

CHAPTER II

THEORY AND LITERATURE REVIEW

Natural Rubber [7, 8]

Nearly 2000 species of trees, shrubs or vines of the tropical and temperate regions produce latex from which natural rubber or a closely related substance can be obtained. However, the latex from the tree of *hevea brasiliensis* is the only important commercial source of natural rubber. The tree is indigenous to the Amazon valley. Natural rubber has been known to the inhabitants of South America for centuries. Christopher Columbus is considered to be the first European to discover it during his second voyage in 1493-1496

Rubber was introduced to the western world by Charles de la Condamine, who sent samples to France from Peru in 1736 and published the result of his observations in 1745. By the end of the eighteenth century, Europe and America were using a few tons of rubber per year. However, users found it difficult to work with solid rubber. Moreover, articles made from natural rubber turned sticky in hot weather and stiffened in the cold.

Two important developments in the nineteenth century enabled these problems to be solved and laid the foundation for the multibillion-dollar modern rubber industry. In 1820, Thomas Hancock invented a machine called the "masticator" that allowed solid rubber to be softened, mixed and shaped. In 1839, Charles Goodyear discovered the process of vulcanization. He found

that heating a mixture of rubber and sulfur yielded products that had much better properties than the raw rubber.

Soon a variety of articles from rubber started to come into the market and the demand of rubber grew rapidly. Exports of raw rubber increased from a few hundred tons in 1846 to almost 10,000 tons by 1880. It was soon apparent that Brazil would not be able to meet future demand. The British considered the possibility of cultivating rubber in Asia and by 1880 Hevea seeding were widely distributed in Asia.

The land used for rubber cultivation and the production of natural rubber has grown steadily as expected since World War II. In 1983, more than 7.5 million hectares of land in the world were under rubber cultivation and about 4 million metric tons of rubber were produced. The Southeast Asia region accounted for about 80 % of the total production. Thailand was the biggest producer, followed by Indonesia and Malaysia. The world production of natural rubber is shown in Table 2.1.

Table 2.1. World production of natural rubber (1993)

country	tons (10^3)
Thailand	1.50
Indonesia	1.35
Malaysia	1.07
India	0.425
China	0.325
Philippines	0.172
Srilanka	0.106
others	0.482
Total	5.43

Source : XIRSG, Rubber Statistical Bulletin

Natural Rubber in Thailand [2]

The data from the Industrial Economics & Planning. Division, Ministry of Industry showed that in 1992, Thailand produced 1,520,000 tons of natural rubber and exported 1,400,000 tons or 92.1% of total production. The remaining 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 air dry sheet, smoked sheet, block rubber, crepe rubber and concentrated latex. There are various products made from different type of rubber which are produced in Thailand as shown in Table 2.2

Table 2.2. Rubber products produced from different types of rubber.

No	Productions	Types of rubber
1	Mould foams for mattresses	Concentrated latex 60%
2	Elastic thread for undergarments	Smoked sheet
3	Toyballons	Concentrated latex 60%
4	Inner tubes for motor vehicles	Smoked sheet
5	Belts	Smoked sheet
6	Rubber shoes, slippers	Scraps of smoked sheet, smoked sheet, block rubber, crepe rubber
7	Battery jackets (boxes)	Smoked sheet
8	Spare parts for automobiles	Smoked sheet
9	Rubber soles	Rubber sheet, scraps of rubber sheet, block rubber

Table 2.2. (continued)

No	Productions	Types of rubber
10	Hoses, water pipes	Crepe rubber, scraps of rubber sheet
11	Wheels	Scraps of smoked sheet
12	Medical devices, electric goods, furniture upholstery	Crepe rubber
13	adhesives, adhesives for foot-wear	Smoked sheet, rubber latex
14	Condoms (Contraceptives), rubber dolls	Smoked sheet
15	Spare parts for thermos	Scraps of smoked sheet, block rubber
16	Household gloves, nipples	Concentrated latex 60%
17	Golf balls	Rubber sheet
18	Spread foams for carpets	Concentrated latex 60%
19	Rubber sponge	Concentrated latex 60%
20	Rubber rings	Smoked sheet

Source : Southern Industrial Economics Center, Industrial Economics & Planning Division, Ministry of Industry



Natural Rubber Latex

1. Latex Technology [9, 10]

Natural rubber, on which the technology of the industry was built, is obtained by the coagulation of the milky aqueous dispersion of rubber called latex produced by the tree *Hevea brasiliensis*.

