ungrafted interpolymer depending upon the amount of ungrafted interpolymer in the feedstocks providing the rubber grafts and the total rubber graft content desired in the blend. Alternatively, a mixed latex of the different graft level copolymer may be prepared and coagulated to provide a mixed coagulum containing the rubber grafts of the desired two particle graft levels in the desired proportions.

General the blends may contain 1.0 to 70.0 percent by weight of the rubber grafts combined. Increasing the total amount of rubber graft while maintaining the ratio of low graft copolymer to total graft copolymer constant generally increases the Izod impact strength of the composition but rapidly increases the viscosity of the blend and decreases the tensile stress at yield and fail and the tensile modulus. Accordingly, the preferred blends contain about 10.0 to 50.0 percent by weight of the combined graft copolymers and most desirably about 20.0 to 40.0 percent by weight.

The effect of varying the rubber content of the composition may be seen in Figure 2.6 of the attached drawings wherein a series of compositions were prepared containing the high graft and low graft components in a ratio of 60:40 and in which the content of the rubber substrate in the composition was varied by the addition of increased amounts of the graft components. As can be seen, the Izod impact value rises relatively rapidly as the amount of rubber is increased.

## **2.6 Graft copolymers from natural rubber [7]**

Useful rubbery behaviour in polymers which could be processed as thermoplastic was reported as early as 1958. There was increasing interest in the blending of rubbery and hard polymers to generate materials which had greater flexibility than many of the conventional plastics and rubber like elasticity approaching that of vulcanized rubber. In 1965, the styrene-diene block copolymers were introduced by commercial announcement. Soon after their commercial announcement, the materials of many different types are now used in thermoplastic rubber technology.

The Natural Rubber Research Organizations had investigated process for grafting polymers to natural rubber using free radical chemistry. Materials were obtained which contained both plastic and rubber constituents and Heveaplas-MG, a graft copolymer of natural rubber and poly (methyl methacrylate), became commercially available.

### **2.6.1 Grafting Chemistry of Natural Rubber**

Anionic grafting chemistry is applicable to polyisoprene as well as to polybutadiene, but the process is very sensitive to the presence of protic impurities and must be operated in a hydrocarbon solution of the polymer. On the other hand, free

radical grafting chemistry was demonstrably practicable in the presence of water (i.e., in latex) and of the various non-rubber constituents which are an inseparable part of natural rubber in all its commercial forms. There was therefore a considerable incentive to try to refine the free radical grafting techniques further to provide the molecular architecture that is necessary for thermoplastic rubber properties.

Maximum control of graft chain length and number of graft chains per backbone will be available if the graft chains are prepared as a separate process and are subsequently attached to the backbone by polymer-polymer reaction. Reactions of this type for natural rubber would have a number of additional constraints. Use of a diluent to induce molecular mixing was considered to be commercially impracticable for natural rubber and efficient reaction in latex could almost certainly be discounted. In the latter case, the most favourable situation would arise when the graft chain polymer was water soluble, so that individual molecules could interact with the latex particle. Even then, interaction would be confined to the particle surface if the criterion of polymer-polymer incompatibility was to be set for reaction product. If the graft chain polymer was not water soluble, reaction could only occur via surface to surface contact of the two dispersed polymer phases and this implies instability of the latex towards coagulation. These considerations point directly to mixing of the polymer constituents in an internal mixer as the most appropriate route to successful reaction.

## 2.7 Literature Reviews

G. Gordon Cameron and M. Younus Qureshi [14] studied kinetics and mechanism of styrene grafting to polyisoprene. The radical-induced grafting of styrene onto polyisoprene (PIP) in benzene solution at 60 °C was studied in rubber concentration (up to 0.5 monomer mole liter<sup>-1</sup>) in which the polymerization of styrene showed ideal kinetics with no retardation by PIP. The proportion of polystyrene



incorporated as graft is independent of the initiator (benzoyl peroxide) concentration and was found to be consistent with the kinetic expression derived by Cameron et al. The graft fraction of polystyrene which was higher than in the corresponding styrene-polybutadiene system reflected the higher reactivity of PIP toward radicals. Azobisisobutyronitrile produces no graft copolymer in the system.

D.J. Hourston and J. Romaine [15,16] studied natural rubber poly(methyl methacrylate) composite latexes synthesized using an amine-activated hydroperoxide. Composite latex particles based on natural rubber latex the composite latex was synthesized to yield materials which may be formally regarded as interpenetrating polymer networks and semiinterpenetrating 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. Besides, natural rubber-polystyrene composite latexes synthesized using azobisisobutyronitrile as initiator was studied. Materials which may be classified as interpenetrating polymer networks have been prepared by *in situ* polymerization of styrene in natural rubber latex using azobisisobutyronitrile (AIBN) as the initiator. The resulting materials have been characterized by electron microscopy, Soxhlet extraction coupled with proton nuclear magnetic resonance spectroscopy, dynamic mechanical analysis, and stress-strain analysis. The styrene polymerized within the natural rubber latex particles to give a relatively fine phase-separated morphology with some evidence for a limited degree of segmental mixing. Moreover, it was clear that AIBN despite what was stated in the literature, led to some grafting of polystyrene, and, in addition, caused significant degradation of the natural rubber molecules when the styrene content is low.

