ÇAPRAZ BAĞLI POLİ DİMETİLSİLOKSAN (PDMS) MEMRANLARIN SENTEZİ VE KARAKTERİZASYONU

SYNTHESIS AND CHARACTERIZATION OF CROSSLINKED POLY DIMETHYL SILOXANE (PDMS) MEMBRANES

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ABSTRACT

In this study, the preparation of crosslinked membrane forms from polydimethylsiloxane (PDMS) samples with different end groups and various molecular weights were aimed. PDMS samples with different end groups like hydroxy and diglycidyl ether were reacted with poly(ethylvinyl ether-co-maleic anhydride) copolymer and synthesized poly(maleic anhydride-1,hexene-acrylic acid) terpolmer to form membranes. Terpolymer was synthesized by complex radical terpolymerization of maleic anhydride (electron acceptor), 1-hexene (electron donor) and acrylic acid (electron acceptor) monomers with benzoyl peroxide as the initiator in 1,4 dioxane at 70-75 ^{0}C reaction conditions.

The spectroscopic characterization of each prepared membranes were achieved by different techniques like FTIR, NMR (^{13}C, ^{1}H), the thermal characterization was carried out by DSC, TGA-DTA and DMA studies. Spectral analysis is capable of highlighting and provides very basic information about chemical structure, bond character and secondary interactions. Besides as a consequence of secondary interactions one may easily reach valuable knowledge stressing the polymer-solvent role.

Another progress of our study involved the determination of swelling behavior of the prepared membranes and related parameters were calculated from the graphs.

Finally, each prepared membranes were followed with regard to membrane-solvent diffusion behavior via contact angle measurements. In addition to that, for the polymorphic investigation membranes were analyzed by X-Ray.

Keywords: PDMS, crosslinking, characterization, FTIR, NMR, DSC, TGA-DTA, DMA, swelling, XRD, water contact angle.

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ÖZ

Bu çalışma da farklı uç gruplara sahip, değişik molekül ağırlığındaki poli dimetil siloksan (PDMS) örnekleri ile çapraz bağlı membran formlarının hazırlanması amaçlanmıştır. Hidroksi, diglisidil eter gibi farklı uç gruplu PDMS örneklerinin; poli(etil vinil eter-ko-maleik anhidrit) kopolimerleri ve sentezlenen poli(maleik anhidrit-1-hekzen-akrilik asit) terpolimeri ile çapraz bağlı membranları hazırlanmıştır. Sentezlenen terpolimer maleik anhidrit (elektron çekici), 1-hekzen (elektron verici) ve akrilik asit (elektron çekici) monomerlerinin, başlatıcı olarak benzoil peroksitin kullanılmasıyla, 1,4 dioksan içeren çözücü ortamında 70-75^{0}C arası reaksiyon koşullarında kompleks radikal polimerizasyonu ile hazırlanmıştır. Çapraz bağlı membranlar, termal yolla hazırlanmıştır.

Hazırlanan her bir membranın spektroskopik karakterizasyonu FTIR, NMR (^{13}C, ^{1}H) gibi farklı yöntemler kullanılarak gerçekleştirilmiş. Yapıların termal karakterizasyonu için ise DSC, TGA-DTA ve bunlara ek olarak DMA çalışmaları ile yürütülmüştür. Spektroskopik karakterizasyon kimyasal yapı, bağ karakteri ve ikincil etkileşmeler hakkında çok temel bilgiler sunabilmektedir. Ayrıca, ikincil etkileşmelerin takibinde, polimer-çözücü rolünü de vurgulayan çok değerli bilgilere ulaşılabilmektedir.

Çalışmamızın diğer bir aşamasında ise, her bir membranın çözücülerde şişme davranışları takip edilmiş ve ilgili parametreler hesaplanmıştır.

Son olarak hazırlanan difüzyon davranışları, değme açısı(contact angle) çalışmaları ile izlenmiş ve yapılara ait morfolojik özellikler X Ray ile takip edilmiştir.

Anahtar Kelimeler: PDMS, çapraz bağ, karakterizasyon, FTIR, NMR, DSC, TGA-DTA, DMA, şişme, XRD, değme açısı.

Danışman: Prof. Dr. Günay KİBARER, Hacettepe Üniversitesi, Kimya Bölümü, Fizikokimya Anabilim Dalı.
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ABBREVIATIONS

A	Acceptor
CTC	Charge Transfer Complex
D	Donor
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimeter
DTA	Differential Thermal Analysis
E’	Storage modulus
E”	Loss modulus
FTIR	Fourier transform infrared
MA	Maleic anhydride
S	Swelling degree
Tg	Glass transition temperature
TGA	Thermal Gravimetric Analysis
H-1	1-hexene
PEL	Polyelectrolyte
BP	Benzoyl Peroxide
AN	Acid Number
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
NMR	Nuclear magnetic resonance
DGE	Diglycidyl ether
MVE	Methyl vinyl ether
PDMS	Poly dimethyl siloxane

1. INTRODUCTION

Polysiloxanes, usually referred to as silicones, find numerous applications in the form of coatings and thin films. Common examples are silicone release liners for dispensing pressure-sensitive adhesives used in tapes and labels, oxygen resistant coatings for spacecraft, and biocompatible coatings used on stents and catheters. All of the applications rely on the unique physical and chemical properties of silicones in the bulk form and at interfaces. A three-dimensional silicone network is formed by the crosslinking of linear silicone molecules, usually poly(dimethylsiloxane)(PDMS) (Simpson et al., 2003; Cai et al., 2004)

A marginal use of PDMS is that as a top layer of membranes for the separation of gases, or vapours, from mixture of gases and of liquids. Pervaporation appears apotentially attractive process for this application (Bennett et al., 1997; Adnadjevic et al., 1997; Uragami et al., 2001). PDMS is widelly used in pervaporation of dilute alcoholic mixtures (Mohammadi et al., 2005), pervaporative recovery of p-cresol from aqueous solution (Wu et al., 2002), separation of ethyl acetate-ethanol binary mixtures (Hasanoğlu et al., 2005), for separation of hydrocarbon/methane and hydrocarbon/hydrogen (Pinnau et al., 2004), separation of organic-organic mixtures. In addition to that PDMS can be used in coating for the control of drug release (Nahrup et al., 2004). As the economy of the membrane processes relies partly on the membrane performance, efforts have been focused on creating new PDMS-based membranes by chemical modification (Bennett et al., 1995; Roizard et al., 1996), or by blending it with appropriate zeolites (Hennepe et al., 1987; Vankelecom et al., 1995). However, crosslinking conditions can significantly affect the materials properties.