As methods were discovered of preserving and transporting the latex from the tropical areas, in which they grow, to the USA, Europe and Japan, a separate technology for the manufacture of products direct from latex developed during the 1920s. The several methods of concentrating the latex, by heat, by creaming, centrifugally or chemically, and later by electrodecantation encouraged these developments because less water was transported and because higher solids content increased still further its advantage over solutions of rubber in organic solvents for some manufacturing operations.

2. Composition [9, 10]

The addition of any filler reduces the strength of the rubber obtained from the latex. Nevertheless, for certain applications and because of the high strength of the natural latex rubber, substantial quantities of clay and other cheap fillers, suitably wetted out and dispersed in water, are added. Compounding with curing agents is necessary so that a vulcanized product can be obtained. Because of the ease of incorporation as aqueous dispersions or solution and the absence of any risk of pre-vulcanization by heat, very rapid accelerator can be employed. In this connection, mention should be made of

vulcanized or prevulcanized latex; this latex in which the particles are vulcanized, and the product obtained from it, does not require any heat treatment apart from that to remove moisture.

In addition to antioxidants, pigments and dyes, surface-active agents are incorporated to control stability and impart the necessary processing properties, e.g. fabric wetting and penetration. Gelling and heat-sensitizing agents are also added.

3. The Production of Natural Rubber Latex Concentrate [9, 10]

The latex is normally called "field" latex, and its average rubber content is 30 percent by weight. This material is not utilized in its original form due to its high water content and susceptibility to bacterial attack. It is necessary both to preserve and concentrate it, so that the end product is stable and contains 60 percent or more of rubber. All the important processes of fabrication of latex articles begin with a latex that has a 60 percent minimum rubber content. Extensive blending of the concentrated latex ensures a consistent high quality material meeting national and international specifications.

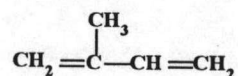
Latex concentrate is differentiated by the method of concentration and type of preservative used. In addition to the general purpose type of latex, there are specialty forms such as double centrifuged latex, creamed centrifuged latex ("sub-stage" latex), and modified types such as prevulcanized latex. Three methods of concentration are employed, centrifugation, evaporation and creaming ; centrifugation is highly preferred method and accounts for 95 percent of total production.

Field latex is collected from the tapping cups, and bulked. Preliminary ammoniation to about 0.05-0.2 percent is carried out to protect it from bacterial attack prior to delivery to the concentrate factory. On arrival, the latex is tested for properties such as rubber content and volatile fatty acid content. If the test results are satisfactory, the latex is put in bulking tanks. From here it is supplied to the centrifuges, where separation occurs, yielding a concentrate (60 percent or more rubber content) and a skim latex (3-6 percent rubber content). The concentrate is ammoniated using ammonia gas and treated with the rest of the preservative system, if necessary. It is kept in storage tanks for quality tests to be carried out. The latex concentrate is transferred to the port installation for shipping to the consumer in bulk containers or drums. Gravitational flow is used wherever possible, otherwise air pressure pumps are employed.

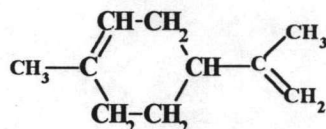
4. The Chemical Formula of Natural Rubber [11]

The empirical formula for the natural rubber 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 . While this result was obtained, using a product which contained associated non-rubbery materials, subsequent studies with highly purified materials have confirmed Faraday's conclusion.

The first, isoprene, was found to have the formula C_5H_8 , for which Tilden proposed the structure.



