CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Natural Rubber

The birth of natural rubber (NR) dates back to the fifteenth century when Columbus first reported that he had been intrigued on his journey through the New World when seeing the native playing with a ball that actually bounced [6].

It has been estimated that some 2,000 different plant species yield polymer akin to natural rubber and use sorts have been obtained from some 500 of them. To all intents and purposes, the natural rubber of commerce is obtained from the latex of *Hevea brasilliensis*. The habitat of the rubber tree is the Amezon rain forest. Today, plantations of *Hevea brasilliensis* are also found in Southeast Asia, principally in Thailand, Indonesia, and Malaysia [7].

Hevea brasilliensis requires temperatures of 25-30°C, at least 2,000 mm of rainfall per year, and high atmospheric humidity. After an initial growth period of 5-7 years, a tree gives latex for as long as 25-30 years. *Hevea brasilliensis* is very suitable for rubber extraction for the following reasons [8]:

1) It can be tapped because of its milk vessels.
2) It does not form resins on tapping.
3) Polyisoprene with almost 100% *cis* double bonds is produced.
4) It tolerates tapping very well for over a period of many years.

2.1.1 Natural Rubber in Thailand

The data from the Rubber Research Institute of Thailand showed that in 1996, Thailand produced 1,970,300 tons of natural rubber and exported 1,762,990 tons or 89.48% of total production [2]. The remaining 10.52% were used in the country. Since1991, Thailand was the biggest producer in world production of natural rubber, followed by Indonesia and Malaysia, Thailand is the largest world production of natural rubber is shown in Table 2.1 along with others. The area about 12 million hectares was employed for rubber cultivation. In 1996, Thailand produced 1.9 million tons of natural rubber. It is very uneconomical to transport preserved field latex form before shipment. After the natural rubber latex has been collected from the field, it is processed into many forms of rubber products, as shown in Table 2.2. Natural rubber latex containing 60% dry rubber content (DRC) by a concentration method is usually obtained.

Table 2.1 World production of natural rubber in 1996

Country	Ton (10^{-3})
Thailand	1,763.0
Indonesia	1,449.8
Malaysia	709.8
Sri Lanka	72.1
Vietnam	69.0
Others	368.6
Total	4,430

Source : Rubber Research Institute of Thailand [2].

Table 2.2 Thailand exports of rubber by types in 1996

Types of Rubber	Ton (10^{-3})
Smoked sheet	1,180,181
Block rubber	259,601
Crepe rubber	1,190
Concentrated latex	202,869
Air dried sheet	17,664
Other rubbers	101,485
Total	1,762,990

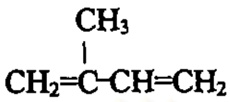
Source : Rubber Research Institute of Thailand [2].

2.1.2 The Chemical Formula of Natural Rubber

The empirical formula for the natural rubber molecule appeared to be first determined by Faraday who reported his findings in 1826. He concluded that carbon and hydrogen were the only elements present and his results corresponded to the formula of 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 as $C_5H_8Br_2$ [7].

Having been 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 that was done by Bouchardat and Greville Williams [7]. These 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



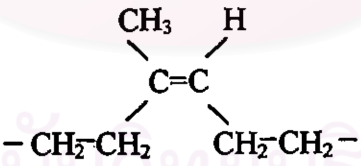
$$CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}CH{=}CH_2$$

I

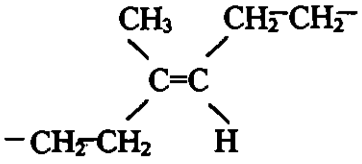
Natural rubber is a polymer of isoprene, in which essentially all the isoprene units are linked together at carbon atom 1 and 4 in a head-to-tail arrangement, and in which all or nearly all the repeating units posses the "*cis*" configuration.

$$-CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}CH{=}CH_2{-}CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}CH{=}CH_2{-}$$

II Head-to-tail arrangment



III *cis*-1,4-polyisoprene



IV *trans*-1,4-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.