For the preparation of membrane forms from PDMS, it was reported that the crosslinked networks were created from the reaction of silicates and silane derivatives as a crosslinker in the presence of a Pt catalyst and inhibitor (Schaefer, 2003; Oh et al., 2001; Smtha et al., 2004)

Crosslinking is extremely important in converting low viscosity liquid PDMS into useful materials (Thomas et al., 1993). This is often accomplished by a peroxide catalyzed cure, by condensation of silanol terminated polysiloxanes or by Pt catalyzed hydrosilylation reactions between Si–H and Si vinyl terminated siloxanes. Ring opening cure of epoxides, used herein, has the advantage that it is perhaps the fastest known method of crosslinking.

In some earlier publications it was reported that synthesis of self-hardenable epoxy-anhydride copolymers was carried out by binary radical copolymerization of unsaturated epoxide monomers of the donor-acceptor type with maleic anhydride. It was shown that in these systems, especially in the high conversion conditions, there is a simultaneous copolycondensation of free epoxide and anhydride fragments via formation of a cross-linked structure (Rzaev et al., 2001)

Poly(methyl vinyl ether-co-maleic anhydride) is widely used for pharmaceutical purposes as a thickening and suspending agent, denture adhesive and adjuvant for transdermal patches. The oral toxicity of all these polymers is quite low (LD50 in guinea pigs is 8–9 g/kg per os from data supplied by ISP Corp.). It is a biodegradable polyanhydride and could be an appropriate copolymer for the preparation of particulate dosage forms with bio-adhesive or muco-adhesive properties.

In this study, the preparation of membrane forms from PDMS samples with different end groups and various molecular weights are aimed in the presence of appropriate copolymers and terpolymers. PDMS samples with different end groups like hydroxy and diglycidyl ether are reacted with poly(methyl vinyl ether-co-maleic anhydride) copolymer and poly(maleic anhydride -1,hexene- acrylic acid) terpolymer to form membranes.

The spectroscopic characterization of each prepared membranes are achived by different techniques like FTIR, NMR. The thermal characterization is carried out by DSC, TGA-DTA, DMA studies. Spectral analysis is capable of highlighting and provides very basic information about chemical structure, bond character and secondary interactions.

Another progress of study involves the determination of swelling behaviour of the prepared crosslinked membranes. Diffusion behaviour was predicted by water contantact angle and crosslinked membranes morphology have also been interpreted by XRD method.

2. THEORY

Organosiloxane polymers, or as they are more commonly called, the silicones, may be defined as polymers with backbones comprising alternate silicon and oxygen atoms in which the silicon atoms are also linked to organic groups. Polysiloxanes belong to the class of semi-inorganic polymers because there are both inorganic silicon atoms and various organic side groups in the structure. Depending on the length of the polymeric chains and their molecular structure, the resulting properties can range from fluids to rubber-like materials to solid resins.

Siloxane materials have a number of properties which make them useful. Among these are low temperature flexibility, high thermal stability, biocompatibility, significant gas permeability, hydrophobicity, and oxidative resistance (Noll, 1968)

High thermal stability, unusually low temperature coefficient of η, unusually large permeability, maintenance of rubber elasticity down to low temperatures, low surface tension, good dielectric properties, weather resistance, release and lubrication properties.

As a result, there are numerous applications for siloxane polymers. For example, prostheses, artificial organs, facial reconstruction and catheters in medical applications take advantage of the inertness, stability, and pliability of the polysiloxanes. The nonmedical applications, such as high-performance elastomers, membranes, adhesives, are also based on the same properties just mentioned.

Poly(dimethylsiloxane) (PDMS), $[-Si(CH_3)_2O-]_x$, is the most important and by far the most used siloxane polymer (Martin et al.,1909; Adrianov, 1965; Barry et al., 1962). It has long been known to be a high-performence material because of its extremely low glass transition temperature and high thermal stability compared with those of other elastomers. But PDMS elastomers in the unfilled state generally lack useful properties simply because of their relatively low strength (Florry, 1968; Noll, 1968; Mark et al., 1976). As a result, most applications require that these elastomers be reinforced by fillers in order to improve their mechanical properties (Polmateen et al., 1975; Wagner et al., 1976; Warrick et al., 1979). As has been known and used for many years, blending of fillers into polymers prior to their crosslinking into network structures is very often used and gives elastomers of greatly improved mechanical properties.

Frederic Kipping is considered the founder of silicone chemistry (Kipping, 1901). Since his synthetic goal was to isolate crystalline silicon-containing small molecules, he had little interest in the polymeric nature of the oily and gelatinous side-products that he had frequently encountered. The importance of these side-products is shown in Rochow's original patent which describes a direct route to the synthesis of the simplest of these polymeric silicones, poly(dimethylsiloxane), PDMS (Rochow, 1941). In comparison to hydrocarbon-based polymers, the higher thermal stability of siloxane-type backbones, $-(Si\text{-}O)_n-$, is also recognized in this patent.

Today PDMS is an extensively studied polymer due to its industrial versality. The chemical inertness of the Si-O linkage is superior to that of the C-C linkage of hydrocarbon polymers and in many aspects results in superior properties including: low tempereature dependence of physical, mechanical, and electrical properties, resistance to oxidation and degradation by light, hydrophobicity, low environmental hazard and essentially nontoxic nature (Clarson et al, 1996). These properties have spurred acedemic interest concerning the performance of PDMS within these applications. A large body of knowledge has accumulated which shows that the exceptional attributes of PDMS stem from unique bond properties coupled with a greater flexibility of the Si-O backbone relative to that of C-C backbone.