In due course the structure was confirmed by synthesis of the isoprene by Euler and by others. The second fraction was separated by Himly and found to have the formula $C_{10}H_{16}$. Today this materials known as dipentene and its structure was confirmed by synthesis of Perkin in 1904 to be:



Clearly dipentene is a dimer of isoprene and the latter may be converted into the former by heating at $270^{\circ}C$ with the process being reversed at higher temperatures.

The linear structure proposed by Pickles provided for the possibility of structural isomerism with both *cis*- and *trans*- repeating units.



It was known at this time that the major hydrocarbon component of both gutta percha and balata (at that time important in belting, submarine cable, golf ball and container applications) was a polyisoprene which when reacted with bromine and ozone gave similar results to those obtained with natural rubber. It was therefore tempting to suggest that one isomer was that of gutta percha and balata and the other that of natural rubber. The earlier work of Staudinger suggested that the *trans*-isomer was natural rubber and gutta percha the *cis*-. However later studies of X-ray fibre diagrams of stretched rubber led Meyer and Mark to the view that natural rubber was the *cis*-polymer, a view reinforced

by Bunn (1942) which elucidated the structure and unit cell of the crystalline stretched rubber molecule (Figure. 2.1).

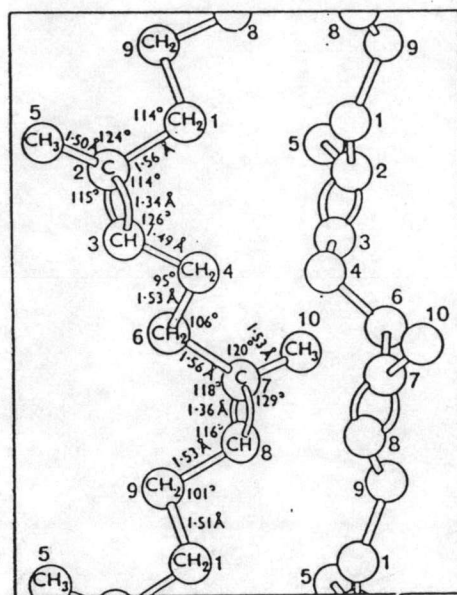
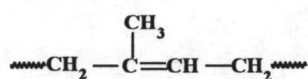


Figure 2.1. Unit cell structure of the natural rubber molecule.

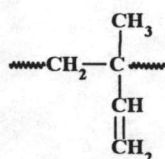
(From Bunn, 1942.) [11]

The possibility that the natural rubber molecule might contain a mixture of *cis*- and *trans*- groups was considered to be unlikely because such a mixed polymer would have an irregular structure and be unable to crystallize in the manner of natural rubber. Infrared studies have subsequently confirmed that natural rubber was the *cis*-polymer.

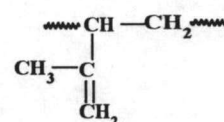
Infrared studies have indeed shown for a long while that natural rubber was at least 97% *cis*-1,4-polyisoprene. The absence of measurable amounts of 1,2-structure but an infrared band at 890 cm^{-1} was at one time thought to be due possibly to the products of a 3,4- structure.



1,4-



1,2-



3,4-

Time-averaging techniques using high resolution NMR which are capable of detecting 3,4-groups at concentrations of less than 0.3% have however failed to establish the existence of any such moiety and have also failed to show up any trace of *trans*-material. The conclusion must therefore be that the molecule is more than 99% *cis*-1,4-polyisoprene. Since all the evidence points to the conclusion that the natural rubber molecule is not obtained in nature by the polymerization of isoprene the absence of detectable pendant groups as would be produced by 1,2- and 3,4- addition is hardly surprising.

Graft Copolymer From Natural Rubber [9]

Natural rubber 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 performed chains of glass polymer to the natural rubber backbone and requires some degree of control over the molecular weight of the glassy polymer and the frequency of attachment to the natural rubber backbone. In comparison with triblock copolymers with carefully controlled molecular weight distribution, the graft copolymers must always have a less than ideal structure for formation of an efficient three-dimensional network, and this is particularly so when, as is normally the case, there is no specific control over the spacing of graft sites along the backbone chain. The technological properties of the natural rubber graft copolymers reflect this fundamental

difference to some extent. This, combined with economic constraints, have so far prevented the commercial development of the materials. The process does, however, have some versatility and, within the constraints imposed by the synthetic chemistry of the prepolymers and the requirement of some double bond unsaturation in the backbone chain, it has provided access to an interesting range of experimental graft copolymers.

