CHAPTER II

Theory And Literature Review

2.1 Natural Rubber

Natural rubber can be isolated from more than 200 different species of plants, including even such surprising examples as dandelions or golderod. However, only one tree source, *Hevea Brasiliensis,* is commercially significant. This naturally occurring polymer is known chemically as cis-1,4-polyisoprene [2].

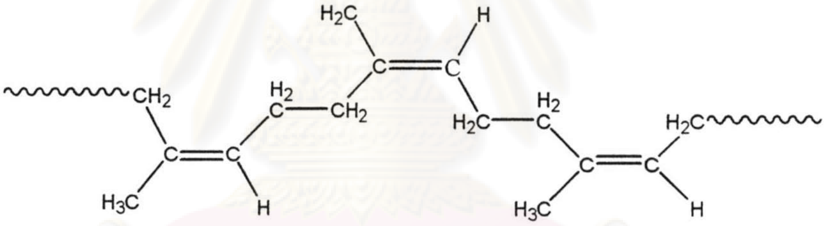

Figure 2.1 Cis-1,4-Polyisoprene [2]

2.1.1 Natural Rubber Latex

Natural rubber latex, collected by tapping from *Hevea* rubber trees, is a colloidal suspension of rubber particles in an aqueous serum phase. The latex that exuded from the cut is called the fresh natural rubber latex or fresh latex. Fresh latex consists of approximately 25-40% dry rubber content (DRC) and 5-10% non-rubber substances. The non-rubber components include proteins, carbohydrates, liquids, and inorganic salts. Its composition varies according to the clones of rubber, age of rubber tree, and tapping method. The composition of typical fresh latex is presented in Table 2.1.

Table 2.1 Composition of Latex Sap [3]

Constituent	% Composition
Total solid	36
Dry rubber	33
Proteinaceous substances	1-1.5
Resinnous substances	1-2.5
Ash	Up to 1
Sugar	1
Water	Add to 100

In general, fresh latex has the density of 0.975-0.980 g/cm^3 with the pH of 6.5-7.0 and a refractive index of 1.5910. Rubber does not dissolve in water, alcohol, and acetone, but it swells and disperses or partly solubilizes in benzene, toluene, gasoline, carbon disulfide, turpentine, chloroform, carbon tetrachloride, and other halogen containing solvents. The chemical and physical properties of latex are influenced by clone, age of rubber, tapping intensity, soil characteristics and season of tapping.

2.1.2 Concentration of Natural Rubber Latex [4]

Fresh field latex from *Hevea brasiliensis* tree has a rubber content of ca. 30-40% DRC, dispersed in water or dispersion medium. The concentration of latex is necessary not only to reduce the volume of latex for transportation, but also to reduce the ratio of non-aqueous substances to dry rubber content. In addition, several of the industrial processes use the latex which has concentration higher than 33%.

There are several concentration methods, such as evaporation, creaming, centrifugation, and electrodecantation, etc. Typical methods are described below.

2.1.2.1 Concentration by Creaming

Concentration by creaming is sedimentation process using creaming agents e.g. ammonium alginate. In natural rubber latex, the density of rubber particles is less than that of dispersion medium. After creaming, therefore, the rubber particles tend to rise to the surface of the dispersion medium. The concentrated latex is known as cream, while the dilute latex forming the lower layer is known as skim. The serum layer is drained off after incubation in the tank for about 40 hours.

2.1.2.2 Concentration by Centrifugation

Among the methods currently used for the concentration of natural rubber latex, centrifugation is the most important, about 90% of concentrated latex used in industrial is produced by centrifugation. Centrifugation is a type of accelerated creaming process, by which successful concentration can be obtained with a significant difference between with the density of the rubber particles that of the aqueous phase. The centrifuge concentrate is known as skim.

Concentrated latex consists of approximately 60% DRC with a lesser amount of non-rubber substances. The most of rubber particles in this cream phase are large particles, which show a size distribution ranging from 0.1-0.3 μm. The molecular weight of the rubber from cream phase is a typical bimodal molecular weight distribution, with peaks at $\overrightarrow{M}_W$ of 2.0×10^6 g/mol and 1.2×10^5 g/mol [4].