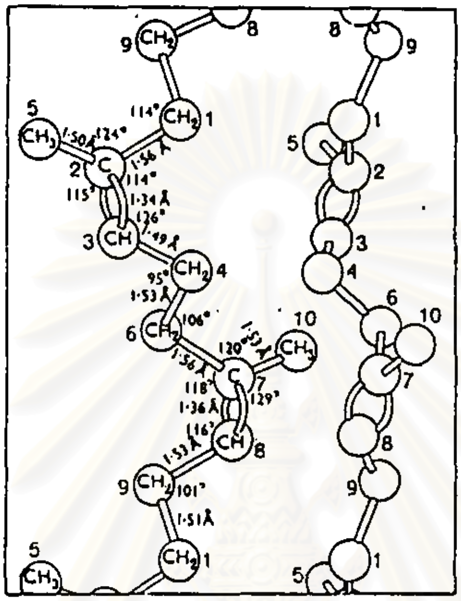


Figure 2.1 Unit cell structure of the natural rubber molecule [7].

2.1.3 Composition of Natural Rubber Latex

Natural rubber latex is essentially a dispersion of *cis*-1,4-polyisoprene in water. The average particle size is between 0.15 and 3.0 μm. The particle-size distribution is very broad. The aqueous dispersion contains between 30 and 38% solid materials, depending on the time of the year and the age of the tree. Other components of the latex are 1-2% protein and phosphoproteins, 2% resins, 1% fatty acids, 1% carbohydrates, and ca. 0.5% inorganic salts. The rubber particles are surrounded by protein anions and are thus effectively negatively charged, which hinders coagulation of the latex. These proteins are decomposed rapidly by bacteria and enzymes when exposed to air, and the rubber then coagulates. In addition, in the presence of air, cross-linking of the rubber occurs within the latex particles, with gel formation and subsequent degradation of the polymer chains [8].

2.1.4 Processing of Natural Rubber Latex

About 3 to 4 hours after tapping, the latex is collected from the tree, treated to prevent premature coagulation and brought to a factory or a smallholder processing center. Ammonia (about 0.05%) is, the most common stabilizer added to the latex though others such as sodium sulfite and formaldehyde are also still used. Mixed stabilizers such as boric acid-ammonia and hydroxylamine-ammonia are used to make certain special grades of rubber for export or local processing.

About 7-10% of world's natural rubber is converted into latex concentrate. Concentration is achieved by centrifugation (most common), by creaming, or by evaporation. The centrifuged latex is shipped as latex concentrate containing 60% dry-rubber content. The remainder of the latex and field coagulum are processed into conventional types of rubber such as ribbed smoke sheets (RSS), pale crepes, and brown crepes, or into the newer forms of technically specified "block" rubbers (TSR) [10].

2.1.5 Modification of Natural Rubber

Since 1801, natural rubber has been modified in many different ways, and modified forms have been available commercially since 1915. The degree of modification can vary from a few percent to complete modification of the polymer chain. Modification highly affects its physical properties. Even thermoplastic or resinous material can be obtained by a modification of rubber.

The most wellknow types of modification are hydrogenation, chlorination, hydrohalogenation, cyclization, resin modification, methyl methacrylate grafting, superior-processing, polystyrene grafting, and epoxidation [8].

a) Poly (methyl methacrylate) Grafted Natural Rubber

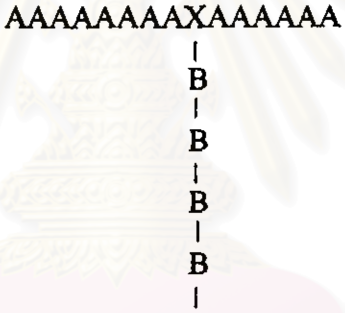
Several monomer can be grafted onto natural rubber (e.g. styrene, vinyl acetate, acrylonitrile, and methyl methacrylate). Peroxides or hydroperoxides are used as initiators. The most important graft polymers are those with methyl methacrylate that are marketed under the trade name Hevea Plus MG. Their main areas of use are in self-reinforcing vulcanizates and adhesives. Three qualities of Hevea Plus MG are available commercially: MG 30 with total content of 30 wt% methyl metharylate, MG 40 with 40 wt%, and MG 49; the latter consist of 80% graft polymer, 10% free methyl metharylate, and 10% free polyisoprene. One use of these materials is for poly(vinyl chloride) adhesion. For this application a free flowing powder form of Hevea Plus MG 49 is available, which dissolves rapidly in toluene or methyl ethyl ketone.

b) Polystyrene-Grafted Natural Rubber

Polystyrene-modified natural rubber was developed for the production of a thermoplastic elastomer. Thermoplastic elastomers frequently have an ABA block structure, where A is styrene . The desired structures cannot be obtained by a common grafting process, as used for grafting with methyl methacrylate. A longer route via special polystyrene having azodicarboxylates as the terminal group must be used. With simultaneous disintegration of the azo groups a polymer of defined structure is formed, but not a pure ABA block. Since thermoplastic natural rubber is also obtained through blends of natural rubber with polyolefins, the graft products with styrene have not gained any commercial importance.

