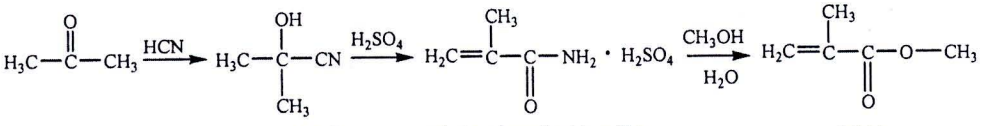
CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Methyl methacrylate and poly(methyl methacrylate) (Fred, 1971)

Methyl methacrylate (MMA) is a monomer used for production of the transparent plastic poly(methyl methacrylate) (PMMA). Generally, MMA is synthesized from acetone and hydrogen cyanide as shown in eq. 2.1:



(2.1)

In a typical process, acetone is treated with hydrogen cyanide at 40°C in the presence of ammonia used as a catalyst to produce acetone cyanohydrin. Then, the acetone cyanohydrin is treated with concentrated sulfuric acid at 100°C to form methyl methacrylamide sulfate which is directly fed into an aqueous methanol to produce MMA. The MMA product is separated by steam and purified by distillation. The MMA or acrylic monomer is colorless liquid with a characteristic sweet odor. Its boiling point is ca. 100.5°C. For shipping and storage, hydroquinone or *p*-methoxyphenol is commonly used as an inhibitor for MMA monomer to inhibit the self-polymerization of MMA (Ghosh, 1990).

The first acrylic polymer commercially produced was poly(methyl acrylate) . Its production was begun in 1927 by Rohm and Haas AG in Germany. In about 1930, Hill of Imperial Chemical Industries Ltd. (UK) prepared acrylic or MMA sheets which are potentially useful material for various applications. However, the high raw material cost prohibited the commercial development. At that time, MMA was obtained by dehydrogenation of hydroxyisobutyic ester. In 1932, Crawford synthesized MMA based on cheap raw materials: acetone and hydrogen cyanide. Thus, PMMA or acrylic plastic became a feasible proposition and commercial

production in 1934. The acrylic sheets were used during the Second World War for aircraft glazing. After the world war, the acrylic sheets have been used in various applications such as display signs, lighting fittings and bathroom fittings. PMMA can be melted by heat to replace the casting process. This causes the enhancement of the cost effective means. PMMA is also extensively used for the production of dentures.

The polymerization of MMA is readily accomplished by bulk, solution, suspension and emulsion techniques. Among these methods, bulk and suspension polymerization methods are mainly used for the production of the homopolymer. The production of cast sheets, rods and tubes is carried out by bulk polymerization, starting in most cases with syrup of partially polymerized MMA with a convenient viscosity for handling. In addition, the shrinkage and heat evolution during polymerization are reduced by the use of syrup. PMMA sheets are also commonly made by extrusion. Alternatively, they may be casted in cells consisting of two glass sheets separated by a coated rubber gasket. The polymerization is carried out at 60-70°C in an air oven or water bath, with a finishing treatment at 100°C. Normally, peroxide or azo initiators may be applied as initiators. PMMA prepared by free radical polymerization is amorphous because of its lack of complete stereoregularity and its bulky side groups. It is therefore soluble in aromatic and chlorinated hydrocarbons including esters. However, it has high resistance to water, alkali, solution, inorganic solvent and most dilute acids. PMMA has more resistance to hydrolysis than poly(methyl acrylate), probably by virtue of the shielding presented by the α-methyl group (Brinkmann, 2006).

PMMA is a linear, hard, polar and rigid transparent thermoplastic with a higher softening point, better impact strength, and better weatherability than PS. The typical properties of PMMA are given in Table 2.1. An outstanding property of PMMA is its clarity. Thus, the transmission of normal incident light through a sheet of the polymer is about 92%. A further outstanding property of PMMA is the good outdoor weathering. After several years under tropical conditions, the color change is extremely small. The mechanical and thermal properties of PMMA such as tensile

Table 2.1 Typical properties of poly (methyl methacrylate) (Katsikis et al., 2007)

Property	Value
Density, g/cm^3	1.15-1.19
Water absorption, %	0.3-2
Hardness, Rockwell M	63-97
Young's modulus, GPa	1.79-3.38
Tensile strength, MPa	55-85
Elongation at break, %	1-30
Charpy Impact, J/cm^2	0.2-0.4
Specific heat capacity, J/(g·K)	1.46-1.47
Thermal conductivity, W/(m·K)	0.19-0.24
Glass temperature, °C	100-105
Melting point, °C	130-140
Vicat Softening Point, °C	47-117
Transmission, %	80-93
Refractive index	1.49-1.498

strength, impact strength, etc. are also good. Electrical properties are fair. A limitation of the optical uses of PMMA is its poor abrasion resistance compared to glass. Although it has been found the techniques to improve the scratch resistance, it also deteriorated other properties such as impact strength.

