

CHAPTER 7

INTRODUCTION

1. INTRODUCTION

The high costs required for developing a new polymer have pushed scientists to innovate new polymers by modification and blending rather than synthesis of a new monomer or polymer. Polymer modification has become a major route to get new polymer properties and wide polymer applicability. Indeed, while the modification of polyolefins, especially polyethylene (PE), polypropylene (PP), polyisobutylene (PIB), poly(1-butene) and their copolymers, are used in a wide range of applications as they incorporate an excellent combination of mechanical, chemical and electronic properties, processibility, recyclability and low costs. Nevertheless, the lack of reactive groups in the polymer structure may limit some of their end uses. Accordingly, the chemical modification of polyolefins has been used as a route to produce valuable products. Methods for polymer functionalization [Pinazzi, 1977, Chung, 1988 and Chung, 1989] have been employed to alter their chemical and physical properties. It is very desirable to prepare polyolefin block and graft copolymers containing functional polymer segments for improving the interfacial interaction between polymers and other materials as compatibilizers [Lohse, 1991].

1.1 GRAFT MODIFICATIONS OF POLYMERS

In recent years, increasing activities have been directed towards chemical modification of existing polymers in order to obtain new materials [Sherrington, 1988 and Lambla, 1993]. Chemical modifications of existing polymers are important for at least two reasons: first, they can be an inexpensive and rapid way of obtaining new polymers without search for new monomers; second, sometimes they may be the only way to synthesize intended polymer. One of the

important chemical modification methods is the free radical grafting of reactive monomers. This involves reaction of a polymer with a vinyl-containing monomer or a mixture of monomers capable of forming grafts onto the polymer backbone. If the grafts are long chain segments, the modified polymer becomes a true graft copolymer, the properties of which will be very different from those of the original polymer substrate. When the grafts are short segments, less than five moieties, most of the physical and/or mechanical properties of the original polymer substrate will be retained. However, the chemical properties of the modified polymer may become quite different, this often being the ultimate object. All possible chemical modification methods -free radical grafting is probably the oldest- are widely practiced and most inexpensive one. These grafts are gained with the use of batch mixers or screw extruders as chemical reactors, which allow the free-radical grafting reaction to occur without solvents. Free radical grafting has been used to promote mechanical properties of various types of polymers of polyolefins such as polyethylene (PE) and polypropylene (PP). However, their applications are limited in various important fields, for example their lack of chemical functionalities, low paint ability and dye ability, poor adhesion to metal or glass, high sensitivity to photo- and/ or thermal oxidation, low elastic modulus, limited impact strength and poor compatibility with other polymers including engineering plastics.

1.1.1. Grafting of Monomers onto Polymers

Grafting polymerization reaction can proceed by various mechanisms and can be catalyzed by different initiators. For addition polymerization of single compounds, initiation of chains may occur via radical,

cationic, anionic, or so-called coordinative-acting initiators, but some monomers cannot be polymerized by more than one mechanism. A free-radical grafting system usually contains three types of reactants: polymer, unsaturated molecule, such as vinyl monomer, and free radical initiator. Free radical initiators are sources of free radicals necessary for initiating a free-radical graft process. Those used to initiate a grafting reaction are organic peroxides and, less commonly, air or ionizing radiation. Free radicals may also be generated by pure thermal or mechanical means. But under normal grafting conditions, in solution or in the melt, free radicals can be formed by thermo-mechanical means at ambient atmosphere. Therefore, thermo-mechanically induced formation of free radicals must be considered as a minor source of radicals, which must be supplemented, by other sources. The most useful source is, of course, organic peroxides, (ROOR') which are often added in small amounts to the grafting system. Organic peroxide supplies free radicals by the homolytic cleavage of the labile oxygen-oxygen bond of the peroxide at appropriate temperatures. Free radical species generated from peroxides have an unpaired (free) electron and are very reactive intermediates with short lifetimes, i.e half-lives of less than 10^{-3} s [Griller and Ingold, 1976]. The only useful peroxides are those of which the primary free radical should be sufficiently reactive to abstract hydrogen atoms from the polymer chain to form the corresponding macroradicals. Because of their short half-lives and low hydrogen abstracting capacity, azo initiators are rarely used in free radical grafting. For example, Smets, Roovers and van Humbleek [Smets et al., 1961] attempted to graft methyl methacrylate (MMA) onto polystyrene. When azo-bis isobutyronitril (AIBN) was used as initiator no grafting was achieved,

as neither the isobutyronitril radical nor the propagating MMA radical is sufficiently reactive to abstract hydrogen from polystyrene. However, when benzoyl peroxide (PB) was used as initiator, grafted polymer was achieved owing to the more reactive phenyl and benzoyloxy radicals having a higher capacity of abstracting hydrogen from polystyrene backbone. Reaction condition and reactivity of initiators should take into consideration when selecting a proper initiator for a given radical process. They must be matched so that the grafting reaction can be successfully completed.

Free radical grafting of selected monomers onto polymer chains occurs when the macroradical reacts with the double bond of the vinyl monomer, forming a branched macroradical. If this branched macroradical continues to react with more vinyl monomer molecules, longer grafts will form. The grafts onto the polymer chain are responsible for property improvement. A notable commercial example are grafting of maleic anhydrid (MA) onto polyolefins, and PP in particular. MA possesses a double reactivity: free radical reactivity and functional reactivity (cyclic anhydride). Another example is grafting of vinyl acetate monomer onto chitin with redoxy initiator in presence of cerium ammonium nitrate as redoxy initiator [Don et al., 2002]. Once grafted onto a polymer backbone in the form of a substituted succinic anhydride (SA), it provides a polymer substrate with higher reactivity towards various nucleophilic groups (amines, alchols, thiols, etc.) or electrophilic groups (epoxies) in the presence of a catalyst. This high reactivity of SA has been explored for numerous industrial applications, included adhesion, painting [Trivedi and Culberson, 1982].