The Interpolymer [5, 12, 13]

The interpolymers (thermoplastic moulding composition) of the present invention 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-chloro-styrene, 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.

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 effect polymerization of the ungrafted superstrate, i.e., mass, suspension and emulsion, or combinations thereof. Such techniques are wellknown and are also described herein with respect to the graft copolymerization reactions.

The Rubber Substrate [3, 5, 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 thereof. 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 thereof. 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. In practice, however, it is preferable to produce small particles within reasonable cycle times. The final particle size is adjusted afterward by agglomeration techniques; this approach leads to a bimodal particle-size distribution of unagglomerated and agglomerated particles (Figure 2.2).

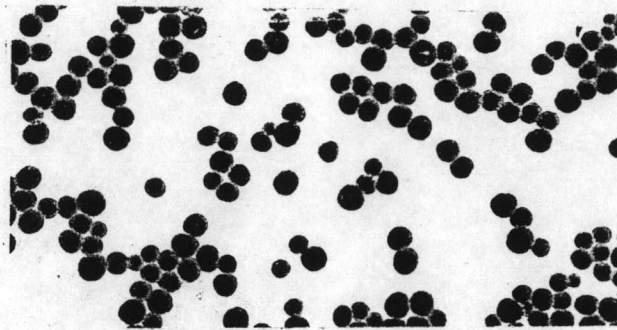


Figure 2.2. Bimodal particle-size distribution in ABS by agglomeration [3].

In ABS polymers, the optimum particle size is much smaller than in HIPS. Because of the polar character of the matrix, the material tends to deform by shear yielding at low deformation rates. At higher deformation rates, crazes are nucleated. Very small particles make the ABS resins stiff, glossy, and less tough; big particles impair stiffness and gloss, but improve toughness (Figure 2.3). The optimum mean particle size for a good combination of toughness, stiffness, and surface gloss is about 0.3-5.0 μm . Measurements of specimens processed under identical conditions show that gloss can be related exponentially to particle size.

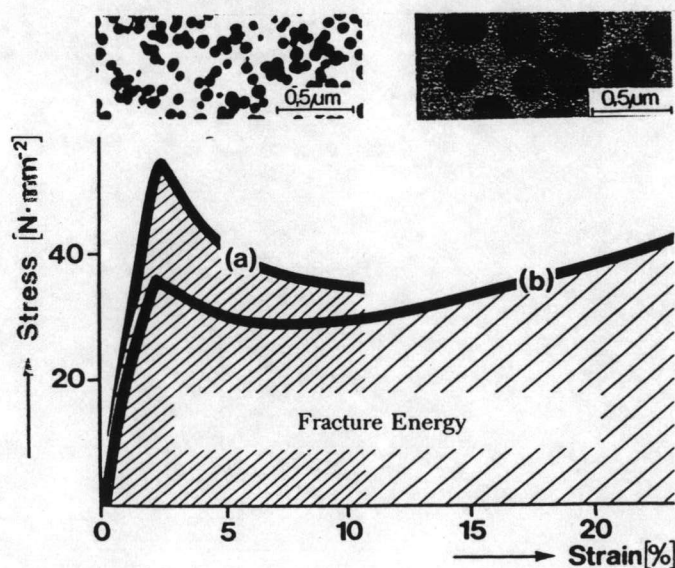


Figure 2.3. Particle size and mechanical properties of ABS [3].

Graft Copolymerization Processes [3, 5, 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 1.0 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 [5, 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 [12, 13].

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, di-isopropylbenzene hydroperoxide, p-tert-butyl-cumene hydroperoxide, pinane hydroperoxide, 2,5-dimethylhexane-2,5-dihydroperoxide, 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, 14], 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, 12, 13].