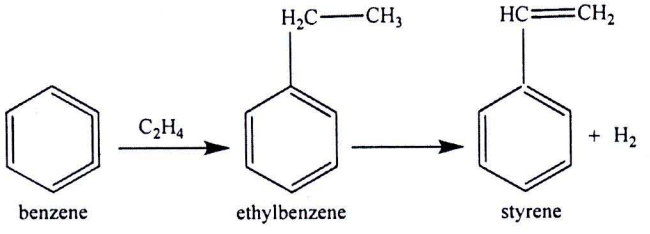
It is generally accepted that the decomposition of PMMA in nitrogen atmosphere consists of three stages: the first stage (100–200°C) is ascribed to the rupture of weak head-to-head linkages in the main chain. The second stage (200–300°C) is decomposition of the terminal vinyl group. Finally, the degradation in the third stage (300–400°C) is related to the random scission of polymer main chain (Hwu et al., 2002). For the decomposition of PMMA in the presence of oxygen, the first peak disappears and the second peak either merges with the third peak or becomes a shoulder to the third peak depending on the heating rate. This phenomenon has been explained by the dual function of oxygen in PMMA decomposition.

At lower temperatures, oxygen inhibits PMMA decomposition by reacting with a polymeric radicals and forming new polymeric radicals with higher stability. Above 270°C, these new polymeric radicals are decomposed and release more reactive radicals resulting to the acceleration of PMMA decomposition (Peterson et al., 1999).

2.2 Styrene and polystyrene (Ghosh, 1990)

Styrene (ST) or vinyl benzene is an organic compound with the chemical formula $C_6H_5CH=CH_2$. Under normal conditions, this aromatic hydrocarbon is an oily liquid and slightly polar compared to ethylene and α-olefins. It is also easily evaporated and smells sweet. It often contains other chemicals having sharp and unpleasant smell.

The bulk of commercial ST is prepared from benzene by the following route (eq. 2.2):



(2.2)

In the first stage, Friedel-Crafts reaction is commonly carried out by treating benzene with ethylene in the liquid phase at 90-100°C at slightly above atmospheric pressure. The catalyst is aluminum chloride (with ethyl chloride as catalyst promoter) to produce ethylbenzene. The second stage involves with the dehydrogenation of ethylbenzene. This reaction is carried out in the vapor phase at 600-650°C over catalyst based on either ferric or zinc oxide with lesser amounts of other metallic oxides such as chromic, cupric, and potassium oxides. The reaction is favored by low pressure. In order to reduce the partial pressure of the ethylbenzene, the feed is mixed with superheated steam before passing over the catalyst. ST is colorless liquid with a characteristic odor and could be refined by distillation.

The production of ST in the United States was dramatically increased during the 1940's to supply the war to be used as the raw material for synthetic

rubber. Because the ST molecule has a vinyl group with a double bond, it can be polymerized. It is normally used as a monomer to make plastics such as polystyrene (PS), acrylonitrile-butadiene-styrene rubber (ABS), styrene-butadiene rubber (SBR) and unsaturated polyesters. These materials are used in rubber, plastic, insulation, fiberglass, pipes, automobile parts, food containers and carpet backing etc.

Polystyrene (PS) is a polymer made from polymerization of ST in four techniques: bulk, solution, suspension, and emulsion polymerizations. Although solution or emulsion polymerization may generally be used, most PS is made either by suspension or bulk polymerization. The chemical structure of PS is shown in Figure 2.1. At room temperature, PS is normally a solid thermoplastic. It can be melted at higher temperature for molding or extrusion.. Commercial interest in PS began in the 1930s when the material was found to have good electronic insulation characteristics. The production was started by I.G. Farben industries (Germany) and Dow Chemical Company (USA) before the Second World War. Application of PS was vigorously explored and quickly adopted in many fields. PS is now one of the major commercial plastics, which are very extensively used such as food containers, packaging, toys and thermal insulation. Straight PS is a hard, rigid and rather brittle material. Some properties of PS are shown in the Table 2.2. It has a relatively low softening point and cannot withstand the temperature of boiling water. PS is a low cost material with high transparent property with 90% of transmission value (Billmeyer, 1984).

2.3 Ethylene propylene diene rubber (EPDM) (Morton, 1973)

The first commercial ethylene propylene rubbers were made by the random copolymerization of ethylene and propylene in solution catalyzed by using Ziegler-Natta catalyst. The dienes most commonly used today to produce the ethylene-propylene diene rubber (EPDM) are 1,4 hexadiene, ethylidene, norbornene and dicyclopentadiene, each conferring a different rate and state of cure to the polymer.

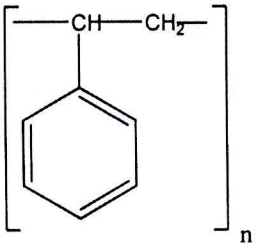


Figure 2.1 Structure of polystyrene.

Table 2.2 Typically properties of polystyrene (Odian, 1991)

Property	Value
Density, g/cm^3	1.04-1.07
Water absorption, %	0-0.1
Hardness, Rockwell M	70-74
Young's modulus, GPa	1.79-3.38
Tensile strength, MPa	25-69
Elongation at break, %	1-45
Charpy impact, J/cm^2	0.2-0.4
Specific heat capacity, J/(g.K)	1.2-2.1
Thermal conductivity, W/(m.K)	0.12-0.193
Glass temperature, °C	83-100
Melting point, °C	240
Vicat softtening point, °C	1.03-110
Transmission, %	80-90

In general, the ethylene propylene rubbers are compounded to provide good low-temperature flexibility, high tensile strength, high tear and abrasion resistance, excellent weatherability (ozone, water, and oxidation resistance), good electrical properties, high compression set resistance, and high heat resistance. Many different types of EPDM are available with different properties. The ethylene content ranges between 45 (amorphous types) to 55-65 wt% (semi-crystalline types) and 70 wt% (crystalline types). For EPDM containing ethylene content below 50 wt%, the crystalline fraction is zero, but it can increase to 20% for EPDM with 80 wt% of

ethylene. The high molecular mass crystalline EPDM can incorporate high levels of fillers. Ethylene propylene rubber (EPMs) and EPDM have low resistance to hydrocarbon oils and their lack of building tack must be compensated by using the addition of resin. In this work, the EPDM containing 9.2 wt% of 5-ethylidene-2-norbornene (ENB) (Figure 2.2) was used as a raw material for graft copolymerization.