The extent to which a vinyl monomer is grafted depends very much on the reactivity of monomer and macroradical combinations. However,

little direct information pertinent to such combination is available. Nevertheless, the reactivity of such combinations may be analogous to that of copolymerization systems. In this latter case, the process is governed primarily by reactivity ratios. This may allow one to appreciate the inherent reactivity of a monomer A with a series of other monomers. In this case, the reciprocal of the ratio, $1/r_a$, is a direct measure of the reactivity of this series of monomers towards the radical A^* as:

$$1/r_a = k_p^{ab} / k_p^{aa} = \text{specific rate of } (A^* + B) / \text{specific rate of } (A^* + A) \quad [1.1]$$

and the rate coefficients of all reactions of radical A^* are measured with reference to a common standard, the homopropagation rate coefficient for monomer A (k_p^{aa}). In general, the order of inherent reactivity of radicals is approximately the inverse of the order for monomers, most reactive monomers yielding the least reactive radical and vice versa. The reactivity ratios for the classical copolymerisation systems may be of use for free radical grafting and especially for selecting comonomers in order to promote the grafting of otherwise unreactive monomers onto polymer substrates.

Apart from a lack of well-established correlation between the structure and reactivity of monomer and radical combinations, another difficulty encountered in free radical grafting lies in the fact that the initiating species for grafting are macroradicals. This type of radical is highly bulky, therefore rendering bulky monomers, which have difficulty-accessing these sites. In other words, the steric effect on reactivity of monomers should be much more important for free radical grafting than for classical copolymerisation. Hence, bulky monomers that are copolymerisable may become reluctant to be grafted onto polymer backbones.

Ide, Kamada and Hasegawa [Ide et al., 1970] published pioneering work on the melt grafting of MA onto an isotactic PP in a Brabender batch mixer using benzoyl peroxide PB or Dicumyl peroxide (CDP) as a free radical generator. Høgt [Høgt, 1988] carried out the melt free radical grafting of MA onto PP in a Berstorff 25 mm co-rotating twin-screw extruder using 1,3-bis (t-butyl peroxyisopropyl) benzene (DTBPIB). He found that, further PP degradation occurs with increasing peroxide concentrations although the MA grafting yield was increased. Early attempts made by some researchers were aimed to minimize PP degradation or PE cross-linking without inhibiting grafting involved adding organic substances. Studies on such type of addition that have initially been made by Gaylord et al. [Gaylord et al., 1973, 1975, 1981, 1982, 1983 and 1988] concerned with the melt free radical grafting of MA. They have tested numerous electron donating organic additives such as dimethyl formamide (DMF) and dimethylacetamide (DMAC). They found that PP degradation or PE cross-linking also was reduced and MA grafting yield was also decreased. This was explained on the basis that the organic additive such as DMF or DMAC would simply behave as a free radical scavenger.

1.1.2. Electron Beam Radiation Graft Modification

Radiation-induced grafting can be performed using different radiation sources. The graft copolymer will have slightly different characteristics depending on the type of radiation used. Three different types of radiation have been used: γ -rays, electron-beam and ultraviolet (UV) radiations. There are mainly two different methods of radiation-induced grafting: the simultaneous and the pre-irradiation methods.

In the simultaneous method, the polymer is irradiated in the presence of the monomer to be grafted. This procedure has drawbacks in case of the grafting, where it is difficult to control and there is a considerable amount of photopolymer is formed. Work has been carried out to improve this method, for instance addition of Mohr's salt [Ishigaki et al., 1982 and Bett et al., 1989] or FeCl_3 [Hegazy et al., 1989, 1990] which showed a reduction in the formation of photopolymers.

Upon using the pre-irradiation method, on the other hand, photopolymer formation can be greatly reduced. Pre-irradiation method can be performed either in presence of oxygen - a case in which peroxides are formed which can be stored for a considerable period of time before activation by UV-light for instance - or under inert atmosphere where radicals are formed and will be ready to react immediately upon contact with other monomers. The principle of pre-irradiation electron beam, EB, grafted in inert atmosphere is that, the electron beam give high-energy electrons which initiate chemical and structural changes in polymer. The radiation is the source of radical formation on the chains of the irradiated polymer. These radicals may lead to chain scission which in turn react with each other causing cross-linking, or they may remain as trapped macroradicals. The relationship between the competing reactions was defined by Charlesby and Pinner [Charlesby and Pinner, 1959].

Grafting can be initiated from the trapped macroradicals by exposing the irradiated polymer to a solution containing a monomer that polymerizes by a radical mechanism. Most of the monomers that form radicals upon irradiation can be grafted onto polymers and form radicals upon irradiation. This makes radiation-induced grafting, using EB technique, a convenient method for modifying a large number of

polymers. Among these polymers, PET which is one of the most radiation stable fiber-forming polymers. Upon gamma irradiation, two major forms of radicals have been suggested to be mostly on the paraffinic segment and to a much lesser extent on the aliphatic segment of the PET chain [Campbell et al., 1966, 1967 and Turner, 1973]. Irradiation of PET in air has shown to produce chain scission at 12-500 Mrad [Basinski, 1974].

Polymerization of vinyl monomers onto PET has been studied mostly using either the pre-irradiation or the mutual-irradiation processes. The former method involves pre-irradiating the substrates prior to the reaction with the monomer. In mutual irradiation, both polymer and monomer are present during irradiation. It is usually performed in aqueous solutions of monomers. The monomers evaluated with either process have included acrylic acid [Anvy et al., 1978 and Kale and Lokhande, 1975], acrylonitrile [Anvy et al., 1978 and Kale and Lokhande, 1975], hydroxy ethylmethacrylate, methylmethacrylate [Hebeish, 1982], 2-methyl-5- vinyl pyridine [Hebeish, 1978], vinyl alcohol [Faterpeker and Potnis, 1982], vinyl acetate [Faterpeker and Potnis, 1980], styrene [Sakunada et al., 1973 and Viaggiu and Stannett, 1973] and several other vinyl monomers. The process of radiation grafting of vinylalkoxy silane monomers in free radical polymerization onto PP was performed by Ivanchev et.al. [Ivanchev et.al., 2001]. Parameters affecting electron-beam grafting are irradiation dose, appropriate solvent, the reaction temperatures, and surface area of the polymer to be grafted.

Grafting of styrene acrylic acid polymer onto fluorinated ethylene propylene copolymer (FEP) was carried out by pre-irradiation of FEP with gamma rays. Effect of reaction conditions on the degree of

grafting such as total radiation dose, monomer concentration, temperature and time of grafting has been studied [Anbarasan et al., 2003].