2.2 Graft Copolymers

A graft copolymer is a polymer comprising molecules with one or more species of block connected to the main chain as side chains, having constitutional or configurational features that differ from those in the main chain, exclusive of branch points. In a graft copolymer, the distinquishing feature of the side chains is constitutional, ie, the side chains comprise units derived from at least one species of monomer different from those that supply the units of the main chain. The simplest case of graft copolymer can be represented by structure V,



V

where a sequence of A monomer units is referred to as the main chain or backbone, the sequence of B units is the side chain or graft, and X is the backbone to which the graft is attached [10].

Graft copolymers produced by causing a post polymerization of vinyl monomers such as styrene, acrylonitrile, or methyl methacrylate either independently or as a mixture of a plurality thereof to a rubber-like polymer latex have been well known.

These graft copolymers have good mechanical strength and have, therefore, been used independently for various shaped articles. In addition, these graft copolymers have been mixed with other resins such as poly(vinyl chloride) to improve the impact resistance of shaped articles of the other resins.

2.3 Graft copolymers from natural rubber

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 processes for grafting polymers to natural rubber using the free radical chemistry. Materials were obtained which contained both plastic and rubber constituents. Heveaplas-MG, a graft copolymer of natural rubber and poly (methyl methacrylate), became commercially available [11].

2.3.1 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 contituents, 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 the number of graft chains per backbone will be available if the graft chains are prepared as a separated 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, the interaction would be confined to the particle surface if the criterion of polymer-polymer incompatibility was to be set for the reaction product. If the graft polymer chain was not water soluble, the reaction could only occur via surface to surface contact of the two disperse polymer phases and this implies instability of the latex towards coagulation. These considerations point direct mixing of the polymer constituents in an internal mixer as the appropriate route to successful reaction.

2.4 Core-Shell Emulsion Copolymerization

The core-shell emulsion copolymerization is a well known process used to control latex particle morphology. According to the polymer particle morphology, there are two main kinds of core-shell copolymers: soft core-hard shell and hard core-soft shell. Usually, polymers such as polybutadiene (PB), styrene-butadiene rubber (SBR), and poly(butyl acrylate) (PBA) are chosen as the soft components, whereas the polymers of methyl methacrylate (MMA), styrene (S), acrylonitrile (AN), vinyl chloride (VC), vinyl acetate (VAc) and so on are chosen as the hard components. There exist graft polymers on the interface between the core and the shell. Polymers with a soft core and a hard shell are used as impact modifiers, toughened plastics, and damped oscillation materials, whereas polymers with a hard core and a soft shell are usually applied in the coating and adhesive fields [12].

2.5 Impact Modifiers for PVC

2.5.1 Impact Modification Theory [13]

During the period shortly after World War II, plastics products were either soft and flexible or hard and brittle. The soft and flexible plastics frequently had short useful lives after which they became too brittle. The lack of permanence of the plasticizers (for flexible) and adequate toughness (for rigids) threatened to destroy the plastics industry that was just beginning to establish itself with new and innovative products. The flexible plastics were rescued by the development of higher molecular weight and less volatile and/or extractable plasticizers. Rigid plastics (primarily styrenics) survived and business prospered because technology was developed to incorporate rubbery components in the polymer structures, which included copolymerization, grafting, and/or occlusion during polymerization [13].

Dow Chemical Company in the early 1950 began developing technology to incorporate rubbery polymers, such as polybutadiene (PBD), during the bulk polymerization of styrene to yield high impact polystyrene (HIPS). In situ modification is practical for large-volume plastics that have properties broadly applicable to many applications and where the polymerization of the base polymer is amenable to this technique.

A second approach to toughening brittle plastics is the introduction of a lower T_g monomer into the polymer backbone. This process, like the one above yields a toughened product with a set of properties that make it useful for selected applications without further modification. Often the structure of these materials, e.g., bisphenol-A polycarbonate (PC), is such that good toughness is obtained, but at the expense of ease of processing. Of course, further chemical modification is possible to alter the balance of properties, but this approach has not thus far proved economically attractive, especially in today's regulatory climate.