EPDM rubber was developed and commercialized in the late 1950s. With an annual production capacity of more than 1,000 kilotons in 1998. EPDM is currently counted as the fourth elastomer by volume to become a commodity rubber. Actually, EPDM is the largest non-tire rubber. The annual growth rate is about 4%. Exxon mobil, Dow and DSM are market leaders. The outstanding property of the ethylene-propylene rubber (EPM) and EPDM are their good weather-resistance compared with polybutadiene, polyisoprene and styrene/butadiene copolymer, due to less C=C double bond content in the structure of the polymer chains. Thus, they are less sensitive to oxygen and ozone including UV-light. Other excellent properties of these rubbers are high resistance to acid and alkali with high insulation properties. Some properties of rubber are shown in the Table 2.3. The EPM and EPDM are also used in the automotive industry for windows, hoses, gaskets, wipers, bumpers, belts, door seals, etc. They are also used for cable insulation and roofing. Moreover, this can be applied for white sidewall compounds of tire production. A large number of commercial EPM and EPDM grades are produced. The main structural characteristics are depended on the factors as followed (Noordermeer, 2002).

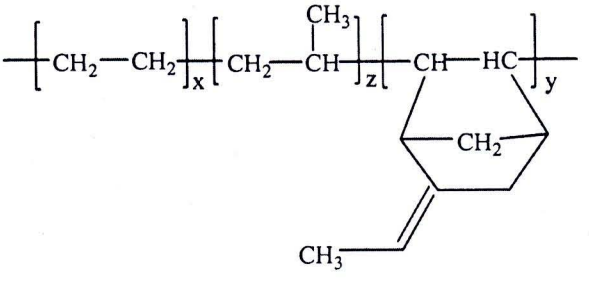


Figure 2.2 Structure of ethylene-propylene-diene rubber (Morton, 1973 and Ciesielski, 1999).

- Concentration ratio of ethylene and propylene chain units (amorphous or crystalline grades)
- Co-or terpolymerization of ethylene, propylene and diene monomers (EPM or EPDM)
- Type and amount of termonomer (chain branching, type of crosslinking and mechanical properties)
- Molecular weight and molecular weight distribution
- Chain branching (differences in viscosity and processability)
- Processability and price

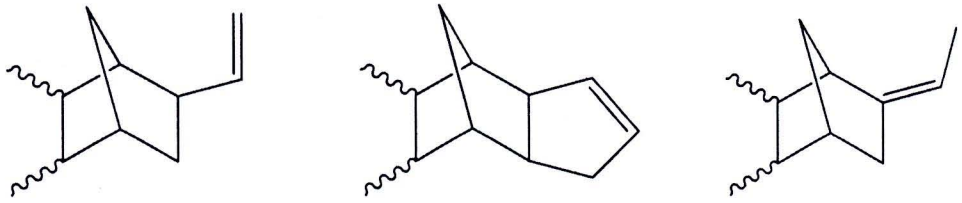
EPM and EPDM containing below 55 wt% of ethylene section are completely amorphous and are not self-reinforcing. At higher ethylene contents of (60-70 wt.%), the polymers can form crystalline domains. These polymers are referred as "sequential" grades and their processing behavior considerably differs from that of the normal amorphous grades. The form with partially crystalline domains is thermally reversible physical crosslinks, which is thermoplastic elastomer to provide higher mechanical strength without chemical crosslinks. However, its tensile properties in vulcanisates are low. Most applications require crosslinking. Traditionally, sulfur vulcanization requires unsaturation and therefore fully saturated EPM cannot be crosslinked by using sulfur. Non-conjugated diene monomers have been introduced in EPM, yielding EPDM for sulfur vulcanization. For peroxide crosslinking, the presence of the diene increases the crosslinking efficiency. The termonomer used must have one of its C=C double-bonds sufficiently reactive to copolymerize randomly with ethylene and propylene, while the other must be unreactive in the polymerization. Normally, the unsaturated termonomer is present on the side chain rather than in the main chain. For various compounds in tire industry, only three types of unsaturated termonomer are widely used (Figure 2.3). From a practical point of view, ethylidene norbornene (ENB) and dicyclopentadiene (DCPD) are the most important diene termonomers due to the high amounts of diene that can be easily incorporated in commercial EPDMs (Hofmann, 1989).