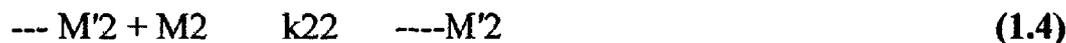
Introducing a suitable organic vapor into the plasma of inorganic gases performs plasma-induced grafting. Polymerization of the vapor takes place and a polymeric film is deposited. The plasma-induced grafting are used to produce excellent mechanical, chemical and optical properties that can be obtained for ultra thin highly-crosslinked polymeric coatings. A drawback, from an academic point of view, is centered on the large number of reactive species formed in the plasma, makes chemical characterization of the system extremely difficult.

1.2. COPOLYMERIZATION AND COPOLYMER COMPOSITION EQUATIONS

The simultaneous polymerization of two or more monomers is called copolymerisation. A copolymer is thus defined as a polymer having at least two different monomers incorporated into one polymeric chain. It can be prepared either by condensation or addition copolymerisation. Of the latter, free radical copolymerisation is the most widely used and the work presented in this thesis is mainly concerned with this type.

The copolymer composition and the mechanism of copolymerization have been first elucidated by Dostal [Dostal, 1936] through practical and theoretical studies. It has been assumed that the rate of addition of monomers to a growing free radical depends only on the nature of the end group on the radical chain. The four possible propagation steps in copolymerization are the following:





Where M1 and M2 are the monomer molecules and M' and M'2 are the growing radicals. While, K11, k12, k21 and k22 are the reaction rate constants.

Wall [Wall, 1941] derived an equation relating the distribution of chemical composition to degree of conversion. Mayo and Lewis [Mayo and Lewis, 1944] and Alfrey and Goldfinger [Alfrey and Goldfinger, 1944] independently derived a differential equation relating the reactivity ratios to the change in monomer mixture composition during the course of a binary polymerization. According to "steady state assumption", they developed the so-called "copolymer composition equation".

$$d[\text{M1}] / d[\text{M2}] = \{ [\text{M1}] (r_1 [\text{M1}] + [\text{M2}]) \} / \{ [\text{M2}] (r_2 [\text{M2}] + [\text{M1}]) \} \quad (1.5)$$

Where $r_1 = k_{11} / k_{12}$ and $r_2 = k_{22} / k_{21}$ and $d[\text{M1}] / d[\text{M2}]$ is the molar ratio of the monomer units in the copolymer. While r_1 and r_2 are the monomer reactivity ratios of the M1 and M2, k_{11} / k_{12} are rate constants for a given radical addition to its own monomer to that for its adding to the other monomer. Thus, when $r_1 > 1$ means that the radical M' prefers addition to M1 rather to M2 and $r_2 > 1$ means that the radical M'2 prefers addition to M2 rather to M1. Equation (1.5) can be written in terms of mole fractions instead of concentrations as follows:

$$F_1 = F_2 - 1 = (r_1 f_1^2 + f_1 f_2) / (r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2) \quad (1.6)$$

where F_1 and F_2 are the mole fractions of monomers M1 and M2 in the feed, and f_1 and f_2 are the mole fractions of monomer units M1 and M2 in the copolymer.

1.2.1. Chemical Heterogeneity of Copolymers

For all copolymerization except azeotropic one, the comonomer feed and the copolymer compositions are different. The comonomer feed changes in compositions as one of the monomers preferentially enters the copolymer. Thus, there is a drift in the “residual monomer” composition towards the less reactive monomer as the degree of conversion increases. This manner, in which copolymer compositions vary as the reaction proceeds, is of great importance to understand the copolymer compatibility. Simha and Branson [Simha and Branson, 1944] have investigated the additional features, which affect the heterogeneity of the copolymer mixture with regard to composition, the average molecular weight and the average composition of the monomer residue. Skeist [Skeist, 1946] has developed a simple and convenient approach for determining copolymer composition and its distribution as a function of a conversion.

$$\ln(1-C) = \int_{f_{1i}}^{f_{1j}} df_1 / (F_1 - f_1) \quad (1.7)$$

where C is the fractional conversion; f_{1i} and f_{1j} are mole fractions of monomer M1 in the feed at two different stages of conversion i and j , F_1 is the instantaneous mole fraction of monomer unit M1 in the copolymer, at any given finite stage of conversion.

In 1965, an analytical solution to the Skeist equation was developed by Meyer and Lowry [Meyer and Lowry, 1965]. They have derived the following equation:

$$C = 1 - (f_{1j}/f_{1i})^\alpha \left\{ \frac{(1-f_{1j})}{(1-f_{1i})} \right\}^\beta \left\{ \frac{(f_{1i}-\delta)}{(f_{1j}-\delta)} \right\}^\gamma \quad (1.8)$$

where, $\alpha = r_2/(1-r_2)$; $\beta = r_1/(1-r_1)$; $\gamma = (1-r_1r_2)/(1-r_2)$

and $\delta = (1 - r_2)/(2 - r_1 - r_2)$

The solution can be conveniently applied to yield the change in composition of a binary monomer mixture, which occurs during the course of copolymerization. Equation (1.8) was later confirmed by Kruse [Kruse,1967].

1.2.2. Reactivity ratios of monomers

Reactivity ratios are among the most important parameters for composition equation of copolymers, which can offer information such as relative reactivity of monomer pairs and estimation of the copolymer composition. Many reports have been published on the correlation between the structure and the reactivity of vinyl monomer in their radical polymerization and copolymerizations [Otsu, 1967, Yokota et al., 1968, Cameron and Kerr, 1967, Chikanishi and Tsuruta, 1965 and Bevington and Maipass, 1965]. The calculation of the monomer reactivity ratios requires the mathematical treatment of experimental data on the composition of copolymers and monomer in feed mixtures. The copolymer composition was evaluated by several techniques; elemental analysis [Neoh et al., 1989 and Sailaja and Kumar, 1995], ^{13}C NMR [Gorda et al., 1990, Cho et al., 1994, Thomas et al., 2003, and Cengiz and Ibrahim, 2003], ^1H NMR [Kim et al., 2003, Wamsley et al., 2004, Cengiz and Ibrahim, 2004 and Nanjundan et al., 2005] and FTIR [Liu et al., 1996, Mohammed et al., 1998 and Senthilkumar et al., 2003]. Copolymerisation is the most successful and powerful method that affecting systematic changes on polymer properties [Tirrell et al., 1985]. The incorporation of two different

monomers, having diverse physical and/or chemical properties, in the same polymer molecule in varying proportion leads to the formation of new materials with great scientific and commercial importance [Ress and Vaughan, 1965]. Copolymerisation modulates both the intramolecular and intermolecular forces exercised between like and unlike polymer segments and consequently properties such as glass transition temperature, melting point, solubility, crystallinity, permeability, dyeability, adhesion, elasticity and chemical reactivity. The utility of copolymerization is exemplified by the fundamental investigations of structure property relations [Liaw et al., 2000 and Fernandez et al., 2000, 2001] and on the other hand, by the wide range of commercial applications [Choudhary and Varma, 1983 and Schoonbrood et al., 1995]. However, deviation is observed due to reactivity differences on account of various structural factors like, for example proximities of the functional groups and whether the functional groups is primary or secondary, etc,. It is natural that in such situations, the more reactive monomer would enter into the polymer first [Bilmeyer, 1984 and Sundarrajan et al., 2003].