A third approach to toughening brittle plastics is by the addition of an impact modifier to the brittle polymer during the melt compounding of the thermoplastic. This approach allows the compounder the freedom to build into a specific compound a desired set of physical properties. Benefits of using impact modifier additives are many: flexibility in compounding, simplified inventory of base resin and additives, and economy in selecting competitive base materials. We will consider the theory of impact modification of PVC through the incorporation of impact modifier additives later. Because profitable production of PVC resins is an art in itself, the availability of additive impact modifiers frees the PVC producer from concerns of introducing such components during polymerization and allows the producer to concentrate on efficiently producing PVC.

2.5.2 Internal Modification of PVC

The early commercial development of PVC products (and its copolymers) was limited to the availability of existing processing equipment which was, at the beginning extruders, calenders, molding equipment designed for processing and fabricating rubber and rubber products. Operating temperatures for most of this equipment was less than 150°C. Therefore, various vinyl chloride and other vinyl ester copolymers with softening temperatures below 150°C were used primarily in flexible (plasticized) products.

As the need for better economics and higher performance properties developed, rubber processing and fabricating equipment was modified and equipment was specifically designed to operate in a range of 150-1900°C. This availability allowed the use of the less expensive and tougher PVC homopolymers. Because the bulk of PVC applications was in flexible PVC, internal modification of PVC was described as early as 1936 and continued to be explored to yield flexible articles that would have extended service life as the result of having little plasticizer to migrate or be extracted from the compound. As the utility of rigid PVC for packaging and building products became more obvious in the United States as a result of European and British success in the World War II era, internal modification of PVC was explored as a means to improve both the processability and toughness (impact resistance) of rigid PVC compounds. It was a natural sequence that the major rubber companies would become producers of PVC and PVC compounds. It was also predictable that early attempts would involve grafting or alloying elastomers to or with PVC. Other definitions of graftable components included "Hard Tough Polymers" (e.g., Acrylonitrile). Standards for impact have changed since the earlier days so that "impact-resistance" compounds developed during the early 1950 would probably not be acceptable today for overall performance and processing properties [13].

2.5.3 Elastomers as PVC Toughners

As early as 1951, patents began to appear for rigid PVC compositions containing elastomeric toughners as additives. Through 1953-1955 several patents were issued to various rubber companies covering blends of PVC and various elastomers including EPDM. Most, if not all, were probably in the flexible to semi-rigid area. A Uniroyal patent in 1955 and a US Rubber Co., 1956, patent claimed "tough rigid" PVC compositions containing rubber diolefin/acrylic ester copolymer or neoprene rubber. Elastomer modified PVC compositions continued to proliferate through the 1960 with the compounds being sold by the rubber/PVC companies for use "as is" for fabricating various PVC articles. Whether these compounds were and are "Impact-Modified PVC" or "PVC/Elastomer Alloys" was and remains a non-productive, semantic exercise. Morphologies of the blends or mixtures might provide a source of categorizing the materials, but the end results are similar: the basically PVC compositions are tough.

In the 1950 , Acrylonitrile/Butadiene/Styrene (ABS) terpolymer became popular as an impact modifier for rigid PVC and as a low temperature enhancer for plasticized

PVC. Patent on ABS compositions began to appear in 1957 and in 1960 Borg-Warner patented ABS graft polymers specifically as impact modifiers for PVC. The ABS family of terpolymers consists of products varying widely in performance depending on the monomer ratios used. Impact efficiency can range from fair to excellent and clarity can range from opaque to clear by adjusting components, refractive index, and particle size. In a sense, ABS may be considered a transition from elastomers to "modifiers" in the modern context [13].

2.5.4 Modern Impact Modifiers

In 1956, Rohm and Haas Company introduced the first Methyl Methacrylate/Butadiene/Styrene (MBS) impact modifier for PVC (Acryloid KM-220). The Newer patent described the first emulsion polymerized, core-shell copolymer coagulated MBS powder that could be added to PVC formulation by independent PVC formulators/processors. This innovation accelerated the growth of the PVC powder blend technology by allowing an end-user of PVC to have the freedom of compounding in-house, thereby increasing compound design flexibility and economy. Both of these factors led to a growth spurt in PVC products that brought the industry to the forefront in plastics products and production.