Table 2.3 Qualitative comparison of properties of rubbers (Indian Rubber Institute, 1998)

Properties	Class				
	Unsaturated carbon chains				Saturated carbon chains
	NR	BR	NBR	SBR	EPDM
Glass transition temperature (Tg, K)	203	168	232	217	213
Density (Kg/m^3)	920	910-940	1,000	933	860
Tensile strength (MPa)	22-25	5	3	2-3	5
Hardness (IRHD)	30-90	35-90	30-90	40-90	40-90
Tear resistance	G	E	F/G	P/F	F/G
Abrasion resistance	G	E	G	VG	E
Compression set	F/G	G	G	P/G	G
Rebound resilience Cold	E	VG	VG	VG	VG
Rebound resilience Hot	E	VG	VG	VG	VG
Electrical properties					
- Dielectric strength	E	E	F	E	VG
- Electrical insulation	E/G	E	F	E	E
Resistance to ageing					
- Oxidation	G	G	F	G	E
- Ozone	P	P	P	P	E
- Sunlight	P	P	P	P	O
- Flame	P	P	P	P	O
- Heat	G	G	G	VG	E
- Cold	E	E	F	G	G

Note: E=excellent F=fair G= good O=outstanding P=poor VG=very good

The increase in the amount of diene causes the enhancement of crosslink densities resulting the corresponding changes in mechanical and elastic properties. The preferred third monomer for peroxide cure is 1,4 hexadiene (VNB).



(a) (b) (c)

Figure 2.3 Chemical structure of diene third monomers: (a) VNB, (b) DCPD and (c) ENB (Noordermeer, 2002).

The commercial grades of EPDM differ in composition (ethylene and termonomer content), molecular mass and amount of extender. They are broadly following categories:

(i) Random polymer with roughly equal ethylene/propylene ratio

(ii) Sequential polymers with higher ethylene content. The ethylene is incorporation ratio into the molecular chain partially in the form of sequences to produce a partially crystalline molecular structure.

(iii) Oil extended polymers: the advantages of EPDM are that they can tolerate large amounts oil and black in the compound and being fully saturated. They are not subjected to ozone or oxidative attack and have good resistance to heat aging. Characteristic properties of EPDMs are good weatherability and excellent ozone and heat resistance.

2.4 Elastomer blends

Various polymers or rubbers are often blended to reach required properties for any application. To obtain a desired combination of properties, both theoretical and technical aspects should be taken into account. Compatibility of rubber ingredients is vital for rubber blends to achieve optimum properties. Blending is an effective and economic approach to achieve desired properties compared to synthesize new elastomers. Potential merits of rubber blends are: (1) improvement of solvent resistance; (2) improvement of processability; (3) better product uniformity; (4) quick formulation changes and manufacture flexibility and (5) improvement of productivity. *The rubber blends, based on the miscibility of constituent polymers, can be divided*

into three broad classes: a) miscible blends (interpenetrating networks), b) partially miscible blends and c) immiscible blends (e.g. polymer alloys which are immiscible but compatibilized). Although the polymer alloy has two or more different phases on a micro-scale, it exhibits macroscopic properties as a single-phase material (Brydson, 1988). The immiscibility and phase separation are normally occurred in the rubber blends. The homogeneity at a fairly fine level instead of molecular miscibility is sufficient for optimum performance. It is usually desirable to have a certain degree of micro-heterogeneity to preserve the individual properties of the respective rubber components. (Kraus, 1978)

2.4.1 Miscibility of polymers (Brydson, 1988)

Miscibility of polymers is determined by thermodynamic phenomena in a term of the Gibbs free energy change of mixing (ΔG_m) as shown in eq. 2.3

$$\Delta G_m = \Delta H_m - T\Delta S_m \leq 0 \tag{2.3}$$

where, ΔH_m is the enthalpy of mixing (J), ΔS_m is the entropy change of mixing (J/K) and T is the absolute temperature (K). Polymers are only miscible when the Gibbs free energy of mixing is negative. Normally, the most polymer blends are immiscible because mixing is endothermic and the entropic contribution is small due to the high molecular weights of the constituent polymers. Miscibility can also be predicted from the solubility parameters. The relationship between the enthalpy change of mixing and the solubility parameters is governed by eq. 2.4.

$$\Delta H_m / v = k(\delta_1 - \delta_2)^2 \phi_1 \phi_2 \tag{2.4}$$

where, V is the volume of the two polymers, k is a constant value close to 1, δ_1, ϕ_1 and δ_2, ϕ_2 are the solubility parameters and volume fractions of components 1 and 2, respectively. Polymer miscibility is possible only when the difference in solubility parameters is small enough (< 0.1 $(J/cm^3)^{1/2}$)) or if there are specific interactions existing which contribute to a negative ΔH_m. The solubility parameters of some

relevant polymers, determined by Gas Liquid Chromatography (GLC), viscometry, swelling measurements together with the calculated data are given in Table 2.4.

2.4.2 Compatibility of rubber blends (Ghosh, 1990)

The lack of miscibility and technological compatibility of the rubberic component severely restricts the application of rubber blends. It is very often that the rubberic components are grossly immiscible as well as technologically incompatible. The mutual compatibility is essentially governed by the thermodynamic compatibility of the rubber components involved in blending. The better compatibility between two phases in the blend shows the smaller dispersed phase domains. To concern the morphology of phase separated rubber blends, the main influences governing the structure of the entire system are: (1) the interfacial tension, which affects the size and shape of the phases; (2) the viscosity of the matrix; and (3) the shear stress. Co-continuous blend morphology is observed for rubbers with similar viscosities.

Generally, the matrix is formed by the phase with lower viscosity, while the one with higher viscosity forms the dispersed phase. Homogeneity of mixing can be controlled by using either proper mixing conditions or by addition of compatibilizers (Grulke, 1994 and Ebewele, 2000).

Table 2.4 Solubility parameters of various polymers determined with different methods (Hofmann, 1989)

Elastomer types	GLC	Solubility parameters $((J/cm^3)^{1/2})$		
		Viscometry	Swelling	Caculated*
EPDM	15.9	15.8	15.9	15.8
NR	16.6	16.8	16.7	16.7
Cis-BR	17.2	17.0	16.7	17.1
PS	19.9	-	-	19.0

* Calculated from eq. 2.4.