1.2.3 Characteristics of Reactivity Ratios

There is a number of different reactivity ratio values that are of a special interest:

a) $r_1 r_2 = 1$

A copolymer that is described by the above reactivity ratios is termed as ideal or random copolymer in which the monomer units are randomly distributed throughout the chain.

b) $r_1 = r_2 = 0$

This type of copolymerisation is referred as alternating copolymer in

which the mole fraction of either the monomer or copolymer is 0.5, i.e.,

$$d[M1]/d[M2] = r_1[M1]/[M2]$$

c) $r_1 > 1$ and $r_2 > 1$

In this case there is a tendency to form a block copolymer. In the limit with $r_1 > 1$ and $r_2 > 1$, i.e., with the reactive species preferring to add to their own monomers. Exclusively, each monomer will independently homopolymerize, a case which rarely happens.

d)-Azeotropic copolymerization

This describes the situation in which the copolymer and feed compositions are identical. In this case, copolymer equation with $d[M1]/d[M2] = [M1]/[M2]$ gives the critical composition $(f1)_c$ as follows:

$$(f1)_c = (1-r_2) / (2-r_1-r_2) \quad (1.9)$$

All the above characteristics for r_1 and r_2 are equally applicable to radical, cationic and anionic polymerization mechanisms. However, the value of the reactivity ratios for a given pair of commoners markedly depends on the polymerization mechanism [Cowie, 1973]. It was also evidenced from a number of recently published papers [Ito and Otsu, 1969 and Saini et al., 1971] in contrast with earlier reports [Lewis et al., 1948 and Price and Walsh, 1951], the medium affects the reactivity ratios in some free radical copolymerizations. For example, the copolymerization of acrylic acid with methyl acrylate or N-vinyl pyrrolidone is markedly influenced by the nature of the solvent [Ryabov et al., 1970 and Chapiro, 1974]. The same phenomenon was observed in the copolymerization of acrylamide with styrene or with methyl methacrylate [Jacob et al., 1972] for which the addition of water to the reaction medium increases the overall rate and degree of

polymerization. The influence of the solvent is particularly strong for these copolymerization where at least one of commoners might be associated by hydrogen bonding [Perec, 1973, Senogles and Thomas, 1975 and Makrikosta et al., 2005].

The effect of temperature on reactivity ratios is fairly small and has been studied for a number of systems [Rudin and Yule, 1971, Barson and Turner, 1974, Bajaj and Buba, 1976, and Buba et al., 1982]. However, Odriscoll [Odriscoll, 1969] suggests the effect of temperature is experimentally significant only for reactivity ratios that are very large (>1.0) or small (<1.0).

1.3. CROSSLINKING POLYMERIZATION

Crosslinking is the general term meaning the process of forming covalent bonds or relatively short sequences of chemical bonds joining two polymer chains together by a branch. Crosslinking will also occur in other polymerizations involving reaction between vinyl monomers having functionalities greater than two. Crosslinking is distinguished by the occurrence of gelation at some point in the polymerization, this point termed as gel point. The gel point is alternatively taken as the point at which the system loses fluidity as measured by the failure of an air bubble to rise in it. The gel is insoluble in all solvents at elevated temperatures under conditions where polymer degradation does not occur. The gel corresponding to the formation of an infinite network in which polymer molecules have been crosslinked to each other to form a macroscopic molecule. The gel, in fact is considered as one molecule. The uncrosslinked portion of the polymer remains soluble in solvents. As the polymerization and gelation proceed beyond the gel point, the amount of gel increases at the expense of the sol as more and more

polymer chains in the sol are crosslinked to the gel. There is a dramatic physical change that occurs during the process of gelation. The reaction mixture is transformed into a polymer of infinite viscosity.

Crosslinking with chemical covalent bonds linking the crystalline and amorphous domains is responsible to three-dimensional network structure that characterize these materials. This drastically improves a large number of low-, room- and especially high temperature properties such as heat deformation, abrasion, viscous deformation, chemical and stress- cracking resistance impact and tensile strength and also adds new useful properties such as shape memory. Properties are attributed to the presence of physical or chemical crosslinks within polymer chains.

The early history of crosslinking polyolefins was presented by Dole [Dole, 1981]. Sultan and Palmlof [Sultan and Palmlof, 1994] reviewed the advances in crosslinking technology. Chodok has recently reviewed [Chodok, 1995] the properties of crosslinked polyolefin-based materials. The crosslinking reaction is an extremely important one from the commercial standpoint. Crosslinked plastics are increasingly used as engineering materials because of their excellent stability towards elevated temperatures and physical stress. They are dimensionally stable under a wide variety of conditions due to their rigid network structure. Such polymers will not flow when heated and termed as thermosetting polymers or simply thermosets. The commercial importance of the thermosets is seen from the fact that of the over 30 billion pounds of plastics produced annually in the United States, almost 5 billion pounds were crosslinked plastics. Usually, elastomers need to be cured for better mechanical properties. Depending on the elastomers type, different curing modes can be used [van Drumpt, 1988, Akiba and Hashim, 1997 and Ogunniyi, 1999]. Sulfur based

crosslinking systems are the most popular ones. It leads to C-S bonds and various polysulfidic bonds. However sulfur curing can only be used with partially unsaturated polymers. Peroxide crosslinking is the second most popular curing mode. More stable C-C bonds are formed than with sulfur based systems. Furthermore, it can be used for both saturated and unsaturated polymers. In both peroxide and sulfur curing methods, no heating of the material is necessary. Electron beam and gamma irradiation are also employed to cure elastomers.