K. Hyungsu et al., [17,18] studied toughened of SAN copolymers by an SAN emulsion grafted rubber. A series of styrene/acrylonitrile (SAN) copolymers have been blended with an SAN grafted butadiene rubber to form ABS type materials. The major focus has been the effects of composition of the SAN matrix copolymer, for a fixed SAN graft, on blend toughness, deformation behaviour and morphology. The acrylonitrile content varied from 0 to 40% in the matrix copolymers, while the acrylonitrile content of the emulsion graft was fixed at 22.5%. Maximum strength and toughness were observed for compositions based on SAN matrices containing 34% AN. Mechanical dilatometry revealed no major changes in deformation mechanism as the acrylonitrile content of the matrix changed. Most of the deformation was due to dilatational processes, presumably crazing. Transmission electron photomicrographs showed differences in rubber particle dispersion. The morphology revealed by scanning electron microscopy of fracture surfaces distinguished the ductile and less ductile blends. The effects of acrylonitrile content on the toughness of ABS materials were studied. Styrene/acrylonitrile (SAN) copolymers were toughened by addition of several SAN emulsion grafted rubbers. The main variables of the study included the AN content of the SAN graft (14.2-37.5 %) and the AN content of the SAN matrix (14.7-40 %). The aim was to develop general principles underlying the properties of rubber toughened SAN or ABS materials. Rubber-matrix adhesion, state of rubber particle dispersion and the inherent ductility of matrix polymer were evaluated, and the trends found in the mechanical behavior of the blends were reasonably well explained by these three factors. The concept of inherent ductility, in particular, was effectively utilized and its importance in the ultimate properties of rubber toughened SAN was emphasized.

H. Nai-Jen and C.S. Donald [19] presented a new method of measuring the efficiencies of free radical grafting reaction which utilized the compositional analysis of capability of dual-detector (ultraviolet and refractive index) gel permeation chromatography (GPC) in which the mixture of polymers resulting from the graft copolymerization reaction was also subjected to separation by molecular size. Samples of the reaction mass drawn from a reactor were diluted with GPC eluent and injected directly into the chromatograph without any other preparative step. Grafting efficiency, graft ratio, molecular weight distributions and the frequency of graft chains along the backbone polymer were simultaneously determined. Low molecular weight diluents (residual monomer, solvent, initiator, etc.) were readily separated from the polymer within the chromatograph, allowing for the determination of the fractional conversion of graft monomer (to grafted and ungrafted polymer) from the same analysis. This simple technique overcame the need to separate or purify the polymer mixture prior to analysis, as required for most other methods. Experimental results were presented for the grafting of styrene onto *cis*-polybutadiene. Gelled samples could not be analyzed by this new technique.

Rusdan Dalimunthe [20] studied the effects of the styrene monomer on colloid stability of natural rubber latex which may affect the grafting reaction and hence decreasing or increasing the efficiency of grafting of the monomers to natural rubber. It has been shown that styrene acts as a destabiliser for natural rubber latex. The destabilisation was due to the swelling effect of rubber particles in styrene and forming a monomer-swollen rubber. Consequently, the average distance between rubber particles decreased thereby reducing the mechanical stability time (MST) of natural rubber. It has also been shown that to provide a favourable condition of colloid stability for the polymerization of styrene in natural rubber latex, the DRC of natural

rubber (60%) was preferably diluted to about 45 % and the temperature of polymerization was preferably kept at 65°C.

C. Rujinirun [25] studied the preparation of graft copolymer of styrene and acrylonitrile onto natural rubber. Process for the preparation of copolymer of styrene and acrylonitrile on natural rubber latex has been studied. The graft copolymerization was carried out varying concentration of styrene and acrylonitrile monomers, emulsifier concentration and reaction temperature. The grafting efficiency of graft natural rubber determined by solvent extraction technique and degree of conversion were studied and discussed. The copolymer composition was determined by Infrared spectroscopy (FTIR) and CHN/O analyzer. The characterization also included Gel permeation chromatography (GPC) and Differential scanning calorimetry (DSC). Blending is widely employed as a simple and practical means of obtaining new materials with special properties. The blends of graft natural rubber and SAN were formulated. The effect of graft natural rubber and SAN ratio on impact strength, flexural strength, tensile strength, hardness, melt flow index and heat distortion temperature were investigated.

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