2.5 Graft copolymerization methods (Bemiller, 1976 and Mark, 1994)

For graft copolymerizations, side chains of the backbone polymer are formed by attachment of macromolecules with different chemical composition. The simplest case of graft copolymer can be represented by the model as shown in Figure 2.4 where a sequence of monomer units (A) is referred as the main chain or backbone, a sequence of B units is the side chain of graft and X is the grafting position on the polymeric backbone (Bayer, 1992). Graft copolymerization is defined as a post polymerization. The vinyl monomers such as styrene, acrylonitrile and MMA are normally used to graft on the backbone.

The synthesis of graft copolymers is much more diverse, but it can be divided into 5 groups related to the reaction processes.

2.5.1 Chain transfer

In a free radical polymerization, the chain transfer is an important reaction. The chain transfer to a monomer, solvent, mercaptan, or other growing chain can take place. When the chain transfer reaction to another chain takes place, it creates radicals which act as sites for further chain growth and grafting. The simplest technique is to dissolve the polymer in the appropriate solvent and initiate with the peroxide initiator to abstract a hydrogen radical and generate a radical on the polymer chain as the grafting sites for the fresh monomer. In many cases, when grafting is carried out in latex form, it has been product is normally used in thermoplastic applications.

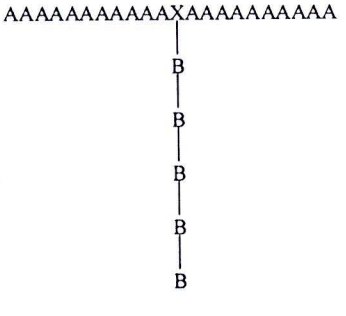


Figure 2.4 Model of graft copolymer (Bayer, 1992).

2.5.2 Copolymerization via unsaturated groups (Schulz, 1982)

Redox polymerization is the most popular techniques for grafting reactions. A hydroperoxide or similar group is reduced to a free radical plus an anion, while the metal ion is oxidized to a higher valency state. At the same time, a monomer is added. When the reducible group is attached to a polymeric chain, the free radical grafting sites formed on the macromolecular backbone acting as initiators for graft copolymerization. Hydroxyl polymers can be grafted by redox polymerization by using water soluble peroxide, such as hydrogen peroxide in conjuction with ferrous ions. The produced hydroxyl radicals abstract hydrogen atoms from the hydroxy groups in the polymer to give free radical grafting sites on the backbone. The advantage of this reaction lies in the fact that only hydroxyls on the polymer are converted into R-O radicals, so that no homopolymer can be produced and pure graft is obtained.

2.5.3 High-energy reaction techniques

The irradiation synthesis may be carried out in solution, either in contact with liquid monomer (with or without a diluent) or in contact with monomer in the absence of air to produce free suspension. The rubber may be pre-irradiated in the absence of air to produce free radicals for later monomer addition, but the life of these radicals is short as a result of mobility within the rubber matrix. The irradiation at very low temperature is possible process to use the trapped radical technique for a variety of synthetic rubbers.

2.5.4 Photochemical synthesis

Macromolecules containing photosensitive groups which can absorb energy from ultraviolet frequencies are often degraded by free radical processes. The degradation processes as a rule is fairly slow, but by the addition of photosensitizer, such as xanthone, benzyl, benzoin and 1-chloroanthraquinone can be speeded up to enable graft copolymerization to take place in the presence of monomers.

2.5.5 Metallation using activated organolithium with chelating diamines

Unsaturated elastomers can be radily metallated with activated organolithium compounds in the presence of chelating diamines or alkoxides of potassium or sodium. They can also be grafted with ionically polymerizable monomers to produce comblike materials.

Although graft copolymerizations are widely practiced with vinyl monomers and polymers, especially for improving compatibility, impact, and low temperature properties of thermoplastics, the technology has been based more upon art than upon science. Often small proportions of actual grafting have been sufficient to give worthwhile modification of properties. If grafting does not give directly the properties desired, it may improve morphology or compatibility with specific added polymers or plasticizers that impart the desired effect. In addition, these graft copolymers have been mixed with other resins such as poly(vinyl chloride) to improve compatibility, impact strength and low temperature properties of thermoplastics.

2.6 Bulk copolymerization (Odian, 1991, Drive, 1979 and Michaeli, 1995)

Bulk or mass polymerization of a pure monomer is the simplest process with a minimum contamination in the resulting product. Monomer, polymer and initiator are the only components in the bulk polymerization. Polymerization apparatus is shown in Figure 2.5. However, the bulk polymerization of vinyl monomer is more difficult, since the reactions are highly exothermic. The usual thermally decomposed initiators proceeds at a rate which is strongly dependent on temperature. Thus, the problem of coupled heat transfer is normally incurred because of the viscosity development at the early stage of reaction, resulting to the difficulty in control. The advantages and disadvantages of the commercial polymerization systems are shown in Table 2.5. In the bulk copolymerization, the monomers and initiators are mixed in a reactor consisting of heating or cooling unit. Many reactions are carried