Radiation crosslinking has many advantages [Bly, 1983] such as being fast, energy saving, and without pollution. But the necessary curing dose for rubbers was very high and deterioration of properties was caused by main-chain degradation. For these reasons radiation vulcanization has not yet been widely adopted in the rubber industry except in precuring of some types of tires. Yunshu et al. [Yunshu et al, 1997] discuss the electron beam irradiation curing of cis-1,4 polyisoprene rubber containing polyfunctional monomers to lower the curing dose and to optimize the properties of cured rubber.

The efficiency of crosslinking mode depends not only on the chemical composition of the polymer, but also on the presence of additives, such as antioxidants, which are generally incorporated to reduce excessive degradation while curing at high temperature and during subsequent aging [Vallat et al., 2004]. The mechanical properties of the networks are drastically dependant on the curing mode. One reason for that is the nature of the chemical bonds formed between the chains and the functionality of the crosslinkers. The other is attributed to the differences of heterogeneity i.e. distribution of crosslinks and defects in the structure [Gehman, 1969 and Mark, 1988]. Grobler et al. [Grobler et al., 1994] found that the heterogeneity of polyisoprene

network decreased in the following order: conventional sulfur > efficient sulfur > peroxide > γ -irradiation.

1.4. SWELLING BEHAVIORS OF CROSSLINKED POLYMERS

When a crosslinked polymer is placed in a liquid, which is a solvent for the uncrosslinked polymer, it swells to an extent, which is dependent upon the interaction between the polymer and the solvent, and it is depend on:

1. A swelling potential
2. The elastic potential (which is determined by the crosslink density).

Equilibrium is reached when these two potentials, which act in opposite directions, are equal (the increase of elastic energy of the chains forming the network balances the decrease in the free energy consequent to mixing of polymer segments with solvent molecules). This leads to the well-known Flory equation [Flory and Rehner, 1943]:

$$\frac{1}{M_c} = - \frac{2}{M_0} \frac{(\bar{v} / V_1) [\ln (1 - \Phi_p) + \Phi_p + \chi \Phi_p^2]}{[\Phi_p^{1/3} - \frac{1}{2} \Phi_p]} \quad (1.10)$$

where

M_c is the number-average molecular weight between two successive crosslinks,

M_0 is the number-average molecular weight of a network primary chain (a primary chain is in the linear molecule before crosslinking),

\bar{v} is the specific volume of polymer.

V_1 is the molar volume of the solvent,

Φ_p is the final swollen equilibrium polymer volume fraction,

χ is the Flory polymer- solvent interaction parameter

The Flory interaction parameter χ is a measure of the interaction between any given solvent and a given polymer. It is a free-energy parameter and contains both enthalpy and entropy terms. It is also a temperature-dependant quantity and is also concentration dependant over a wide range of polymer concentrations. The parameter χ must be measured for every polymer- solvent pair. It can be calculated by different methods. Among theses methods, equilibrium swelling [Mullins, 1959, Manjarai et al., 1963 and Biskup and Cantow, 1973], osmotic pressure [Okazawa and Kaneko, 1971 and Sugamiya et al., 1974], vapor pressure [Allen et al., 1964 and Okamoto and Overberger, 1974], sedimentation-equilibrium ultracentrifugation [Chu and Munk, 1977], viscosity [Cowie, 1969 and Bristow and Watson, 1987], optical studies [Ammon et al., 1965 and Desphande et al., 1974, 1978] and inverse gas chromatography [Reese and Tucker, 1965, Tait and Abushihada, 1977 and Galin and Rupprecht, 1978].

The value of the swelling equilibrium is related to the nature of the polymer solvent system and provides information concerning the nature of the crosslinking and reinforcement. In order to determine the final swollen equilibrium (polymer volume fraction%), it is necessary to place a sample of known density in the chosen solvent until weight measurements indicate the saturation of the polymer by liquid. Assuming that no extractables are present, and that all the absorbed solvent causes swelling.

Polymer volume fraction (Φ_p) is given by:

$$\Phi_p = \frac{(W_1 - W_0) \rho_p}{W_0 \rho_s} \times 100 \quad (1.11)$$

Where

W_0 is the sample weight before swelling ,

W_1 is the sample weight after swelling,

ρ_p is the density of polymer sample,

ρ_s is the density of the solvent.

In order to obtain the curve of swelling rate, it is necessary to make a series of gravimetric measurements and determine the percentage volume swelling or weight increase as a function of time. Accurate determination of the swelling-time relationship requires a large number of experimental measurements, especially in the early stages of swelling. The gravimetric method usually requires an interruption of the swelling process, and this involves experimental difficulties. The accuracy of data obtained by this method is low. Sol-gel analysis is carried out by soaking polymer sample in a solvent at constant temperature for a given time (from minutes up to hundreds of hours). After the soaking, the gel is obtained by drying the residual sample in vacuum at room temperature. The sol is determined as the difference in weight before and after the swelling experiments.

The sol fraction (in percent) is expressed by:

$$\text{Sol fraction} = \frac{\text{Sol}}{\text{Sol} + \text{Gel}} \times 100 \quad (1.12)$$

Goiti et al. [Goiti et al., 2004] study some properties of networks produced by the Diels-Alder reaction between poly (styrene-co furfuryl methacrylate) and poly (styrene-co furfuryl methacrylate) networks. The resultant crosslinked polymers were swollen to equilibrium in toluene at 25 °C and swelling properties measured by gravimetric and

dimensional measurements. The swelling behavior of these organogels is dependant on the composition of the copolymer and the concentration of bismaleimide.

1.5. APPLICATION OF CROSSLINKED POLYMERS

Crosslinked polymers are important in chemical research and practice owing to their wide range of other applications. Chemical resistance, water treatment, chromatographic techniques, biomedical and biochemical applications, solid phase organic synthesis, enzyme immobilization, soil conditioning, solvent, ion separation, organic coating and oil sorber are using crosslinked polymers as the principal substrate. Crosslinked polymer networks are excellent materials for multiple applications [Malik et al., 2002].

Crosslinked reactive polymers with novel structures have been prepared from the corresponding monomers or by newly developed chemical modification reaction. These include the preparation of polymers with two or three carbon spacer groups between backbone and crosslinkers. Novel applications of these polymers in asymmetric synthesis pregnable polymeric protecting groups, supernucleophilic catalysts, polymeric separation media for HPLC, as well as aids in the determination reaction mechanisms have been investigated [Deratani et al., 1987]. Microenvironmental effects within the polymer beads are shown to be important when considering the use of an insoluble reactive polymer.