The serum or skim latex contains a small amount of rubber particles, 4-10% DRC, with a high amount of non-rubber components, including amino acid, proteins, carbohydrates, organic acid, inorganic salts and nucleotidic materials. The rubber particles in serum phase are small particles and show a size distribution in a range of

0.05-0.3 μm. The molecular weight distribution is a unimodal, with a peak at 1.0 x 10^6 g/mol [5]. The $\overline{M}_n$ obtained by osmometry is higher than that of cream phase but no significant difference in the $\overline{M}_w$.

2.2 Standard Thai Rubber [6]

STR (Standard Thai Rubber) has been proposed to replace "TTR" (Thai Test Rubber) according to the reason of international image that Thai Technically Specified Rubber attains the international standard instead of just passing the test as implicity by the name "TTR". Furthermore, new name, STR is also followed the international style of calling this type of natural rubber.

Material to be processed for STR must be derived from *Hevea brasiliensis* tree. The processing materials of the various STR grades for improved consistency and quality within grades are shown in Table 2.2.

Table 2.2 Processing Materials of STR Grades [6]

Grade	Processing Materials
STR XL, STR 5L	Whole field latex bulked and formic acid coagulated under strictly controlled conditions.
STR 5	Either whole fresh coagulum or unsmoked sheet (USS) or blend of them subjected to further crumb processing.
STR 10, STR 20 STR 10 CV, STR 20 CV	Field grade materials based on USS, lump, scrap, green crepe or mixture.

Lump and scrap are field grade materials derived from latex naturally coagulated in different manner such as in the tapping cup or other suitable vessels, and

Table 2.3 Standard Thai Rubber (STR) Scheme [6]

Parameter	STR XL	STR 5L	STR 5	STR 5 CV	STR 10	STR 10 CV	STR 20	STR 20 CV
	Latex		Latex/Sheets		Lump/Sheets/Green Crepe			
Dirt retained on 44 μ aperture (max.% wt.)	0.02	0.04	0.04	0.04	0.08	0.08	0.16	0.16
Ash (max.% wt.)	0.40	0.40	0.60	0.60	0.60	0.60	0.80	0.80
Nitrogen (max.% wt.)	0.50	0.60	0.60	0.60	0.60	0.60	0.60	0.60
Volatile Matter* (max.% wt.)	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80
Initial Plasticity (Po) (min)	35	35	30	-	30	-	30	-
Plasticity Retention Index (PRI) (min)	60	60	60	60	50	50	40	40
Colour Lovibond Scale (individual value, max.)	4.0	6.0	-	-	-	-	-	-
Mooney Viscosity ML (1+4) 100°C	-	-	-	**	-	**	-	**
Colour Coding Marker	blue	light green	light green	white on light green background	brown	white on brown background	red	white on red background

Note Provision of Rheograph with basic cure data as consumer or ACS 1 based recipe will be offered as additional test.

* Producer limit is not more than 0.50% ** Producer limit of 70 (+7, -5), 60 (+7, -5) and 50 (+7, -5) for STR 5 CV ; 60 (+7, -5) for STR 10 CV and 65 (+7, -5) for STR 20 CV

in the trace of tapping etc. Field grade materials are USS or green crepe or cuplump or field coagulum or scrap or mixture which contain certain proportion of each of them according to the STR grade intended to process.

2.3 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 the following structure.

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 of graft, and X is the backbone to which the graft is attached [7].

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

2.3.1 Glycidyl Methacrylate [8]

Glycidyl methacrylate (GMA) monomer is dual functional, containing both acrylic and epoxy groups. The fact that both of these groups readily react with a wide range of monomers and functionalized molecules provide the user with maximum freedom and flexibility in polymer design.

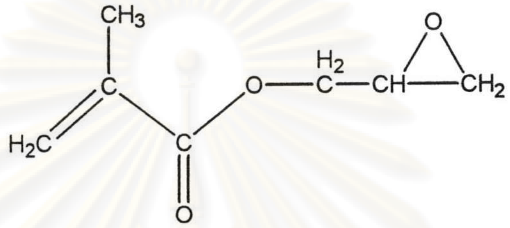

Figure 2.2 Glycidyl Methacrylate Chemical Structure

The dual functionality of GMA also brings together desirable properties of both acrylics and epoxides. For example, now the weatherability of acrylics and the chemical resistance of epoxides are available in one product. The physical properties of GMA are shown in Table 2.4