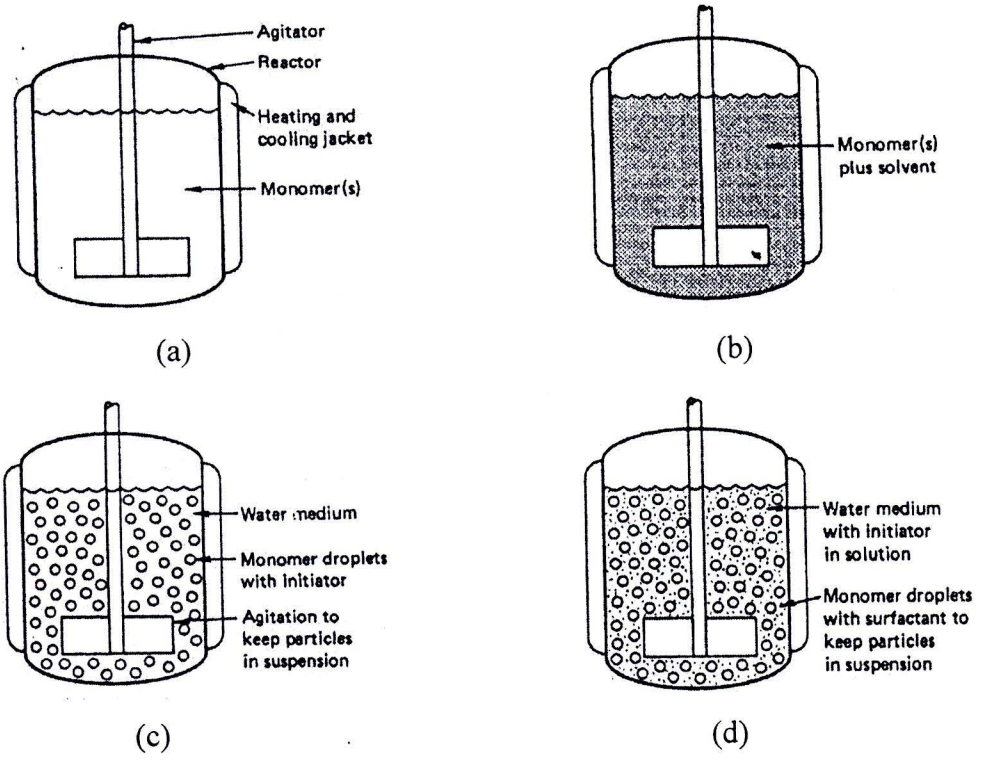


Figure 2.5 Diagrams of polymerization apparatus: (a) bulk, (b) solution, (c) suspension and (d) emulsion polymerization (Grulke, 1994).

out by charging one monomer into the reactor and/or slowly adding the second monomer.

In addition, the reaction is often too exothermic for the bulk process resulting to the requirement of careful temperature control. Therefore, the special steps must be taken to remove heat during polymerization. It can be differentiated between quiescent and stirred bulk polymerization. Both methods are applied to system which polymer is stable in monomer and progressively increases viscosity with conversion. In quiescent systems, gel formation, corresponding to infinite viscosity, can occur. However, the reaction rate of this system is difficult to be controlled due to the released heat during polymerization.

Table 2.5 Commercial polymerization systems (Grulke, 1994)

Type	Advantage	Disadvantages
Bulk: batch	• Minimum contamination • Simple equipment for making castings	• Strongly exothermic • Broadened molecular weight distribution at high conversion • Complex if small particles required
Bulk: continuous	• Lower conversion per pass leads to better heat control and narrower molecular weight distribution	• Requirement of agitation, material transfer, separation, and recycling
Solution	• Ready control of heat of polymerization	• Not useful for dry polymer because of difficulty of complete solvent removal
Suspension	• Ready control of heat of polymerization • Suspension or resulting granular polymer may be directly usable	• Requirement of continuous agitation • Contamination by stabilizer • Requirement of washing and drying processes
Emulsion	• Rapid polymerization to high molecular weight and narrow distribution with ready heat control	• Contamination with emulsifier, etc., almost inevitable, leading to poor color and color unstability • Requirement of stability washing and dryingprocess

2.7 Casting process (Drive, 1979 and Grulke, 1994)

Casting is a manufacturing process and involves the pouring of a liquid resin into a mold to allow it to harden with little or no pressure. The liquid may consist of a melted or dissolved thermoplastic, thermosetting resin, or thermoplastic monomer. Hardening takes place by cooling, evaporation of solvent or chemical reaction (Drive, 1979). Casting method requires simpler machines for making products with more economical practice of small quantities. It is also lower expenses for molds (Michaeli, 1995). The configuration of the conventional mold for preparing the general thermoplastics is shown in Figure 2.6.