Crosslinked water born reactive polymer system has been developed to provide enhanced specific adhesion to plastic film. The system combines low activation temperatures with high solvent and heat resistance. Crosslinked efficiency is evaluated in terms of solvent

resistance, softening point and tensile strength and elongation [Lombardi et al, 1987].

Sambasivam et al. [Sambasivam., 1996] developed new formulations based on proprietary epoxies to apply in microelectronic packaging applications. The features of these formulations are short cure cycle, long term stability at 25 °C, very low cure volatile, low moisture absorption, low coefficient of thermal expansion (CTE), excellent adhesion to various substrates.

Crosslinking modification of two woven (35/65 polyester / cotton and 100% cotton) fabrics and (90/10 cotton /Lycra) can improve esthetical and functional properties. The two woven fibers were treated with two different DMDHEU resins (one unalkylated and the other is a blend of alkylated/unalkylated DMDHEU of low formaldehyde content) and poly ethylene glycol 1,000 solutions. Curing under selective mild conditions produced modified fabrics (containing crosslinked polyols). All treated fabrics have good thermal storage and release properties, enhanced absorbency, flex life, antistatic behavior, and oil soil release than untreated fabrics when the blended resin was used in the crosslinking formulation. The treated cotton/polyester fabrics had the additional benefit of high strength retention, toughness, and elongation. Photomicrographs show that, the crosslinked polymer protects both cotton and synthetic fibers from flexural failure [Vigo et al., 1991].

Fujita et al. [Fujita and Soane 1988] prepared crosslinked membrane with controlled pore size distribution. Membrane reactors are recognized as possessing some unique capabilities [Tundo,1991].

The limitation is presently that the polymeric materials generally tolerate only relatively mild reaction temperatures. Hollow fibers are frequently used in membrane reactors when minimal reactor volume is

desired. The main drawback is that they are extremely sensitive to fouling and clogging caused by particles in the feed stream [Cabasso, 1987].

1.6. CROSSLINKED POLYMERS AS OIL SORBERS

Transportation of petroleum from oil fields to consumers may require 10 to 15 transfers. Tankers, pipelines, trains transport petroleum, and tank trucks stored temporarily in a cultivator of facilities. Accidents may occur during each of these transportation and storage steps. Offshore and shoreline waters can be polluted by runoff from offshore oil exploration and production and spills from ship transport of oil. Water can be polluted by runoff from oil fields and refinery areas and, in some cases process effluent from petroleum and petrochemical plants [Johnson et al. 1973]. Under favorable conditions, oil in a clean water body may continue to spread over the water surface and form a monomolecular layer. The oil film on the surface of water impairs the exchange of energy, heat, moisture, and gases between the water reservoir and the atmosphere [Pushkarev et al., 1983]. Crude oil consists of different hydrocarbons that range from a light gas (methane) to heavy solids. The most important and prevalent elements in petroleum are hydrogen and carbon. Which comprise up to 98% of some crude oils and 100% of many refinery products. Other constituents of petroleum are hydrocarbon derivatives containing oxygen, sulfur, nitrogen, and inorganic metal such as vanadium, nickel and mineral salts. When oil is spilled on water or on land, the physical and chemical properties of oil change progressively. This process is referred to as weathering. The volatile components evaporate quickly. Some of the medium-sized polycyclic aromatic hydrocarbons are

slightly soluble. Some of the products, which are degraded by sun and microorganisms, become highly soluble. Weathering rates are not constant but are usually highest in the first few hours. Major processes of weathering of oil spilled on water include evaporation, dissolution, oxidation, emulsification, and microbial degradation. If the residue oil is adsorbed to other material of high specific gravity such as silt or clay suspended in the water, the specific gravity of the residual oil may exceed 1.0 and sink. The residue continues to spread from an area of denser saline water to less denser freshwater and may then sink. In the case of crude oil evaporation, it plays an extremely important role in its volumetric loss after a spill. It was reported that 25% of the total volume of spilled crude may be evaporated within one day. Gasoline loses about 50% of its original volume within 7 to 8 min at 20 [Galt et al. 1991].

The spilled oil contributes an undesirable taste and odour to drinking water and causes severe environmental damage [Blumer, 1969]. Contaminated water cannot be used for municipal water supply, for industry, nor for irrigation [Blumer, 1969. Morita et al., 1987]. Public concern for sustaining a healthy environment has resulted in stronger environmental regulations regarding water quality and use of hazardous chemicals and substances. This concern has resulted in the need for improved techniques and methods for the use and reuse of hazardous chemicals where contacts with the environment occur. Improved techniques for control and removal of oil slicks is an area of research under active development. Natural cleaning oil spill, allowing oil to be degraded and removed by natural means, takes long time to be fully effective. Oil dispersant or an oil-sinking agent can enhance this method. Oil gelling act as a surface-tension modifier, coagulating the

spilt oil, and enhance the potential for mechanical removal techniques, for example recovery of solidified oil with a net. In both cases the disadvantage is that the spilt oil cannot be reused. Therefore, recent trials of spilt oil treatment have been focused on oil absorbents.

1.6.1 Mechanical Recovery of oil spill

Mechanical recovery is the transfer of oil from the spilled area to some transportable form as temporary stored by the help of oil-booms or skimmers. Oil booms are floating barriers, used to prevent spreading of oil on water, and sometimes to thicken the layer of oil by reducing the area into which it has spread [Milgram, 1977, Bellier, 1979 and Greene et al., 1979]. Oil skimmer is a mechanical pick up device, which physically removes oil from the seawater surface. It contains three basic components: the pickup head, the pump system, and the oil water separator.

Various types of skimmers are available, most of which rely on the ability to physically skim the oil off the water surface, to adhere the oil to a solid surface, or to absorb it into a porous material.

a-Adhesive surface devices:

This group of oil recovery units relies on the adhesion of oil to a solid surface. This type employing a rotating drum or cylinder covered with oil absorbent materials that have ability to absorb the oil from an oil and water mixture. Oil adheres to the drum can scraped off the surface by a knife blade or by rollers and transferred to a storage tank.

b-Weir devices

The weir type of skimmer depends on gravity to drain the oil off the

surface of sea-water. The weir devices employ adjustable weirs over which the oil film, riding on the surface of the water, may flow. The recovered liquid usually collected may be pumped away. Once oil collected, it may be pumped into a gravity separation tank as a secondary operation. The oil separates and floats to the surface. The sea-water is discharged through valves in vessels bottom weir type skimmers generally work best with heavier, thicker oils [Walkup, 1971, Sittig, 1974 and Schwartz, 1979].