Rohm and Haas Company followed the success of Acryloid KM-220 in supplanting a significant portion of the competitive ABS modifiers by introducing Acryloid KM-227 in 1958. This product was used in clear as well as opaque PVC compounds and offered advantages in impact efficiency, thermal stability, and processability over those of the then popular ABS or MBS modifiers. The first phase of Rohm and Haas Company's leadership culminated in Acryloid KM-228 (in 1961) as the first MBS impact modifier for PVC bottles in the US. and Europe. Acryloid KM-228 was the first spray-dried impact modifier as Rohm and Haas pioneered this process to reduce the cost of impact modifiers. Its superior cost-performance allowed the MBS family of impact modifiers to capture approximately half of the impact modifier business at the time. In1960, Rohm and Haas Company, and ICI Ltd., patented PVC compounds modified with butadiene/MMA copolymers.

In the mid 1960, Japanese chemical companies, notably Kureha and Kanegafuchi, began to seriously develop and promote impact modifiers for the European PVC bottle and packaging market. The modifiers were MBS or MABS (acrylonitrile modified MBS) emulsion polymers isolated by various coagulation and attrition techniques similar to those used by Rohm and Haas Company in its introductory product, Acryloid KM-220. The coagulated products were generally not as impact-efficient as spray dried products by Rohm and Haas, but they did have an advantage in better clarity and low contribution to taste and odor in packaged foods and liquids. In 1973 the market for PVC bottles in Europe was of sufficient size to encourage Rohm and Haas Company to resume development of coagulated products having superior impact efficiency. These research efforts came to full fruition in 1982 when Rohm and Haas concluded a purchase of Kureha licensing and European production facilities from Borg-Warner. This event provided the means to manufacture Rohm and Haas coagulated products for world-wide distribution. Approximately two years later, the Louisville, Kentucky, plant was expanded specifically to produce new and unique Rohm and Haas coagulated modifiers.

In 1960, Rohm and Haas Company began development of all-acrylic impact modifiers to take advantage of the unparalleled weathering resistance of acrylic compounds. It was not until 1968, however, that business and technology criteria were right for the introduction of Acryloid KM-323 (current product trade name is Paraloid). The all-acrylic technology would gradually generate products that world be the industry standard for weatherability and toughness. In the middle 1970, M & T Chemical Co. bought a Union Carbide patent that covered butadiene modified acrylic impact modifiers. Rohm and Haas Company had earlier investigated this type of polymer system, but had concluded that the impact/weathering balance favored all-acrylic elastomers. M & T marketed this toll-produced product, designated Durastrength 200, until mid 1984 when they brought the production in-house. The economics and marketing aspects of the building products area made it necessary for Rohm and Haas Company to develop unique technology for the production of more efficient all-acrylic impact modifiers without sacrificing the ultimate in weatherability. Paraloid KM-334 was the first of the new technology products [13].

2.5.5 Effect of PVC-Impact Modifier Morphology and Interaction

Owing to the previously described relationship of PVC morphology to its toughness, was suggested that chemically different modifiers be operated by somewhat different mechanisms. A common factor is that all effective impact modifiers must have a degree of compatibility in order to provide adhesion to PVC. Pure rubbers, such as SBR and nitrile cross-linked rubbers, lack the necessary adhesions and are generally ineffective by current standards. For convenience, the current types of Impact Modifier may be classified as follow [14]:

Type I. These are the core-shell multipolymers that are made, via emulsion polymerization, to specific sizes (submicron) and compositions. The core can either be hard or soft, and is surrounded by a shell consisting of a polymer made from one or more monomers that impart the proper degree of adhesion to the PVC particles. As supplied, the powders resemble PVC powders in particle-size range, but upon being sheared during processing in the PVC melt, they are reduced to their ultimate particle size and spherical shape formed during polymerization. Therefore, the size and shape of the core-shell modifiers remain constant over wide ranges of processing time, temperature, and shear rates. The MBS and all-acrylic modifiers are typical core-shell modifiers.

Type II. These are amorphous polymers that have a relatively high degree of compatibility with PVC. They are also called network polymers (NP), a term that describes their mode of operation. The two compositions that are most typical of this class are CPE and ethylene-vinyl acetate copolymers (EVA). In each, the compositions may be varied to adjust compatibility with PVC to allow them to be used as plasticizers for PVC, as impact modifiers for PVC, or as stand alone polymers. Because of their nature, NP modifiers assume different configuration in the PVC melt as processing conditions vary. The processing window for the NPs is relatively narrow. Jones and Righter have shown detailed electron micrographs of CPE in PVC under various processing conditions. As indicated by the term network polymer, these materials will be most effective when PVC particles are bound together by a network of the CPE or EVA. At 150°C or so, the melt does not form this configuration. At temperatures over 200°C, the thoroughly melted PVC converts the NPs into spherical lumps dispersed in the PVC matrix, resulting in poor impact strength.