A marginal use of PDMS is that as a top layer of membranes for the separation of gases, or vapours, from mixtures of gases, and of liquids (Blume et al., 1996). Although the quantity of PDMS used in membranes is very small, the separations made with these membranes save very large amounts of chemical products, and greatly reduce pollution. As the economy of the membrane processes relies partly on the membrane performance, efforts have been focused on creating new PDMS-based membranes by chemical modification (Bennet et al., 1995; Roizard et al., 1995) or by blending it with appropriate zeolites (Hennepe et al., 1987; Vankelecom et al., 1995). However, crosslinking conditions can significantly affect the material properties.

Crosslinking is extremely important in converting low viscosity liquid PDMS into useful materials (Thomas et al., 1993). This is often accomplished by a peroxide catalyzed cure, by condensation of silanol terminated polysiloxanes or by Pt catalyzed hydrosilylation reactions between Si–H and Si vinyl terminated siloxanes. Ring opening cure of epoxides, used herein, has the advantage that it is perhaps the fastest known method of crosslinking.

2.1. Membrane Technology

Membranes have gained an important place in chemical technology and are being used increasingly in a broad range of applications. The key property exploited in every application is the ability of a membrane to control the permeation of chemical species in contact with it. In separation applications, the goal is to allow one component of a mixture to permeate the membrane freely, while hindering the permeation of the other components. Since the 1960s, membrane science has grown from a laboratory curiosity to a widely practiced technology in industry and medicine. This growth is likely to continue for some time, particularly in the areas of membrane gas separation and pervaporation separation.

Until 30 years ago, membrane separations were mainly of academic interest and not yet considered technologically significant. Today however, they are used in a wide range of applications and the number of applications is steadily growing. From an economic point of view, the present time may be regarded as intermediate between the development of first generation membrane processes and their general use in industries and someday perhaps even domestic use.

2.2. Historical Development of Membranes

Systematic studies of membrane phenomena can be traced to the eighteenth century philosopher scientists. Abbe Nolet coined the word osmosis to describe permeation of water through a diaphragm in 1748. Through the nineteenth and early twentieth centuries, membranes had no industrial or commercial uses but were used as laboratory tools to develop physico-chemical theories.

The measurements of solution osmotic pressure made with membranes by Traube and Pfeffer were used by Van't Hoff in 1887 to develop his limit law, which explains the behavior of ideal dilute solutions. This work led directly to the Van't Hoff equation. At about the same time, the concept of a perfectly selective semipermeable membrane was used by Maxwell and others to develop the kinetic theory of gases. In 1907, Bechhold devised a technique to prepare 10 nitro cellulose membranes of graded pore size, which he determined by a bubble test. Other workers (Elford, 1937; Zsigmondy, 1918; Ferry, 1936) improved on Bechhold's technique, and by the early 1930s, microporolls collodion membranes were commercially available. Over the next 20 years, this early microfiltration membrane technology was expanded to other polymers, notably cellulose acetate. Membranes found their first significant application in the filtration of drinking water samples at the end of World War II. Drinking water supplies serving large communities in Germany and elsewhere in Europe had broken down and filters to test for water safety were urgently needed. The research effort to develop these filters, sponsored by the U.S. Army, was later exploited by the Millipore cooperation, the first and still the largest microfiltration membrane producer in the world.

By 1960, the elements of modern membrane science had been developed, but membranes were still used in only a few laboratories and small, specialized industrial applications. Membranes suffered from four problems that limited their widespread use as a separation process: they were too unreliable, too slow, too unselective, and too expensive. Partial solutions to each of these problems have been developed since the 1960s and by the 1990s membrane-based separation processes had become common place.

The seminal discovery that transformed membrane separation from a laboratory to an industrial process was the development, in the early 1960s, of the Loeb-Sourirajan process for making defect-free, high flux, asymmetric reverse osmosis membranes (Loeb et al, 1963). These membranes consist of an ultra-thin, selective surface film on a microporous support, which provides mechanical strength. The flux of the first Loeb-Sourirajan reverse osmosis membrane was 10 times higher than that of any membrane then available and made reverse osmosis commercializable.

The 20-year period from 1960 to 1980 produced a significant change in the status of membrane technology. Building on the original Loeb-Sourirajan membrane technology, other processes, including interfacial polymerization and multilayer composite casting and coating, were developed for making high performance membranes (Kroschwitz, 1985).

2.3. Definition of a Membrane

For practical purposes, a membrane may be defined as a selective barrier between two phases, the term 'selective' being inherent to a membrane or a membrane process. It should be noted that this is a macroscopic definition while separation should be considered at the microscopic level. In fact, in membrane separation processes, the membrane acts as a semi-permeable barrier through which components pass due to a gradient force between the two sides. A schematic representation of membrane separation is given in Figure 2.1.

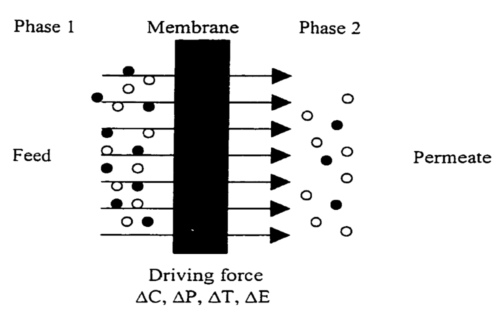


Figure 2.1. Schematic representation of a two-phase system separated by a membrane.

Phase 1 is usually considered as the feed or upstream side phase while phase 2 is considered the permeate or downstream side. Separation is achieved because the membrane, by its nature, allows the transport of one component from the feed mixture more readily than any other component or components.

The performance or efficiency of a given membrane is determined by two parameters: 'selectivity' and 'flow' through the membrane. The latter, often denoted as the flux or permeation rate, is defined as the volume flowing through the membrane per unit area and time.

2.4. Membrane Materials

A membrane can be thick or thin and its structure homogeneous or heterogeneous while transport can be active or passive and passive transport can be driven by a pressure, concentration or temperature difference. In addition, membranes can be natural or synthetic, neutral or charged. For practical understanding, membranes can be classified according to different criteria. One classification is by nature, i.e. biological or synthetic. This is the clearest distinction possible. It is also an essential first distinction since these two types differ completely in structure and functionality. Synthetic membranes can be divided into organic (polymeric or liquid) and inorganic (ceramic, metal) membranes.