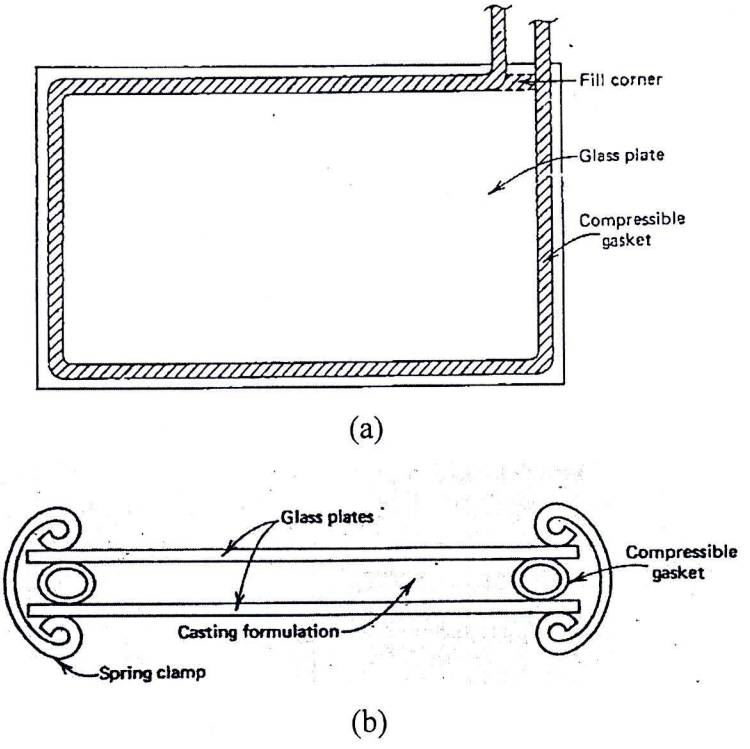


Figure 2.6 Conventional cell casting mold configuration: (a) face view and (b) edge view (Drive, 1979 and Grulke, 1994).

2.8 Impact modifier (Lutz, and Grossman, 2001)

In the early days of the thermoplastic industry, the commercial polymers such as PS, rigid PVC and PMMA exhibited low impact strength in their homopolymer forms. In the case of PS and styrene-acrylonitrile copolymer (SAN), rubbers such as polybutadiene or natural rubber are incorporated to such polymers during polymerization in order to increase their toughness.

2.8.1 Effect of secondary glass transitions temperature

The impact resistance of the brittle polymers is correlated to the presence of a secondary glass transition temperature of polymer. This temperature locates below the primary glass transition temperature. The secondary glass transition temperature is associated with the motion of the polymer backbone, not pendant side-chain groups. This is effective to improve the impact resistance. Because the definition of impact strength is the ability of the material to undergo massive yielding at impact speeds, the main-chain motions that can be activated at impact speed are expected to correlate with impact strength. Thus, a low secondary glass transition temperature is an indication of chain segments that possess some degree of mobility at impact speed. This mobility can be translated into the large-scale deformation of the polymer chains.

2.8.2 Interaction of additive impact modifier and polymer matrix

There are relatively few polymers, such as polycarbonate, that manifest the secondary glass transition temperature that to yield high impact strength with maintaining a sufficiently high primary glass transition temperature for acceptable engineering properties. Polymers having low secondary glass transition are PVC and polyphenylene oxide. These require impact modifiers to yield high impact resistance. However, some polymers, such as PS, do not have the secondary glass transition temperature. Consequently, this concept provides the secondary glass transition temperature in the materials for improving their impact strength by the addition of rubber impact modifiers with a low glass transition temperature.

In general, rubbery materials can be used as impact modifiers due to their shear stresses that arise at the rubber-matrix boundaries. When the large numbers of microscopic rubbery phases inclusions are distributed throughout the matrix, this matrix deformation is delocalized throughout the sample and large amounts of energy can be absorbed. Graft copolymers containing identical segments to the blend components can be applied as the compatibilizer to increase the miscibility between the copolymer segments and the corresponding blend components. In the most cases, the compatibilizer possibly affects the final products such as reduction of the interfacial tension during melt mixing resulting to a finer dispersed phase which increases the adhesion at phase boundaries. This gives the improved stress transfer with strengthening the interface in the solid state and stabilization of the dispersed phase by reducing the rate of domain coalescence during melts processing and annealing (Edenbaum, 1996).

2.9 Literature reviews

2.9.1 Graft copolymerization of ethylene propylene diene rubber

Fu et al. (2008) studied the use of EPDM grafted with MMA and ST (EPDM-*g*-MMA/ST) as a toughen agent for methyl methacrylate styrene resin (MS resin). The graft copolymer was synthesized by solution graft copolymerization in toluene/n-heptane co-solvent using benzoyl peroxide (BPO) as an initiator. The effects of reaction conditions on the graft copolymerization such as EPDM/MMA-ST ratio, MMA/ST ratio, initiator dosage, reactant concentration, toluene/n-heptane ratio and reaction time were discussed. EPDM-*g*-MMA/ST/MS resin blends were prepared by melt blending. The effect of EPDM-*g*-MMA/ST on the toughening property of MS resin was also investigated. The results showed that the optimized reaction conditions were 50/50 by wt of EPDM/MMA/ST and 75/25 by wt of MMA/ST initiator dosage of 1%, reactant concentration of 20%, toluene/n-heptane ratio of 75/25 at 80°C for 20 h and EPDM-*g*-MS with the higher EPDM content (56.8%) and grafting ratio (52.8%) was obtained under the optimized reaction conditions. SEM analysis showed that EPDM-*g*-MMA/ST had good compatibility with MS resin. EPDM-*g*-MMA/ST had

excellent toughening effect on MS resin and could be used for toughen agent of MS resin.

Fu et al. (2008) studied the toughening effect of grafted EPDM with MMA and ST (EPDM-*g*-MMA/ST) as a toughening agent for MS resin. The graft copolymer was synthesized by solution graft copolymerization in toluene/n-heptane co-solvent using benzoyl peroxide (BPO) as an initiator. The toughening effects of grafted EPDM on MS resin were discussed. The result showed that the Notched Izod impact strength of MS resin increased with increasing grafting ratio. The differential scaning calorimetry showed that the grafted EPDM and MS resin are partially compatible and the compatibility was improved with increasing grafting chain polarity of grafted EPDM.