Table 2.4 Typical Physical Properties of GMA Monomer [8]

Property	Value
Molecular weight	142.2
Appearance	Clear liquid
Boiling point at 760 mmHg, °C (°F)	195 (383)
Density at 25 °C (77 °F), g/ml	1.074
Flash point , °C (°F)	85 (185)
Pour point, °C (°F)	-81.7 (-115)

Table 2.4 (Continued)

Property	Value
Refractive index at 25°C (77°F)	1.4473
Surface tension at 25 °C (77°F), dynes/cm	33.6
Thermal conductivity at 25°C (77°F), W/(m-K)	0.158
T_g^1, °C (K)	75 (348)
Water solubility at 20 °C (68°F), g/g	0.023
Organic solvent solubility	Soluble
Heat of formation[2], kcal/mol	-91.22
Entropy[2], cal/(mol K)	116.78
Free energy of formation, kcal/mol	-54.74

[1] Tg at infinite molecular weight determined by midpoint technique

[2] Predicted via computer program

2.4 Polymer Blends [9]

By definition, any physical mixture of two or more different polymers or copolymers that are not linked by covalent bonds is a polymer blend, or polyblend. Some scientists like to make an analogy with metals and call such mixtures polymer alloys. There has been a resurgence of interest arising primarity from the demand for engineering plastics and specialty elastomers and fibers. A number of technologies have been devised to prepare polymer blends; these are summarized in Table 2.5. It so happens that most polymers are not compatible. They separate into discrete phase on being mixed, although an increasing number of completely miscible blends are being developed. Differences between the two types are manifested in appearance-miscible blends are usually clear, immiscible blends are opaque-and in such properties as a glass transition temperature- miscible blends exhibit a single T_g intermediate between those of the individual components, whereas immiscible blends exhibit separate T_gs characteristic of each component. Miscibility is by no means prerequisite to commercial utility.

A major problem with developing miscible polyblends is trying to predict miscibility. Attempts to predict miscibility using solubility parameters have been largely unsuccessful because strong dipolar interactions are not taken into account. It has been shown, for example, that compatibility may be greatly enhanced by dipole-dipole attraction, hydrogen bonding, ion pairing, and charge-transfer complexing, as well as by minimizing dipole moment differences between the individual polymers.

Properties of immiscible polyblends are much less predictable. Attempts to develop additivity relationships are complicated by the effects of varying morphologies that might arise as a result of processing variables. Frequently, one polymer will constitute a continuous phase while the second will be dispersed as a noncontinuous phase in the form of fibrils, spheres, lamellae, and so on. Which polymer is the continuous phase largely determines properties. For example, a 50/50 blend of polystyrene (a hard, glassy polymer) and polybutadiene (an elastomer) will be hard if polystyrene is the continuous phase, but soft if polystyrene is the dispersed phase. Alternatively, an immiscible polyblend may have both components dispersed as continuous phases.

The major problem with immiscible blends is the often poor physical attraction at phase boundaries, which can lead to phase separation under stress with resultant poor mechanical properties. To improve compatibility between immiscible phases, a number of ingenious approaches have been adopted. In such cases the polymers are physically “locked” together by the interdispersed tree-dimensional network, a phenomenon referred to as topological bounding. Such mixtures still undergo phase separation into microdomains that vary in size according to the degree of immiscibility.

Table 2.5 Types of Polyblends [9]

Type	Description
Mechanical blends	Polymers are mixed at temperatures above T_g or T_m for amorphous and semicrystalline polymers, respectively.
Mechanochemical blends	Polymer are mixed at shear rates high enough to cause degradation. Resultant free radicals combine to form complex mixtures including block and graft components.
Solution-cast blends	Polymer are dissolved in common solvent and solvent is removed.
Latex blends	Fine dispersions of polymers in water (latexes) are mixed, and the mixed polymers are coagulated.
Chemical blends	
Interpenetrating polymer networks (IPN)	Crosslinked polymer is swollen with different monomer, the monomer is polymerized and crosslinked.
Semi-interpenetrating polymer networks (semi-IPN)	Polyfunctional monomer is mixed with thermoplastic polymer, then monomer is polymerized to network polymer (also called pseudo-IPN).
Simultaneous interpenetrating polymer networks (SIN)	Different monomers are mixed, then homopolymerized and crosslinked simultaneously, but by noninteracting mechanisms.
Interpenetrating elastomeric networks (IEN)	Latex polyblend is crosslinked after coagulation.