C- Centrifugal or vortex devices

Several oil recovery devices based on the use of a centrifugal force to separate oil from water. One of the interest variants of centrifugal devices is the Bertin skimmer [Pinchon, 1975].

d- The floating suction devices

The floating suction skimmer can easily be put into action by placing it on the sea-water and adjusting it to float at the oil/sea water interface. Oil accumulates at surface and sea-water is displaced through a baffled opening in the bottom. When an oil layer of sufficient depth has accumulated it is pumped away by conventional means to storage [Taylor, 1972].

1.6.2. Using of Chemicals as Oil Spill Dispersants

The use of dispersants has been, and still is, the most widely employed and immediately effective method of combating oil pollution both on open sea and on beaches. When oil, which is floating on the surface of the sea, is treated with a suitable surface-active agent the oil is broken up into particles of different sizes. Basically, all dispersants are

chemicals consisting of a polar (water –soluble group) and a non polar (oil - soluble group). Because of its amphipathic nature, the surfactant molecule locates and orients itself at the oil- water interface of an oil slick, its polar end in the water and its non-polar end in the oil. Because of this orientation it is able to reduce the interfacial tension and thereby aids in the generation of finely dispersed oil droplets. Once dispersed, the surfactant will prevent them from coalescing again [Beynon,1971].

In most cases, simply applying the surfactant to the slick is not enough [Churchill et al., 1993]. The water must also be mechanically agitated to enhance breakup of the slick into droplets. This is often done by use of a surface agitator. In recent years, however, self-mixing dispersants have been developed which form droplets on their own and do not require mixing by ships.

Dispersants have disadvantages, the principal one being that many of them are much more toxic than the oil which they are acting on. In addition, dispersed oil may be even more toxic than no dispersed oil because more dissolved hydrocarbons are present in the water column when the oil is dispersed. A great deal of research to produce low toxic oil dispersant was subsequently (after 1967) carried out and new, less toxic and more effective dispersants are developed. They consist essentially of low aromatic content. At present they must be used with extreme care and only after detailed study.

The difficulty with the use of dispersants is how to apply them rapidly and effectively to the very large areas. This can be done by use of ships or aircraft, but the application time is long, the ability to evenly distribute the dispersant is questionable, and the cost is enormous. Application of dispersants in shallow water remains an issue of debate within the spill response community. An experimental oil spill to

evaluate potential environmental impacts and benefits of applying dispersants to spills in shallow water has therefore been under consideration.

Coupled three-dimensional oil spill and hydrodynamic models were used to assist in the design of such an experiment to apply oil spill dispersant. The purpose of the modeling work was to map hydrocarbon concentration contours in the water column and on the seafloor as a function of time following dispersant application. These results could assist in determining the potential environmental impact of the experiment, as well as guiding the water column sampling activities during the experiment itself. Eight potential experimental oil spill scenarios included application of chemical dispersants to the slick shortly after release [Reed et al., 2004].

1.6.3 Using of Oil Sorbers to Control Oil Spill

The most urgent technique of elimination of emergency spread of oil and petroleum products is collecting of thin layers from the water surface with the help of sorbents. Sorbents are materials that soak up liquids. They can be used to recover oil through the mechanisms of absorption, adsorption, or both. Absorbents allow oil to penetrate into pore spaces in the materials they are made of while adsorbents attract oil to their surfaces but don't allow it to penetrate into the material. To be useful in combating oil spills, sorbents need to be oleophilic or hydrophobic although they may be used as sole cleanup method in small spills. Sorbents are most often used to remove final traces of oil or in areas that cannot be reached by skimmers. Once sorbents have been used to recover oil, they must be removed from the water and properly disposed or cleaned for re-used. Any oil that is removed from

sorbent materials must also be properly disposed or recycled.

Retention of oil over time, recovery of oil from sorbents, amount of oil sorbed per unit weight of sorbent, and reusability and biodegradability of sorbent are important properties of sorbent. Sorbent materials applied to oil slick changes from liquid oil to a semi colloid. The oil can then be removed in an efficient and easy manner.

The characteristics of both sorbents and oil types must be considered when choosing sorbents for cleaning up spills:

- Rate of absorption: the rate of absorption varies with the thickness of the oil. Light oils are soaked up more quickly than heavy ones.
- Oil retention: the weight of recovered oil can cause a sorbent structure to sag and deform, and when it is lifted out of the water, it can release oil that is trapped in its pores.
- Ease of application: sorbents may be applied to spills manually or mechanically, using blowers or fans. Many natural organic sorbents that exist as loose materials, such as clay and vermiculite are dusty, difficult to apply in windy conditions, and potentially hazardous if inhaled.
- Good absorption selectivity of oil over water.
- Convenient shipping and storage
- Lower density compared to water to float with or without oil absorbed.

Sorbents can be divided into three basic categories: inorganic materials, natural organic materials and synthetic sorbents.

- Inorganic materials: such as glass wool, vermiculite, and pumice. They absorb oil of low viscosity very well but with heavy oils, the absorbent properties are reduced. However, these materials do not have adequate buoyancy and their oil sorption capacity is generally

low.

- Natural organic materials: such as straw, sawdust and cotton. These absorbents usually work best with crude oils or heavy fuel oils. Cotton have been shown to be effective for oil removal.
- Synthetic sorbent products can be classified in three classes: synthetic polymers and naturally treated materials. The most often used polymers are polypropylene, polyethylene, polypropylene booms and polyurethane foam, which have highly oleophilic and hydrophobic properties and are the most widely used sorbents in the remediation of oil spills [Zahid et al., 1972 and Schrader, 1991]. However, these materials degrade very slowly relative to mineral or vegetable products. In the case of floating polypropylene booms, it is difficult to recover all the absorbent material, the residual nonbiodegradable material contaminates the environment similar to the parent material [Schrader 1991].

The limitations of the above-mentioned method have led to the study of alternative methods for oil removal using biodegradable materials such as lignocellulosic fibers [Bertrand, 1993 and Anthony, 1994]. Also, agricultural products and residues are in expensive and readily available.