Zeng et al., (2004) studies on the synthesis of high rubber styrene-EPDM-acrylonitrile graft copolymer (AES) and its toughening effect on SAN. The graft copolymerization of styrene (ST) and acrylonitrile (AN) onto EPDM were prepared by solution polymerization in n-heptane/toluene cosolvent using benzoyl peroxide as an initiator. The effects of reaction conditions, such as reaction temperature, initiator concentration, EPDM content, the solvent component, and reaction time on the graft copolymerization were discussed. In addition, according to the research on mechanical properties of the SAN/AES blend, the toughening effect of AES on SAN resin was found. By means of scanning electron microscopy, the toughening mechanism was proposed to be crazing initiation from rubber particles and shear deformation of SAN matrix. Uniform dispersion of rubber particles, as shown by transmission electron microscopy, the AES was attributed to the good compatibility of SAN.

2.9.2 Modification of acrylic sheet

Charmondusit et al. (2008) studied the preparation of high impact transparent ST-MMA copolymer cast sheet by using natural rubber (NR) as an impact modifier. The copolymer cast sheets were prepared by bulk polymerization via casting process. The influence factors, such as monomer ratio and NR concentration were

studies. The physical and mechanical properties of the modified copolymer cast sheets were investigated. It was found that the appropriate conditions were 90 and 80 wt% of MMA, 10 and 20 wt% of ST, 0.1 wt% of peroxide as an initiator and 0.03 wt% of azocompound initiator. The highest impact strength of copolymer cast sheet was reached when the cast sheet contained 20 wt% of NR.

Cheng et al. (2004) studied transparent EVA/PMMA sheets produced via *in situ* polymerization of MMA. In the presence of the EVA-graft-PMMA (EVA-*g*-PMMA) prepared by using *tert*-butyl peroctoate (*t*-BO) as an initiator in the EVA/PMMA, EVA can be well dispersed in the PMMA matrix. Both tensile fracture energy and Izod impact strength of the EVA/PMMA blends were higher than those of the neat PMMA. This was confirmed by using Scaning Electron Microscopy (SEM). The copolymer also prevented the dispersed EVA particles from pulling out the fracture surface. The strength of the EVA/PMMA blends were investigated at room temperature over the four stain rates of decadence (from 1.6×10^{-4} to 0.16 s^{-1}). It had an obvious transition, whereas the neat PMMA remained the brittleness over the entire range of strain rates.

Mansour et al. (2004) prepared copolymer films of ST and MMA with different percentage. Differential scanning calorimeter showed a single transition at 50/50 ST/MMA. Thermogravimetry technique was used to compare the thermal stability of the copolymer and homopolymers. The copolymers degradation occured at higher temperatures than pure PMMA indicating the higher stabilization of the copolymer. FTIR spectroscopy was used to give information on the structural changes consequently upon exposure. This indicated that the copolymerization of ST and PMMA improved the photodegradation behavior of PS. The optical absorption (α) and the band gap (*Eg*) of film were determined before and after exposure to UV radiation. The optical transmission and reflection data for 50/50 of ST/MMA copolymer were also analyzed to evaluate the refraction index (*n*) and extinction coefficient (*k*) before and after exposure to UV radiation.

Hinchiranan et al. (2007) reported the improved properties of modified acrylic sheet via addition the graft NR. The mechanical properties of a modified

acrylic sheet prepared by bulk copolymerization of MMA and ST were improved by the addition of a small amount of graft NR (GNR). The graft copolymerization of MMA and ST onto NR latex was carried out by emulsion polymerization using potassium persulfate as an initiator. The properties of the modified acrylic sheet containing GNR with 22.5 wt% graft copolymer were investigated as a function of GNR content. The results indicated that the impact strength, tensile strength and elongation at break of the modified acrylic sheet increased with increasing the amount of GNR in the range of 0.5–4 parts. From the stress–strain behavior, the characteristics of the modified acrylic sheet shifted from brittle to ductile when the amount of GNR was increased. The scanning electron micrographs of the modified acrylic sheets showed the relatively smooth fracture surface with relatively few small cracks. This implies that the GNR could be used as an impact modifier for acrylic plastics.

Thawornwisit et al. (2006) studied the properties of copolymer sheets containing ST, MMA and modified NR prepared by bulk copolymerization using benzoyl peroxide and 2,2'-azobis-(2,4-dimethylvaleronitrile) as initiators. The modified NRs were prepared by graft copolymerization and hydrogenation. The graft NR prepared by emulsion copolymerization using redox initiator consisted of 66.1 wt% NR-*g*-(MMA-*co*-ST), 26.9 wt% of free rubber and 7.0 wt% of free copolymers. The hydrogenation of NR catalyzed by $OsHCl(CO)(O_2)(PCy_3)$ was carried out at 140°C and 400 psig, to obtain the hydrogenation level as 56.5%. The effect of ST, rubber and monomer contents on the mechanical and physical properties including morphology of the modified acrylic sheets was investigated. The results showed that the better mechanical properties of the modified acrylic sheet were obtained from the addition of 2 wt% of graft NR and 1 wt% of hydrogenated NR. The optimum content of ST in the modified acrylic sheets for improving the mechanical properties was 20 wt%. Moreover, the modified acrylic sheet containing the hydrogenated NR had the superior thermal resistance. The tensile fracture surface examined by SEM showed the relatively smooth surface with few relatively small cracks. It implied that the modified NR could be used as an impact modifier for the acrylic cast sheet.