Another approach is to incorporate compatibilizers into the blend to improve adhesion between phases. The most successful approach to compatibilizing polymer blends from the commercial standpoint is to generate graft copolymers *in situ* that help bind the immiscible phases together.

2.5 Compatibilization [10]

Generally, melt mixing of two polymers produces a material that is weak and brittle. The low deformation modulus may follow an approximately linear mixing rule, but the ultimate properties certainly will not follow this rule because of the presence of stress concentrations and weak interfaces between the dispersed phase and a matrix. The process of bridging to enhance the mechanical properties by the addition of a third component, or by *in situ* chemical reaction is termed compatibilization. In most cases, the compatibilizer has many possible effects to the final blend, for example:

i) to reduce the interfacial tension in the melt, leading to a finer dispersed phase

ii) to increase the adhesion at phase boundaries, giving improved stress transfer and strengthen the interface in the solid state.

iii) to stabilise the dispersed phase by reducing the rate of domain coalescence during melt processing and annealing.

2.5.1 The Method of Compatibilization

The method of compatibilization can be broadly grouped into four categories.

2.5.1.1 Thermodynamic Miscibility

This method is a main idea to produce commercial blends. Following the equation 2.1, the miscibility between polymer is determined by a balance of enthalpic and entropic contributions to the free energy of mixing. The change in free energy on mixing (ΔG) is written as

$$\Delta G = \Delta H - T\Delta S \qquad (2.1)$$

Where H is enthalpy, S is entropy and T is temperature. For spontaneous mixing, ΔG must be negative and so

$$\Delta H - T\Delta S < 0 \tag{2.2}$$

The entropy of polymers is almost zero. This inferred that exothermic mixtures ($\Delta H < 0$) will mix spontaneously, whereas endothermic mixtures miscibility will only happen at high temperatures.

2.5.1.2 Addition of Block and Graft Copolymers

The addition of block or graft copolymers represents the most extensively researched approach to compatibilization of blends. It is perhaps not surprising that block and graft copolymers containing segments chemically identical to the blend components are obvious choices as compatibilizers, given that miscibility between the copolymer segments and the corresponding blend component is assured, provided the copolymer meets certain structural and molecular weight requirements, and that the copolymer locates preferentially at the blend interfaces. This action mode is illustrated in Figure 2.3. Better dispersion and adhesion result in improved mechanical properties of the compatibization blend. However, the finest dispersion does not necessary give the best physical properties to the blend. The optimum size of dispersion must be related to the required end-use properties of the blend [10].

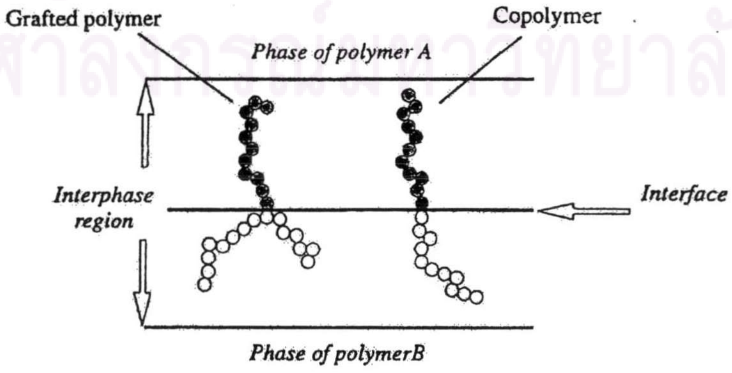

Figure 2.3 Schematic Diagram Showing Location of Block and Graft Copolymers at Phase Interfaces [10]

2.5.1.3 Addition of Functional Polymers

The addition of functional polymers as compatibilizers has been described by many workers. Usually a polymer chemically identical to one of the blend components is modified to contain functional (or reactive) units, which have some affinity for the second blend component; this affinity is usually the ability to chemically react with the second blend component, but other types of interaction (e.g. ionic) are possible. The functional modification may be achieved in a reactor or via an extrusion-modification process. Examples include the grafting of maleic anhydride or similar compounds to polyolefins, the resulting pendant carboxyl group having the ability to form a chemical linkage with polyamides via their terminal amino groups. Functionalised polymers (usually maleic anhydride or acrylic acid grafted polyolefins) are commercially available at acceptable cost to be used as compatibilizers.