In large-scale production, commercial thermoplastics and cellulosics are primarily used. Polymers can be tailored for specific applications, but until the mid-1980s only a few polymers were developed as a result of a need for membranes of very specific selectivity.

In neutral, dense polymer membranes, mass transport takes place only through the amorphous phase, where the solubility and mobility of a permeating species largely depend on the local arrangement of the polymer chains above and below the glass-transition temperature. Semi-crystalline polymers are often considered heterogeneous materials because the type of diffusion differs in the pure amorphous phase and at the crystalline-amorphous interface. Interaction between the diffusing species and the functional groups of the polymer chains depend largely on the distribution of these groups in the amorphous phase. Consequently, materials that would otherwise be viewed as homogeneous are considered heterogeneous on the basis of the permeate diffusion route. For example, aggregation of ionic groups in ionomer membranes, such as Nation, leads to mass transport characteristics quite different from those of membranes characterized by random distribution of the ionic moieties. In this regard, more is known about the structure-property relationship of polymers and membranes that interact with the permeating species through well-defined and relatively large forces, e.g., ion-exchange membranes. Much less is known about the influence of the membrane building blocks on permselectivity resulting from hydrogen bonding, dipole-induced dipole or quadriopole and dispersion type forces and interactions.

Inorganic materials generally possess superior chemical and thermal stability relative to polymeric materials. Nevertheless their use as membrane material has been limited although a growing interest can now be observed. Four different types of inorganic materials frequently used may be distinguished: ceramic, glass, metallic and zeolitic. Ceramics are formed by the combination of a metal (e.g. aluminium, titanium, silicium or zirconium) with a non-metal in the form of an oxide, nitride or carbide. Ceramic membranes prepared from such materials form the main class of inorganic membranes, with aluminium oxide or alumina and zirconium oxide or zirconia as the most important representatives. These membranes are usually prepared by sintering or by sol-gel processes. Glass may also be considered as a ceramic material. Ceramic membranes are used in ultra-filtrations and micro-filtrations in which solvent resistance and thermal stability are required. Glass membranes (silicon oxide or silica*)* are mainly prepared by techniques involving leaching on de-mixed glasses. Metallic membranes, mainly obtained via the sintering of metal powders (e.g. stainless steel). Tungsten or molybdenum), have only received limited attention to date. Dense metal membranes, particularly palladium membranes are being developed for coupled and facilitated transport processes. Zeolite membranes have gained much interest recently. Zeolites are crystalline microporous alumina-silicates. It is built up by a three dimensional network of SiO_4 and AlO_4 tetrahedral. These materials have very small pore size and can be applied in gas separation and pervaporation.

Another means of classifying membranes is by morphology or structure. This is also a very illustrative route because the membrane structure determines the separation mechanism and hence the application.

2.5. Membrane Morphology

The membrane morphology dictates the mode of permeation and separation, as shown in Figure 2.2. The basic morphologies are isotropic (dense or porous) and anisotropic with a tight surface extending from a highly porous wall structure. The tight surface can be a dense, selective skin, permitting only diffusive transport or a porous skin, allowing viscous flow of the permeate, as in conventional ultra-filtration. Membrane separation is achieved by manipulation of these basic morphologies.

The semi-permeability of porous membranes is based on the spatial cross section of the permeating species, that is, small molecules exhibit a higher permeation rate than large molecules, and linear chain molecules permeate better than those with a globular shape. The semi-permeability of the dense membrane or a membrane that exhibits anisotropic morphology with a dense skin is obtained primarily through a solution-diffusion mechanism. The permeating species interact chemically with the dense polymer matrix and selectively dissolve in it, resulting in diffusive mass transport along a chemical potential gradient. Thus, for example, a dense membrane may exhibit semi-permeability toward the large molecules with which it interacts, whereas the smaller, non-interacting species do not permeate. This is demonstrated in the pervaporation process, where ethanol is separated from water by employing membranes made of organic polymers.

The development of anisotropic (asymmetric) membranes in the early 1960s accelerated the progress of membrane separation technology (Loeb et al., 1963). This development is based on the fact that the transport rate through a dense membrane is inversely proportional to the membrane thickness, and that membrane perm-selectivity is independent of thickness. Thus membranes with this structure permit high transport rates, yet yield excellent separation. In addition, the use of anisotropic morphologies eliminates mechanical integrity problems associated with the handling of ultra-thin membranes. The success of the anisotropic membrane led to the development of the thin-film composite membrane.

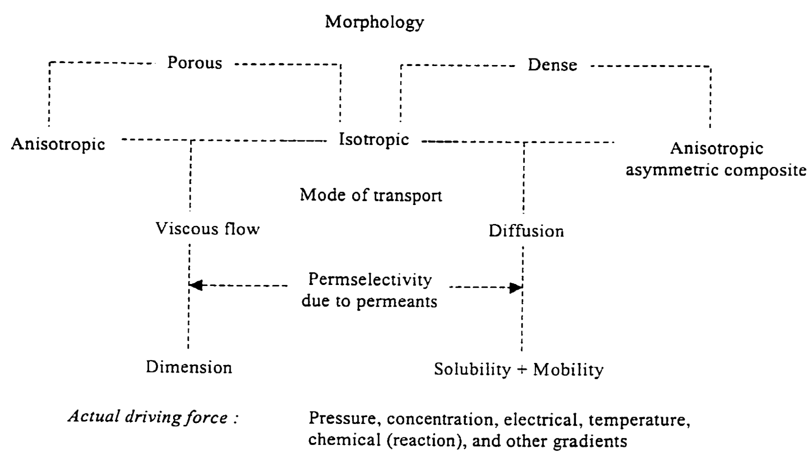


Figure 2.2. Configuration, morphology, transport, perm-selectivity, and driving forces employed in membrane science and technology.