Other authors have reported their results comparing core-shell (all-acrylic) and NP (CPE and EVA) modified PVC, illustrating the sensitivity of NPs in developing physical properties as functions of processing time and temperature. Lower impact, tensile strength, modulus, and heat-deformation values have been reported for NPs as compared with the values obtained with Type I all-acrylics. Rabinovic [15] has generated contour plots of the impact strength of PVC compounds after a variety of combinations of time and temperature in three-roll-mill processed specimens. Figures 2.1-2.3 show the performance of all-acrylic, EVA-modified, and CPE-modified PVC respectively. These contours illustrate the consistent performance of Type I modifiers over a wide range of processing conditions. They further illustrate the relatively narrow processing window that results in the proper network in PVC required for Type II modifiers to be effective. Menges et al.[16], described the changes from PVC granules to primary units as occurring at about 160°C. At around 190°C, the primary particles melt. The curves suggest that the maximum impact for the Type II (NP) modifiers occurs at about 180°C (mill temperature), confirming the fact that primary PVC interact with the NP-modifier network.

Type III. The ABS terpolymers appear to be "transitional" between Type I and Type II. They do contain a cross-linked component (butadiene-styrene rubber) and retain much of their shape during processing. Like the Type I materials, ABS is made in a variety of compositions designed for optimum performance in specific applications.

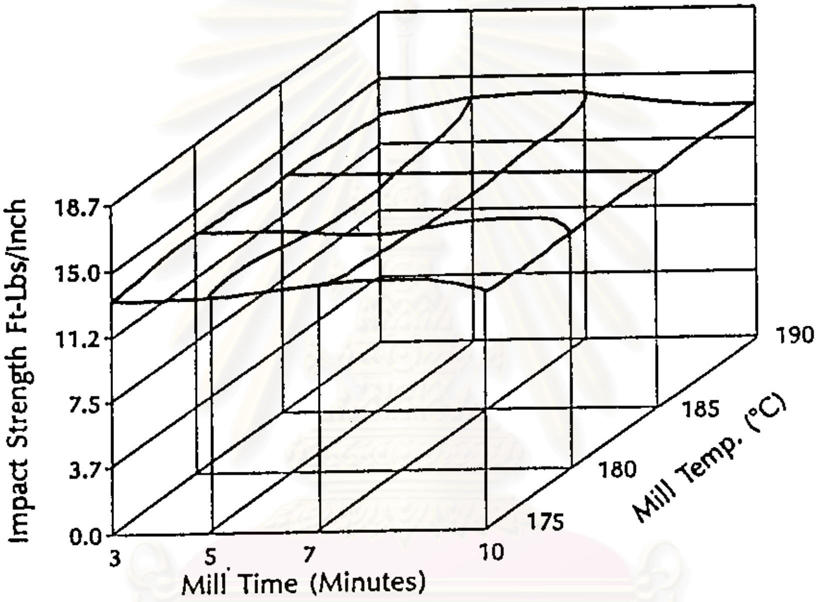


Figure 2.2 Impact vs. Processing conditions for acrylic-modified PVC [13].