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 2.4). 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.

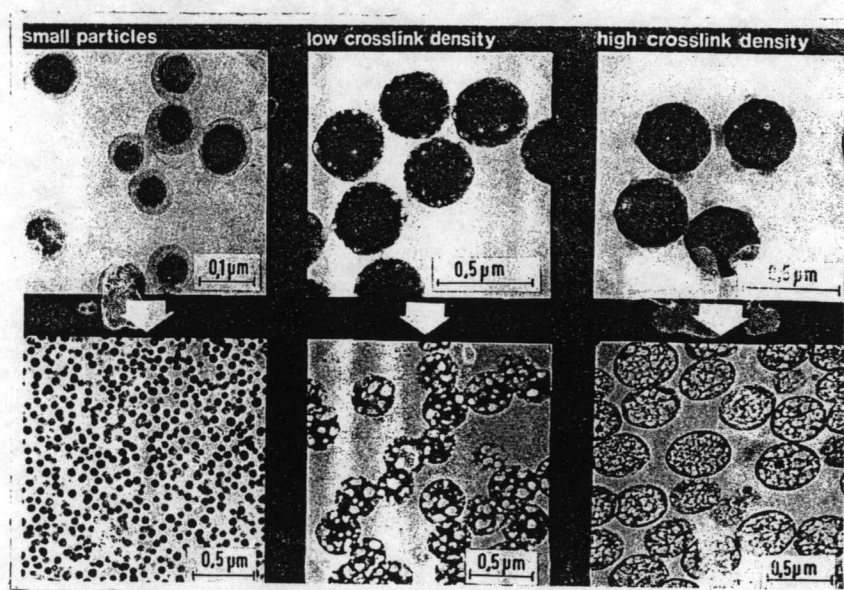


Figure 2.4. Structure of grafted particles in ABS [3].

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 amount 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 2.5). 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.

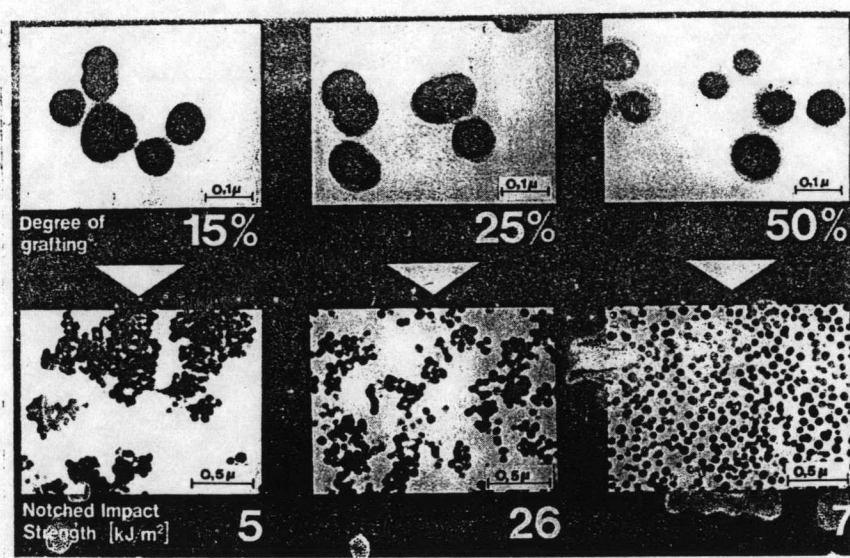


Figure 2.5. Influence of degree of grafting on ABS structure [3].

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.

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.