2.6. Modifications Made to the Polymer for Improving Separation Properties

2.6.1. Crosslinking

In membrane technology, there are two reasons to crosslink a polymer. The first reason is to make the polymer insoluble in the feed mixture and the second reason is to decrease the degree of swelling of a polymer in order to derive good selectivity.

Crosslinking can be executed in three ways. One is via chemical reaction by using a compound to connect two polymer chains, the second by irradiation and third, is a physical crosslinking (Gowariker et al.,1999; Bitter, 1984). A good example of this is the chemically crosslinked PVA top layer of the GFT composite membrane which shows excellent resistance to many solvents. On the other hand, excessive crosslinking has to be avoided as it renders the polymer membrane brittle with a loss in the dimensional stability thereby making it unsuitable for pervaporation application.

2.6.2. Grafting

Grafting is a polymer modification technique where oligomeric chains are attached as side chain branches irregularly to the polymer main chain. This again can be done by chemical reaction or by irradiation. If the molecules to be grafted contain a functional group that is able to react with a functional group of the polymer, grafting by chemical reaction can occur. Grafting by irradiation is a versatile technique for the modification of insoluble polymer films. Polymers with good chemical resistance can be made into films by melt extrusion/ calendering followed by modification through irradiation based grafting. Neel and co-workers (Aptel et al., 1972) and Ellinghorst et al. (Ellinghorst et al., 1972) have performed a lot of research on grafting films by irradiation. They used PVDF, PVF and PTFE as basic polymers and N-vinylimidazole as grafting monomers.

2.6.3. Blending

A mixture of two polymers which are not covalently bonded is called a polymer blend. In principle, blending is an ideal technique for creating optimum hydrophilicity in the hydrophobic membrane. The optimum-blending ratio can be determined by mixing the hydrophilic polymer with a hydrophobic one at various compositions and measuring the permeability and selectivity. Two types of blends can be distinguished: homogeneous blends, in which the two polymers are miscible on a molecular scale for all compositions and heterogeneous blends, in which the two polymers are not totally miscible. In the latter case, domains of one polymer distributed within the matrix of the other polymer can be observed. However, homogeneous blends only are considered as potential membrane materials for PV as heterogeneous blends will not give enough mechanical strength to the thin membranes (Cresa, 1962; Burlant et al., 1960; Buttaerd et al., 1967)

2.6.4. Copolymerization

Copolymerization can be applied for the same reason as the blends are used, but unlike in blends the two polymers are covalently bonded which increases the mechanical stability of membrane. Besides grafted copolymers, block and random copolymers can be formed by this technique. An important aspect in copolymerization is the degree of crystallinity. Random copolymers might be fully amorphous while graft copolymers contain a certain degree of crystallinity. Membrane made of random copolymers cannot be used for PV applications as a certain degree of crystallinity is required for the membrane to show preferable sorption towards one of the two organic components (Govariker, 1999; Spitzen et al., 1988).

2.7. Membrane Processes

Micro-filtration (MF), ultra-filtration (UF) and reverse osmosis (RO) are three developed membrane separation processes which separate components of suspensions or solutions using porous membranes. Micro-filtration refers to membranes with pore diameters from 0.1 μm to 10 μm. Micro-filtration membranes are used to filter suspended particulates, bacteria or large colloids from solutions. Ultra-filtration refers to membranes having pore diameters in the range of 2-100 nm. Ultra-filtration membranes can be used to concentrate dissolved macromolecules such as proteins in solutions. In reverse osmosis membranes, the pores are extremely small, in the range of 0.5-2 nm in diameter. Reverse osmosis membranes are used to separate dissolved micro-solutes such as salt from water (Mulder et al., 1996). Another developed membrane process is electro-dialysis, in which charged membranes are used to separate ions from aqueous solutions under the driving force of an electrical potential difference. The process utilizes an electro-dialysis stack, built on the plate-and-frame principle, containing several hundred individual cells formed by a pair of anion and cation-exchange membranes. The principal current application of electro-dialysis is the desalting of brackish groundwater. However, industrial use of the process in the food industry, for example to deionize cheese whey, is growing, as is its use in pollution control applications.

The semi-permeability of dense membranes or membranes of anisotropic morphology with a dense skin is due to a solution-diffusion mechanism. The permeating species interact chemically with the membrane polymer and selectively dissolve in it, resulting in diffusive mass transport along a chemical potential gradient. A dense membrane may therefore be permeable to larger molecules which are soluble in it and refractory to smaller species which are chemically incompatible with it. Pervaporation and vapor permeation are two processes which separate components in solution using non-porous membranes. In pervaporation, a liquid mixture is contacted with one side of a membrane and permeate is removed as vapor from the other side. Vapor permeation is the same as pervaporation except that the solution on the inside of the membrane is also in the vapor phase. Currently, the only industrial application of pervaporation is the dehydration of organic solvents, particularly of 90-95% w/w ethanol solutions, a difficult separation problem because of the formation of an ethanol water azeotrope at 95% w/w ethanol. The current leader in this field, GFT Co. (Neunkirchen, Germany), built their first major plant using this technology in 1982. More than 100 plants have since been built by this company for this application alone (Bruschke, 1988). Pervaporation is also being developed for the removal of dissolved organics from water and for the separation of organic solvent mixtures (Blume et al., 1990).

Due to the ability of non-porous pervaporation membranes to remove from aqueous organic solvents of larger molecular size than water, the performance of many different polymeric non-porous membranes has been examined. During the past decade, many studies have focused on separating ethanol from dilute aqueous solutions by pervaporation with different polymeric membranes and operating conditions (Mulder et al., 1983).

2.8. Solubility in Rubbery Polymers

The term "solubility" refers to the equilibrium concentration of a penetrant gas or vapor dissolved in a polymer under specified conditions. The penetrant solubility is governed by the laws of thermodynamics (Stern et al., 1981; Marchin et al., 1965; Rogers, 1965; Meares, 1957), and depends on the nature of the polymer and the penetrant, and on system properties such as temperature and pressure.