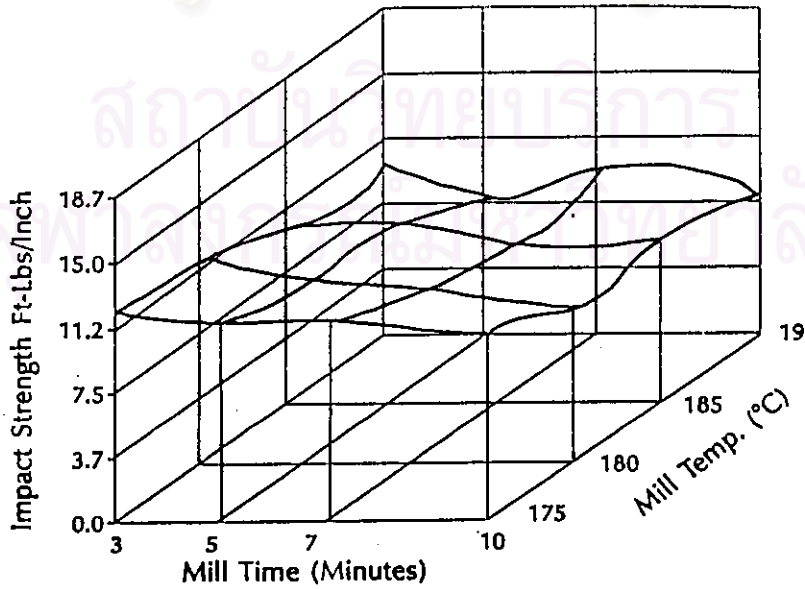


Figure 2.3 Impact vs. Processing conditions for EVA-modified PVC [13].

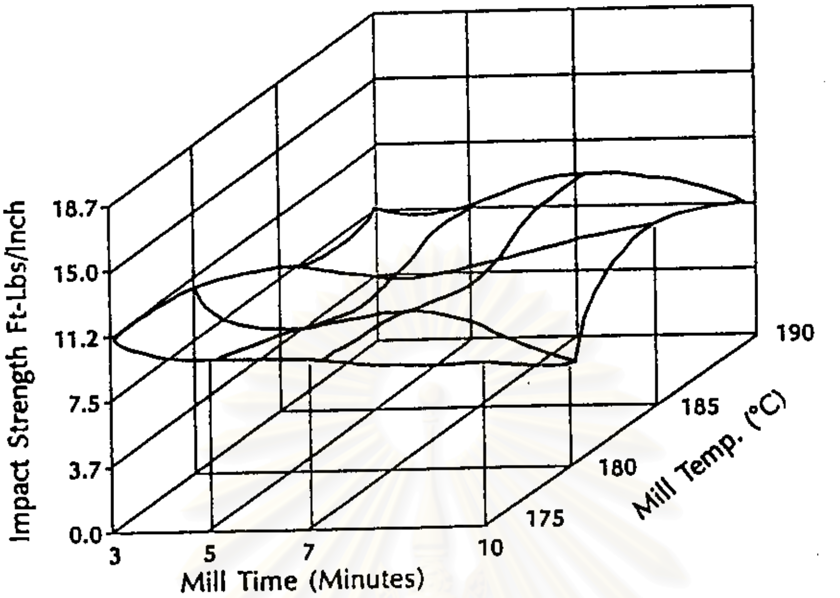


Figure 2.4 Impact vs. Processing conditions for CPE-modified PVC [13].

2.6 Literature Reviews

A.M. Aerdts et al., [17] studied the emulsifier free grafting of styrene (S) and methyl methacrylate (MMA) onto polybutadiene (PB) and the determined the copolymer microstructure. Styrene/methyl methacrylate (25/75) monomer mixtures were copolymerized at 323 K in the presence of polybutadiene seed latex using either a water soluble (potassium persulfate) or an oil soluble (cumene hydroperoxide) initiator. The grafting of styrene and methyl methacrylate onto polybutadiene seed particles, stabilized by sulfate end groups, gave stable composite particles. By using emulsifier free grafting process, a high degree of grafting value was achieved, while neither coagulation nor formation of a new crop of particles occurred. The intramolecular microstructure of S/MMA grafted copolymer shifted more strongly to higher MMA contents than that of free S/MMA. The chemical composition distributions (CCDs) of S-*g*-MMA was broad but not bimodal. Moreover, the lower fractions of S in the grafted copolymer was believed to be caused by the dominant grafting on the PB backbone of polymeric radicals originating from the aqueous phase or by particle precursor coagulation. This mechanism would, of course, depend on the monomer type and its water solubility in reaction temperature, which gained its importance as S becomes depleted.

J. Zhao et al., [12] studied the graft copolymerization of styrene and methyl methacrylate on SBR latex particles in the core-shell emulsion process. It was conducted in a 600 ml. glass stirred vessel with the BPO-Fe^{2+} redox initiator. The influences of the principal factors on the grafting degree and the grafting efficiency were initiator content, reaction temperature, emulsifier content, monomer-to-polymer ratio, and conversion. The local viscosity at the surface of the latex particles was quite large and the graft polymerization was a surface-controlled process.