2.5.1.4 Reactive Blending

In this method, the blend components are either chosen or modified themselves, so the reaction occurs during melt blending, with no need for addition of another compatibilizer. The main point is the *in situ* formation of graft or block copolymer by the following various mechanism:

- Mechanical chain scission and recombination of component polymers, induced by high shear during processing.
- Chemical bonding reaction between reaction groups, may be initiated by free radical initiator.
- Interchange reaction in the backbone bonds of the components, likely in condensation polymers.

These reactions may be occurred either in batch-type melt mixers or continuous processing equipment (such as single and twin screw extruders). However, the disadvantages of this method are the cost is increased and the chemically linked structures may prevent recycling.

2.6 Literature Review

Egboh and Mukherjee [11] studied the grafting of glycidyl methacrylate and N-vinyl pyrrollidone onto natural rubber by irradiation using the cobalt-60 at 32°C. The dependence of the rate of grafting on the monomer concentration was found to be 0.93 and 0.80 for glycidyl methacrylate and N-vinyl pyrrollidone, respectively. Their investigation showed that glycidyl methacrylate and N-vinyl pyrrollidone when grafted onto natural rubber could produce higher percent grafting but the extraction of the gel homopolymers becomes difficult. Differential scanning calorimetry (DSC) thermograms of the graft copolymers showed no observable Tg for the poly(glycidyl methacrylate) (PGMA) branches. However, graft copolymers with 19% grafting have a melting temperature of about 115.87°C and heat of fusion of 1.053 J/g. Furthermore, grafted copolymers based on glycidyl methacrylate were relatively less thermally stable compared with ungrafted natural rubber.

Cartier and Hu [12] studied the free radical grafting of glycidyl methacrylate (GMA) onto polyethylene in the melt by using 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane (DHBP) as free radical initiator. The results show that the use of styrene as a comonomer greatly promotes both GMA's grafting yield and grafting rate onto polyethylene. In the presence of styrene, the dominant mechanism of the free radical grafting of GMA onto polyethylene is that styrene reacts first with polyethylene secondary macroradicals and the resulting styryl macroradicals then copolymerize with GMA leading to grafted GMA. The contribution of styrene is not related to an improved solubility of glycidyl methacrylate in the molten polyethylene. The GMA's grafting yields obtained in the batch mixer are higher than those in the twin screw extruder.

Cartier and Hu [13] studied the efficiency of using styrene as a comonomer to promote the melt free radical grafting of glycidyl methacrylate onto ethylene and propylene rubber (EPR) in the batch mixer and corotating self-wiping twin screw extruder. GMA's grafting yield obtained in the presence of styrene is three times higher than that obtained in the absence of styrene under the same reaction conditions. The conversion of the glycidyl methacrylate monomer to grafted species was more than 80%. Comparison of grafting efficiency of dicumyl peroxide (DCP) was higher than that of α,α'-di(t-butyl-peroxy)-1,3- and 1,4-diisopropylbenzene (DTBPIB). The time required for the EPR/GMA/peroxide system without styrene to reach a given amount of grafted glycidyl methacrylate is at least 10 times that needed for the same system in the presence of an equimolar amount of styrene. This significant reduction of reaction time is crucial for a successful free radical grafting of glycidyl methacrylate on EPR in a corotating twin screw extruder, because the residence time in such a machine is typically on the order of 0.5-5 min.

Sun et al. [14] studied the free radical grafting of glycidyl methacrylate (GMA) onto polypropylene in a corotating twin screw extruder. The presence of styrene as a second monomer increased the GMA's grafting yield greatly with reduced polypropylene chain degradation. The GMA's grafting yield increased with increasing concentration of peroxide, 1,3-bis (tert-butylperoxyisopropyl) benzene and GMA's grafting yield decreased with increasing screw speed or feed rate. For a particular specific throughput (the rate of throughput to screw speed), an increase in throughput with a concomitant increase in screw speed brought about a decrease in GMA's grafting yield.