Polypropylene fiber (Sun et al., 2004) or non-woven fabrics [Radetic et al., 2003, Wei et al., 2003], melt-blown polyesters and polyurethane foam sheets have been used. But these have a serious disadvantage of bulkiness that is, inconvenient shipping and storage. For polyurethane foam these disadvantages were resolved by using an oil-recovery machine designed for an on-site foaming method [Shimizu et al., 1997]. In other words, two of polyurethane liquid components are transported to the site of the oil spill, and mixing the two components

produces polyurthane foams. However, this method also has difficulty in moving the on-site foaming machine to the site of oil spill, and its shipping and storage are very inconvenient [Jang and Kim, 2000].

In spite of the development of polymer for oil absorption, there have been few reports on the synthesis of such polymers. Synthesis of ethylene-propylene-diene polymer (EPDM) containing an aromatic moiety was reported [Davis et al., 1996]. Due to the non-polar hydrocarbon nature of the polymer, EPDM has excellent water resistance but poor oil resistance. As known, ethylene-propylene- diene (EPDM) is an artificial rubber, which has elasticity and outstanding resistance to degradation by heat, light, oxygen, ozone, and water but poor resistance to oil.

It was known that an effective mean to obtain oil absorbent is to synthesize the crosslinked polymer, which does not dissolve in oil [Lu et al., 1995]. The butyl radical of 4-tert-butylstyrene (tBS) may have some stereo effect to produce the crosslinked polymer with a large cavity in which oil will fill. From this point of molecular design, Zhou and Cho [Zhou and Cho, 2002] prepared 4-tert-butylstyrene- EPDM-divinylbenzene (PBED) polymers by graft crosslinking polymerization of (tBS) and divinylbenzene (DVB) onto EPDM in toluene using benzoyl peroxide (BPO) as an initiator to obtain high oil absorbency sorber. DVB is a useful crosslinking agent. The sol PBED can be reused for oil-absorption through crosslinking of ultraviolet (UV) irradiation. The effects of synthesis conditions such as solvent amount, molar ratio of DVB to tBS, EPDM content, initiator concentration, reaction temperature and reaction time were studied. The produced gels show poor gel strength after swelling in oil at high absorbency. Composite technique is one of the available methods for reinforcing

them. Mechanical properties and morphologies of some composites were obtained with a tensile tester and scanning electron microscopy, respectively [Zhou and Cho, 2001].

On the other hand, it has been known that vulcanized styrene butadiene rubber (SBR) has excellent tensile strength, tear resistance, and abrasion resistance. The graft terpolymer, tBS-SBR-DVB (PBSD) was prepared by the graft crosslinking polymerization of (tBS) and (DVB) onto unvulcanized SBR in the solution process using (BPO) as an initiator to obtain high oil absorbency sorber [Zhou and Cho 2001]. The effects of synthesis conditions such as solvent amount, molar ratio of DVB to tBS, SBR content, initiator concentration, reaction temperature and reaction time on conversion, grafting efficiency, and gel fraction were examined. The swelling rates, light resistance, and tensile strength of PBSD were investigated. It was found that the tensile strength is considerably better than that of 4-tert-butylstyrene-EPDM-divinylbenzene (PBED).

Other kinds of polymers have been widely used to absorb oil spilled on water [Bertrand, 1993, Anthony, 1994]. Among them, alkyl acrylate and aromatic polymers, which have hydrophobicity and gel-type structure consisting of an elastic network and interstitial space, have been attracting much interest in the field of environment [Zhou and Cho, 2000, Martel and Morcellet, 1994, Atta, 2002, Monji and Hoffman, 1987, Hoffman et al., 1986, Champ et al., 2001, Dong and Hoffman, 1986, Freitas and Cussler, 1987, Okano, 1993, Sayil and Okay, 2001, Saito et al., 1993]. This hydrophobic network polymers were used as absorbents of oil or some organic solvents spilled on water.

Jang and Kim [Jang and Kim, 2000] studied the copolymerization of

styrene monomer with various long chain alkyl acrylate monomers like, 2-ethylhexyl acrylate (EHA), lauryl acrylate (LA), lauryl methacrylate (LMA) and stearyl acrylate (SA). These acrylates with long chain alkyl groups are generally known as hydrophobic materials. Therefore, a highly oil absorbing property can be obtained by controlling the composition and the crosslinking density of the copolymer. EHA, LA, and SA were chosen to evaluate the effect of hydrophobic chain length of alkyl groups. LMA, on the other hand, was chosen to find the difference between acrylate and methacrylate. Various crosslinked styrene /alkylacrylate copolymers were synthesized. They were prepared by adding (DVB) as a crosslinking agent.

Jang and Kim [Jang and Kim, 2000] conducted a detailed study on the swelling properties of the crosslinked copolymers. The influence of synthetic variables (monomer feed ratio, amount of crosslinking agent, amount of initiator, polymerization temperature, and type of acrylate monomer) of the crosslinked copolymers on the oil absorbency capacity were examined. The effect of moisture was also investigated through a series of oil absorption tests. Sponglike materials using crosslinked styrene-acrylate copolymers was prepared and their oil absorption capacity was evaluated.

The copolymerization of acrylate monomers was carried out by electron-beam irradiation at different dose rates [**Makhaeva et al., 1996, Ichijo et al., 1994**]. Furthermore, the crosslinking of these polymers by a high dose electron-beam irradiation in the presence of crosslinkers has been studied.

[**Atta and Arndt [Atta and Arndt, 2004]** synthesized new oil-absorptive polymers containing alkyl acrylate via different types of chemical crosslinkers and irradiation techniques. They conducted a

detailed study on the swelling properties of the crosslinked 1-octene-isodecyl acrylate copolymers. The crosslinking polymerizations were carried out in presence of different concentrations of ethylene glycol diacrylate (EGDA) and ethylene glycol dimethacrylate (EGDMA) crosslinkers via catalytic initiation and by electron beam irradiation at dose rate 80 kGy. The effect of various crosslinking conditions (amount and types of crosslinking agent, technique of crosslinking and monomer feed ratio) were studied through oil absorption test using petroleum crude oil. The oil absorbency was influenced mainly by the degree of crosslinking and the hydrophobicity of copolymer units. The final equilibrium oil content, volume fraction of polymer and swelling capacity were determined at 294K. The effective crosslinking density ν_e , the average molecular weight between the crosslinks M_c and the polymer-toluene interaction parameter were determined from stress-strain measurements. The efficiencies of EGDA and EGDMA crosslinking agents towards copolymers were determined.