2.9. Diffusion in Polymers

2.9.1. Fickian Diffusion

Crank (Cranck, 1975) has defined *diffusion* as the process by which matter is transported from one part of a system to another part as a result of random molecular motions. This process is quantified for many liquid, gases and vapors in a variety of "rubbery" and "glassy" polymers by Fick's two laws. Fick's first law, which is phenomenological, is based on the hypothesis that the rate of transport of a diffusing species per unit area of a section of a homogeneous and isotropic substance is proportional to the concentration gradient of the species measured normal to the section:

$$J = -D\ (\partial c/\partial x) \qquad (2.1)$$

where J is the rate of transport per unit area of section; D is the local mutual (binary) diffusion coefficient; c is the local concentration of the diffusing molecules; and x is the space coordinate measured normal to the section. D is commonly a constant or a function of the penetrant concentration. If the substance (such as a polymer) is heterogeneous, D can also be a function of position.

Fick's second law, which is derived from equation.2.1, is expressed by the following relation for one-dimensional diffusion, ie., if there is a gradient of concentration only along the x-axis:

$$\partial c / \partial t = \partial/\partial x\ (\ D\ \partial c/\partial x\ ) \qquad (2.2)$$

where D, c, and x are as defined above and t is the time. Solution of this partial differential equation with the initial and boundary conditions appropriate for a given diffusion process will yield c=f(x,t)*, i.e.*, the evolution of the concentration profile of the diffusing molecules in a given substance with time. Three experimental methods have been widely used to determine diffusion coefficients of gases and vapors in polymers:

1) *Concentration-distance measurements,* in which the penetrant concentration is obtained as a function of distance from the surface of the polymer sample by refractive index or radiation absorption methods;

2) Permeability measurements, in which the penetrant flux through a polymer membrane of a known thickness and area or the permeate pressure change in a known volume is measured as a function of time;

3) Sorption-balance measurements, in which the weight change of a polymer sample caused by the absorption or desorption of a penetrant vapor is measured as a function of time. The geometry and dimensions of the polymer sample have to be accurately known in order to solve the diffusion equation.

The diffusion coefficients for many organic vapors or liquids can be determined from absorption and/or desorption measurements by solving Fick's second law for the pertinent initial and boundary conditions. The variaition in the concentration profile in the membrane sample with time during the absorption or desorption process can also be determined from Fick's second law.

The following initial and boundary conditions apply to equation.2.2 for absorption and desorption measurements:

For *absorption* : Initial condition : $c(x,0) = 0$

Boundary condition : $c(-\delta/2,t) = c_0$ and $c(+\delta/2,t) = c_0$

For *desorption* : Initial condition : $c(x,0) = c_0$

Boundary condition : $c(-\delta/2,t) = 0$ and $c(+\delta/2,t) = 0$, where δ is the membrane thickness and t is the time.

2.9.2. Solution of Fick's Second Law for **D =** *Constant*.

Solution of equation.2.3 for the above initial and boundary conditions and a *constant* diffusion coefficient, *D,* yields the following expression for c=f(x,t*) :*

$$\frac{c}{c_0} = 1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)}\exp\left[\frac{-D(2n+1)^2\pi^2 t}{\delta^2}\right]\cos\frac{(2n+1)\pi x}{\delta} \qquad (2.3)$$

Let M_t denote the total amount of vapor absorbed by the membrane at time t*,*

$$M_t = \int_{-\delta/2}^{\delta/2} c(x,t)dx \qquad (2.4)$$

and let M_∞ denote the corresponding quantity after infinite time, i.e., at absorption (solution) equilibrium. Equations 2.4 and 2.5 then yield the relation:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp[-D(2n+1)^2\pi^2 t/\delta^2] \qquad (2.5)$$

where the ratio M_t / M_∞ is the fractional amount of vapor absorbed by the polymer at time t*.* It should be noted that the above equation also holds for desorption measurements except that in this case M_t denotes the total amount of vapor desorbed.

The values of diffusion coefficients, *D,* for penetrant/polymer systems can be determined by several methods from absorption measurements :

(a) The Half-Time Method

The simplest method is to note the time $t_{1/2}$ at which M_t / M_∞ = 1/2. According to Crank , the only first term of equation 2.5 (n=O) is important with the error being about 0.001 %.
Then, for a planar membrane,

$$D = \frac{0.04919\delta^2}{t_{1/2}} \qquad (2.6)$$

(b) The Initial Slope Method

In the early stages of the absorption/desorption measurements, equation 2.5 can be simplified to the following form:

$$M_t/M_\infty = \frac{4}{\delta}\left(\frac{D}{\pi}\right)^{1/2} t^{1/2} \qquad (2.7)$$

where D can be obtained from a slope of a linear plot of M_t / M_∞ versus $t^{1/2}$ at short times.

(c) The Method of Moments

A variation of a method derived by Felder et al. (Felder et al., 1980) for estimating diffusion coefficients from permeation rate data may also be applied to absorption/desorption measurements. Felder et al. (Felder et al., 1975) have defined a function τ_s as follows:

$$\tau_s = \int_0^\infty \left[1 - \frac{M_t}{M_\infty}\right] dt \qquad (2.8)$$

The quantity τ_s in the above equation is calculated by numerical integration. Then, the diffusion coefficients can be estimated from the following relation :

$$D = \frac{\delta^2}{12\tau_s} \quad (\text{for planar membranes}), \qquad (2.9)$$

The method of moments has the advantage of utilizing the entire absorption or desorption curve, rather than a single datum point as in the half-time method, or a portion of the curve within a time interval as in the initial-slope method.

The use of at least two of the above three methods of determining diffusion coefficients and a comparison of the results provides a consistency check on the values of these coefficients. The half-time method and the method of moments were used in this study. The initial-slope method was not suitable for the present measurements due to pressure fluctuations in the initial stages of the measurements.

2.9.3. Solution of Fick's Second Law for D =f(c)

If the diffusion coefficient, D, in equation 2.5 is dependent on penetrant concentration, as in the present study, equations 2.6, 2.7, and 2.9 yield a mean or concentration-averaged diffusion coefficient, $\bar{D}$, defined by :

$$\bar{D} = (1/c_o)\int_0^{c_o} D(c)\,dc \qquad (2.10)$$

According to Crank, a better approximation of $\bar{D}$ can be obtained from the average of the diffusion coefficients obtained from an absorption measurement $(\bar{D}_a)$ and a desorption measurement $(\bar{D}_d)$ at the same equilibrium pressure; i.e., $\bar{D} = 1/2(\bar{D}_a + \bar{D}_d)$ Then, in order to obtain the mutual diffusion coefficient *D(c)* it is necessary to measure $\bar{D}$ as a function of c and differentiate the above equation.