M.E. Enyieybulam and I.U. Aloka [18] studied the grafting 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 one hand, and the attendant influenced 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 decreases both the graft level and graft efficiency but increases the molecular weight of the copolymer. But an increase in the concentration of the benzoyl peroxide initiator at a given monomer concentration exceeds approx. 1.0 X 10^{-2} mol/cm^3. Dilute solution theory applicable to homopolymers could also be applied to the graft copolymers without any adverse effect in technological application.

H.Y. Erbil [19] studied the graft copolymerization of some hydrophilic such as 2-hydroxyethyl methacrylate, n-vinyl pyrollidone and methacrylic acid onto natural rubber (NR) using procedures similar to those for grafting methyl methacrylate monomer onto NR latex in order to use the copolymers as a contact lens material. However, these hydrophilic monomers could not be grafted by hydroperoxide-polyamide and ammonium persulphate-sodium meta bisulphite initiator systems due to their high solubilities in the water phase of NR latex. The monomer, 2-hydroxyethyl methacrylate could not be grafted onto dry NR in benzene solution because of its high self propagation tendency. A blend of homopolymers was produced. The reduction of the pendant methacrylate groups on NR-methyl methacrylate graft copolymer with $LiAlH_4$ in tetrahydrofuran solution introduced hydroxyl groups and hydrophilicity, and reduced the transparency of the reaction product.

H. Nai-Jen and C.S. Donald [20] studied a newly developed test method for graft copolymer analysis which makes use of the compositional analysis capability of the dual-detector gel permeation chromatography (GPC). Utilizing refractive index and ultraviolet light absorption detectors, GPC has been shown to be a sensitive technique for the analysis of composition in polymer blends and copolymers, particularly for the dependence of composition on molecular weight. Samples of the reaction mass drawn from a reactor was diluted with GPC eluent and injected directly into the chromatographer 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 were readily separated from the polymer within the chromatographer, allowing for the determination of the fractional conversion of the graft monomer (to grafted and ungrafted monomer) from the sample analysis. This simple technique overcomed the need to separate or purify the polymer mixture prior to analysis, as required for most other method. Experimental results were presented for the grafting of styrene onto cis-polybutadiene. Gelled samples could not be analyzed by is new technique.

D. Dompas et al., [21] studied the toughening behaviour of rubber-modified thermoplastic polymers involving very small rubber particles: impact mechanical behaviour of poly(vinyl chloride) (PVC)/methyl methacrylate-butadiene-styrene graft copolymer (MBS) blends. The resistance of MBS particles against cavitation increased with decreasing particle size, and there existed a critical particle size below which the MBS particles were unable to cavitate. The inability of small particles to cavitate was the reason for the decrease of the impact properties of PVC/MBS blends with very small MBS particles ($d_o < 150$ nm). A toughening mechanism was proposed for the PVC/MBS blends in which the particle size of the rubber particles and the interparticles distance played equally crucial roles.

C. Rujinirun [22] studied the preparation of graft copolymer of styrene and acrylonitrile onto natural rubber. The process for the preparation of copolymer of styrene and acrylonitrile on natural rubber latex was studied. The graft copolymerization was carried out by varying the concentrations of styrene and acrylonitrile monomers, emulsifier concentration and reaction temperature. The grafting efficiency of grafted natural rubber determined by solvent extraction technique and degree of conversion were reported and discussed. The copolymer composition was determined by Infrared spectroscopy and elemental analyzer. The characterization included Gel permeation chromatograph and Differential scanning calorimetry. The blends of graft natural rubber and SAN were formulated. The effects of graft natural rubber and SAN ratio on impact strength, flexural and tensile strength, hardness, melt flow index, and heat distortion temperature were investigated.

P. Sintoorahat [23] studied the enhanced graft copolymerization of styrene and acrylonitrile onto natural rubber. The effects of initiator concentration, reaction temperature, and pressure on graft copolymerization of styrene and acrylonitrile onto natural rubber latex were studied. The grafting efficiency and graft ratio of the grafted natural rubber determined by solvent extraction technique and degree of monomer conversion were reported and discussed. The average molecular weight of free SAN and the frequency of grafted chains on the backbone rubber were determined by the Gel permeation chromatography technique. The copolymer composition was determined by Infrared spectroscopy and elemental analysis. The blends of grafted natural rubber and SAN were investigated. The effects of grafted natural rubber and SAN ratio on tensile and izod impact strength, and hardness were investigated.