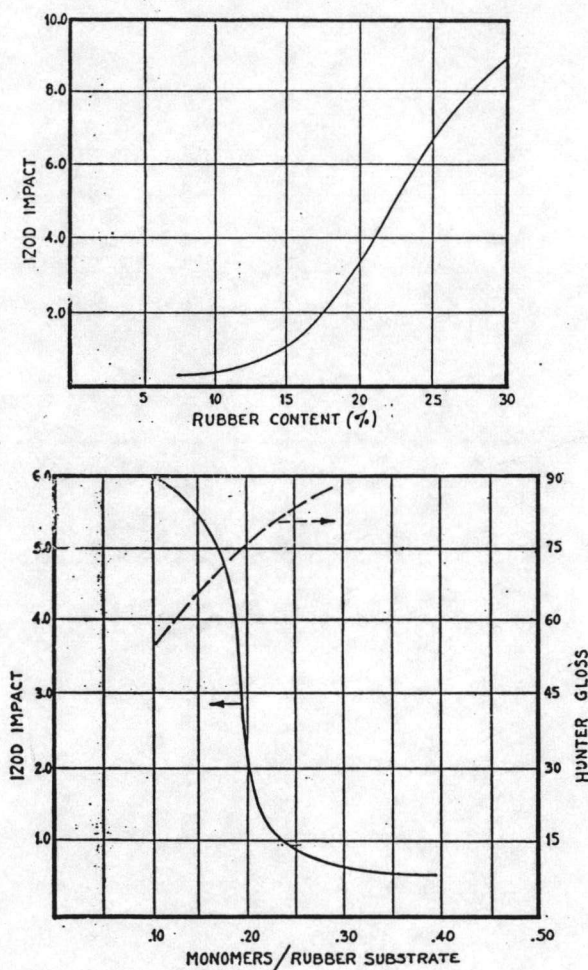


Figure 2.6. The effect of varying the rubber content of the composition in thermoplastic ABS [5].

Generally, the properties of the invention are most dependent upon the level of grafting of the low graft component and its percentage of the total graft copolymer. Accordingly, the composition desirably contain the low graft

copolymer component in an amount which increases as the amount of grafting is increased.

It will be readily appreciated that optional components may be added to the composition such as fillers, antioxidants, stabilizers, etc., depending upon the intended use and the nature.

It has been found that the efficiency of the present invention may be further enhanced by including a small amount of relatively large particle size graft copolymer. Generally, the relatively small particle graft copolymer of the present invention having both high and low graft components when combined with small amounts of graft copolymer having particle size of about 0.8 to 2.0 microns affords a beneficial blend from the standpoint of impact properties commensurate with acceptable gloss [13].

Literature Review

V. Veena and K.R.Animesh [15] studied the characterization of natural polyisoprenes and synthetic polybutadiene. The characterization included IR, NMR, GPC, TGA, contact angle, and viscosity measurements. Spectroscopic characterization helped in the differentiation of InR (India Rubber) and GR (Gayana Rubber). Viscosity data was used in the evaluation of activation parameters at infinite dilution of viscous flow. Viscosity data was also used for the determination of the conformation of the macromolecules in various solvents. Surface characterization confirmed the total hydrophobic nature of the three rubbers. Thermal analysis showed different degradation pattern for natural rubbers than for the synthetic rubber.

M.E. Enyiegbulam and I.U. Aloba [16] studied graft characteristics and solution properties of natural rubber-g-methyl methacrylate copolymer in

MEK/toluene. Despite the long period (25-30 years) of accumulation of research results, in natural rubber-g-methyl methacrylate, technological applications demanded a correlation between grafting efficiency and graft level on the one hand, and the attendant influence on the hydrodynamics of the graft in technologically useful solvent mixture of MEK/toluene on the other hand. An increase in the concentration of methyl methacrylate at a given benzoyl peroxide initiator decreased both the graft level and grafting efficiency but increased the molecular weight of the copolymer. But an increase in the concentration of the benzoyl peroxide initiator at a given monomer concentration decreased the graft level to a constant level when the benzoyl peroxide concentration exceeds approx. $1.0 \times 10^{-2} \text{ mol/cm}^3$. Dilute solution theory applicable to homopolymers could also be applied to the graft copolymers without any adverse effect in technological application.