2.9.4. Classification of Diffusion Processes

The diffusion behavior of penetrants in polymers has been classified by Crank into the following three categories, based on the relative rates of diffusion and polymer relaxation:

a) Case I or "True" Fickian Diffusion

In this case, the rate of diffusion is slower than that of relaxation. "True" Fickian diffusion is characterized by absorption/desorption rate curves described by equation 2.5 with time-independent boundary conditions. The initial absorption rates are then linear up to a time when the M_t / M_∞ ratio (the fractional amount of gas or vapor absorbed) reaches a value of at least 0.5. In some special cases the absorption curves resemble the “true" Fickian curves but the initial linear portion of the curves persists for a shorter time. These special cases were designated by Rogers as *"pseudo-Fickian".*

b) Case II Diffusion

This case occurs when the diffusion is very rapid compared to the relaxation process and the diffusion coefficients are time-dependent. This case is observed when good solvents are absorbed by glassy polymers at temperatures considerably below their glass transition temperature, *Tg.*

c) *Non-Fickian or Anomalous Diffusion*

The diffusion processes which do not show Fickain or Case II type behavior are usually called non-Fickian or anomalous diffusion. This type of diffusion can be caused for many reasons. For example, the case when the rate of diffusion and polymer relaxation are comparable is an intermediate case between Case I and Case II diffusion and consequently would be considered non-Fickian. According to Crank , during the initial period of the absorption measurements, the relationship between the fractional amount of vapor absorbed by the polymer,
M_t / M_∞ , and the time, t, can be expressed by the relation:

$$M_t / M_\infty = k.t^n \qquad (2.11)$$

where *k* and *n* are constants.

Fickian diffusion is characterized by n =1/2 and pseudo-Fickian by $n<1/2$. Case II diffusion is observed when n =1. For non-Fickian diffusion, which, as mentioned above, is an intermediate case between Case I and Case II diffusion, the values of n lie between 1/2 and 1.

2.10. Complex-Radical Alternating Terpolymerization

Among many various molecular complexes it is especially interesting to distinguish charge transfer complexes (CTC) of donor–acceptor monomer system (complexomers) due to their specific function as intermediates in functional macromolecules formation.

The mechanism of the study of the formation of CTC, complexomers spectra, and their action on separate stages of radical copolymerization, terpolymerization and cyclocopolymerization, are of great significance in solving the problem of controlling the chain growth, as well as planning the copolymer structure regularities, rate and degree of polymer formation reaction, and probably, steric structure which were the objective of early investigations. However, in many papers on radical copolymerization of donor–acceptor monomer systems, the role of CTC in elementary acts of chain growth reactions has been either ignored or considered inadequately.

One of the strong electron-accepting monomers able to form CTCs with various types of functional-substituted electron-donor monomers is 1,2-substituted ethylenes including maleic (fumaric) acid derivatives. The formation of a CTC in these monomer systems is the main decisive factor for determination of relative reactivities of monomers involved and for the elucidation of chain growth mechanism of complex-radical copolymerization reactions.

In several reports (Rzaev, 1984; Cowie, 1985; Kabanov et al., 1986) and reviews (Ratzsch et al., 1991; Golubev et al., 1973; Gaylord, 1969; Hill et al., 1982; Rzaev, 1982; Ebdon et al., 1986) investigations on the role of monomer CTCs in radical copolymerization and peculiarities of chain growth reactions in alternating copolymerization of donor–acceptor monomers were considered and the results were summarized. After these publications in recent years considerable progress has been made in the field of complex-radical copolymerization and new aspects of the mechanism of alternating chain growth reactions were revealed, and also many alternating copolymers having excellent properties were synthesized by using complex-radical copolymerization method.

The complex-radical terpolymerization of the donor-acceptor monomer system maleic anhydride (acceptor A1), 1-hexene (donor D) and acrylic acid (acceptor A3) was investigated.

2.11. Classification of Acceptor–Donor Monomers

The classification of monomers from different positions and specific classes of functional monomers were considered in several books (Bergbeiter et al., 1989; Sherrington et al., 1988; Yacum et al., 1973; Amos et al., 1952) and reviews (Varshney, 1986; Warshawsky, 1987; Pomogalio, 1986; Temin, 1982; Biswas et al., 1986; Prasad et al., 1988; Wulf et al., 1989; McCormic et al., 1982). Thus, Arshady (Arshady, 1992) classifies the monomers as structural monomers (styrene, acrylamide, dimethacrylamide, methacrylamide, acrylates, methacrylates and vinylics) and functional monomers (substituted styrenes, *N*-alkylacrylamides, alkyl and aryl acrylates and methacrylates, vinyl and allyl monomers, and maleic anhydride). This designation was employed to emphasize the relationship within and between different monomer types, and hence to better understand their homo- and copolymerization behaviors. Unfortunately, classification of functional monomers based on their position of their acceptor–donor properties was not considered in the above studies.

In general, depending on the type of conjugation of double bond and functional groups, all functional monomers can be categorized into two major groups(Rzaev, 2000): electron-acceptor (A) monomers and electron-donor (D) monomers. Functional substituted ethylenes, containing primary carboxyl, anhydride, ester, amide, imide and nitrile fragments, include a wide range of A-monomers such as: (1) maleic anhydride and its α,β-substituted derivatives (citroconic, dimethylmaleic and halogen-substituted maleic anhydrides), itaconic anhydride and etc.; (2) imides and *N*-substituted imides of unsaturated dicarboxylic acids (maleic and α,β-substituted maleic acids, itaconic acid, etc.); (3) unsaturated mono- and dicarboxylic acids (crotonic, *trans*-cinnamic, maleic, fumaric acids, etc.) and their esters, nitriles and amides and (4) tetrahalogen-substituted ethylenes. Sulfur dioxide (SO_2) can also be included in the above-mentioned group of A-monomers which easily copolymerize with vinyl and allyl D-monomers and form the alternating copolymers.