Tedesco et al. [15] studied polypropylene functionalized with maleic anhydride (PP-MA) and polypropylene functionalized with glycidyl methacrylate (PP-GMA) as compatibilizing agents on polypropylene (PP)/Nylon 6 (Ny6) blends. The crystallinity of the components of the PP/PP-GMA/Ny6 blend was virtually unchanged indicating that the presence of PP-GMA did not distrub the crystalline structure of the blend components. PP/PP-MA/Ny6 presented an improvement in properties when compared with PP/PP-GMA/Ny6 and PP/Ny6. The elongation percentage value of the blend with PP-MA was higher than for the others blends. The compatibilizing effect of the PP-MA for the PP/Ny6 blends was more effective than the PP-GMA.

Chen et al. [16] studied the use of glycidyl methacrylate modified polypropylene copolymer as reactive compatibilizer for polypropylene (PP)/acrylonitrile-co-butadiene-co-acrylic acid rubber (NBR) blends. For the non reactive blend, the particle size is large and the dispersion of the NBR in the PP matrix is poor. As the level of free radical melt grafting of glycidyl methacrylate onto polypropylene (PP-g-GMA) added to the blend was increased, there was a corresponding decrease in the particle size and the dispersion of the NBR became more homogeneous. When PP-g-GMA reactive copolymer was added, up to an eight fold increase in the impact energy of the PP/NBR blend compared to that without reactive copolymer. Reactive copolymers without styrene yielded somewhat higher impact energies than the corresponding copolymers with styrene at the same GMA's grafting level. The number average molecular weight of copolymers is in range from 20 to 37 kg/mol.

Kim and Lee [17] studied the effect of poly(styrene-co-glycidyl methacrylate) (PS-GMA) as an *in situ* compatibilizer on the morphology and rheological properties of the immiscible poly(butylene terephthalate) (PBT)/polystyrene (PS) blend. The epoxy group in PS-GMA reacts with the carboxylic acid group in PBT, thus PS-g-PBT copolymer is formed and acts as a compatibilizer between PS and PBT during the melt blending. Rheological behaviour of blends having *in situ* compatibilizer was investigated by dynamic oscillatory shearing measurement. The amount of graft copolymer formed during blending increases, the viscosity at low shear rates increases but the degree of shear thinning is not pronounced. For polymer alloys prepared at the setting temperature of 230°C, the finer morphology was obtained when more than 5 phr PS-GMA decreased to 3 phr when the setting temperature in the mixer was increased to 240°C since at higher temperature more graft copolymer can be formed.

Oommen and Thomas [18] studied the mechanical properties and fracture behavior of natural rubber/poly(methyl methacrylate) blends. Tensile strength, tear strength and Young's modulus decrease with increase in natural rubber content. Coran's equation is found to agree with the experimental value. Addition of a compatibilizer reduces the domain size followed by a leveling-off at higher graft copolymer concentration. Tensile strength, tear strength, and Izod impact strength show considerable improvement by the addition of the graft copolymer. The properties attain an optimum value when the reduction in domain size is maximum. Interfacial adhesion between the two homopolymers increases by the addition of the graft copolymer and, consequently, the mechanical properties increase. Solution-cast blends exhibit better mechanical properties as compared to melt-mixed samples due to degradation at processing conditions. Scanning electron microscopy (SEM) studies of the failure surfaces indicate no adhesion between the components in the uncompatibilized system. The presence of microfibrils on the fracture surface of the compatibilized system indicates improved interface adhesion.

Thiraphattaraphun [19] studied the effects of initiator concentration, reaction temperature, monomer concentration, and reaction time on the grafting of the methyl methacrylate (MMA) monomer onto natural rubber using potassium persulfate as an initiator. The graft copolymer was carried out by emulsion polymerization. The appropriate conditions for the preparation of grafted natural rubber were found to be 100 parts by weight of the monomer per 100 parts by weight of the dry rubber content, 0.75 phr of the initiator concentration, and a reaction temperature of 55°C for 8 hours, which gave a high monomer conversion and grafting efficiency. The tensile strength, tear strength, and hardness increases with an increase in poly(methyl methacrylate)

(PMMA) content. The tensile fracture surface examined by scanning electron microscopy disclosed that the graft copolymer acted as an interfacial agent and gave a good adhesion between the two phases of the compatibilized blend.