L. Sharon and R. Alfred [17] studied the mechanism of core-shell inversion in two-stage latexes. In two-stages where the first polymer was more hydrophilic than the second, inversion of the core and shell could occur. The mechanism of core-shell inversion during the initial and final intervals of the second-stage polymerization was investigated using model PMMA/PS systems. The phase behavior of polymer solutions intended to model the two-stage system during the initial interval of the second stage polymerization has yielded some insight into the thermodynamics of phase inversion. If the second stage monomer dissolved first stage polymer, the latter would tend to precipitate at the water/monomer interface, particularly in the presence of surfactant. The energy of the oil/water interface was thereby reduced. In the final interval, when much of the second monomer had polymerized, phase mobility was crucial to the inversion process.



N.E. Aubrey et. al., [5] founded the foregoing and related objects and advantages may be readily attained in a composition comprising a polyblend of (A) a matrix of an interpolymer consisting at least principally of a monovinylidene aromatic hydrocarbon and an ethylenically unsaturated nitrile; (B) a first graft copolymer having a graftable rubber substrate containing a diene monomer component and a superstrate of an interpolymer consisting at least principally of a monovinylidene aromatic hydrocarbon and an ethylenically unsaturated nitrile ; and (C) a second graft copolymer having a graftable rubber substrate containing a diene monomer component and a superstrate of an interpolymer consisting at least principally of a monovinylidene aromatic hydrocarbon and an ethylenically unsaturated nitrile. One of the graft copolymers had 0.7 to 5.0 grams of superstrate per square centimeter of substrate surface and the other graft copolymer had 7.0 to 35.0 x 10⁻⁷ grams of superstrate per square centimeter of substrate surface. The two graft copolymers each had a particle size of about 0.03 to 0.6 micron and the total thereof comprised 1.0 to 70.0 percent by weight of the total blend. The first graft copolymer comprised about 20.0 to 97.0 percent of the total weight of the graft copolymer combined.

The theory of operation was not fully understood, but it was believed that the low graft particles had a tendency to cluster and simulate relatively large particles which provided a high degree of toughness which was then extended by the highly grafted rubber particles which did not exhibit this tendency. By proper combination, the two graft components cooperated in a manner such that the gloss and tensile properties of the composition were maintained at desirable levels.

J. Swoboda et al., [12] studied the molding compositions of impact resistant thermoplastic. The thermoplastic contained a hard component

comprising a styrene/acrylonitrile copolymer and a soft component comprising a graft copolymer of styrene and acrylonitrile on a rubbery polymer containing butadiene. The rubbery polymer serving as base for the graft copolymer was produced by polymerization of the monomer or monomers forming said polymer in aqueous emulsion and in the presence of a small amount of an alkanol of from 1 to 4 carbon atoms. The compositions had improved color and color stability and was processed by conventional methods to form shaped articles.

Eichenauer et al., [13] studied the process for preparation of thermoplastic molding composition. Process for the preparation of a thermoplastic molding composition of 10 to 65 % by weight of at least one graft polymer which was obtained by emulsion polymerization of styrene and acrylonitrile in a weight ratio of 90:10 to 50:50, it was possible for all or some of the styrene to be replaced by α -methylstyrene or methyl methacrylate, in the presence of at least one rubber base, and the weight ratio of monomers employed to rubber polymer employed being 20:80 to 70:30, and 90 to 35 % by weight of a copolymer of styrene and acrylonitrile in a weight ratio of 90:10 to 50:50, it was possible for all or some of the styrene to be replaced by α -methylstyrene or methyl methacrylate, wherein, to prepare the graft polymer, the grafting monomers and 0.05 to 1.00 part by weight (per 100 parts by weight of grafting monomer) of a mercaptan were added stepwise to the latex of the rubber base over a period of time, the part amount of the monomer added in each time interval ΔT_{n+1} being 0.30 to 0.95 times the amount of monomer added in the preceding time interval ΔT_n at least in the first half of the period of time, and the total period of time comprising n time intervals where $n = 3$ to 30, and each time interval Δt being 5 to 100 minutes long.

H. Nai-Jen and C.S. Donald., [18] studied a new method of measuring the efficiencies of free radical grafting reactions. This technique utilized the compositional analysis 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.

K. Hyungsu et al., [19] studied the effect of acrylonitrile content on the toughness of ABS materials. 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.