D-type of monomers which copolymerize with the above-mentioned A-monomers by mainly complex-radical alternating chain growth mechanism comprise also a wide range of monomers and can be divided into the following groups(Rzaev, 2000):

(1) D-monomers with π–σ-conjugation (α-olefines, cycloalkenes, vinylcycloalkanes, allyl monomers, etc.);
(2) D-monomers with π–ρ-conjugation (vinyl ethers, vinyl sulfides, dimethoxyvinylene, *N*-vinylamides, *N*-vinylamines, vinylhalide, etc.);
(3) D-monomers with π–π-conjugation (vinylaromatic monomers, *trans*-stilbene, phenanthrene, acenaphthylene, indene, vinylpyridine and other vinyl-substituted heterocyclic monomers with pseudoaromatic character, phenylacetylene, etc.);
(4) D-monomers with π–ρ–π-conjugation (vinyl esters, *N*-vinylcarbazole, *N*-vinylpyrrolidone, *N*-vinylsuccinimide, *N*-vinylphtalimide, etc.);
(5) Heterocyclic monomers with π–ρ- or π–π-conjugation (furan, benzofuran, dihydrofuran, thiophene, benzothiophene, dihydropyrane, *p*-dioxene, etc.);
(6) Elementorganic monomers of vinyl and allyl type (Si-, Ge-, Sn-, Fe-, P- and other metallorganic monomers with different types of conjugation).

Bifunctional monomers containing two D- and/or A-type of double bonds in molecule comprises the following types of monomers:

(1) Monomers of D–D-type (divinyl and diallyl ethers, sulfides, esters, amines, and metallorganic derivatives, divinyl- and diallylarylenes, conjugated and nonconjugated dienes and cyclodienes, etc.);

(2) Monomers of D–A-type (vinyl and allyl esters of unsaturated mono- and dicarboxylic acids, *N*-vinyl- and *N*-allyl-substituted maleimides, etc.);

(3) Monomers of A–A-type (diacrylates, dimethacrylates, bis-maleimides, etc.).

2.12. Phenomenon of Charge Transfer in Radical Copolymerization

In a wide range of known molecular complexes, the CTCs from A–D monomer system attract interest and have great importance because of their specific role in the formation reactions of functional macromolecules.

Progress in the field of radical copolymerization was considerably more, thanks to discovered effect of complex-formation and possibility to control radical chain growth reactions, and also due to advanced principle about structure of monomer CTC and their relationship with kinetic parameters of reactions.

The role of monomer CTC in radical copolymerization and particularly in alternating chain growth reactions of A–D monomers was considered in particular and generalized in earlier published reviews (Golubev et al., 1973; Gaylord, 1969; Hill et al., 1982; Ebdon et al., 1986; Yasuhiko et al., 1977) and reports (Rzaev, 1984; 2000; Cowie, 1985; Kabanov et al., 1986).

Geometry and structure of molecular A–D complexes and their relationship with mechanism of reactions were considered by Andrews and Keefer (Andrews et al., 1964) and Briegleb (Briegleb, 1961), where mechanism about alternating copolymerization of some monomers was also mentioned.

π-electrons of double bond and/or functional group (COOH, COOR, C=O, CN, etc.) of A-monomers can take part in complex-formation depending on the nature of second component (X) of A...X complex (Rzaev, 2000), where X can be:

(1) D-monomers;
(2) organic compounds with electron-acceptor or electron-donor functional groups or bonds;
(3) polar organic solvents and
(4) acids, inorganic and organometalic compounds of Lewis-acid-type.
(5) On the other hand, D-monomers at the same time can take part in complex-formation through other functional groups.

2.13. Polyelectrolyte Behavior of Polymers

Polyelectrolyte (PEL) is the term used to classify macromolecules that have many charged or chargeable groups when dissolved in polar solvents, predominantly water. The polyelectrolytes dissociate into a macro ion and counter ions in aqueous solution. One typical feature of polyelectrolytes is the extremely low activity coefficient of the counter ion. If the charge density of PEL is high enough a fraction of counter ions is located in the vicinity or 'at' the surface of the macro ion (condensed fraction of counter ions). The physical background of the counter ion–condensation effect is the competition between a gain in energy in the electrostatic interaction and a loss of entropy in the free energy. Another typical feature of polyelectrolytes is the high expansion or 'stretching' of the poly ion chain due to the strong electrostatic repulsion between charged segments. The abnormal viscosity behavior of the diluted salt-free PEL solution, i.e. the strong increase of the relative viscosity with decreasing polyelectrolyte concentration, has for many years been explained by the conformational change of the extended chain (empirically described by the Fuoss–Strauss law (Fuoss et al., 1948). However, recently a series of papers has been published, showing a maximum viscosity at very low polyelectrolyte concentrations (Cohen et al., 1988). Extending the theory of dilute solutions of highly charged spherical particles (Hess et al., 1983) to solutions of rodlike polyelectrolytes, the maximum in the concentration dependence can be qualitatively described (Rabin, 1987). A quantitative description of the intrinsic viscosity of branched polyelectrolytes is given in Antonietti et al., (Antonietti et al., 1997). Nonetheless, these features cannot be understood as a simple superposition of electrolyte and polymer properties. The interference between the polymer and electrolyte character has generated considerable interest in the field and opened new areas of application.

Polyelectrolytes and self-assembly. The self-assembly of matter is of interest as a fundamental prerequisite of life. According to Oparin's approach (Oparin, 1938), life originated via a spontaneous increase of molecular complexity and specificity. That is why biologists and biochemists proposed the polyelectrolyte RNA as one of the major macromolecules in living systems. Another approach in investigating the origin of life starts from the self-assembly of phospholipids to lipid vesicles, considered as precursors of the living cell (Deamer, 1997). The ability of a solution to self-organize is now emerging as an approach to many new synthetic architectures, unique properties and commercial applications. Industrially important examples include micelles, bilayers, vesicles, bicontinuous structures as well as helical and folded polymers.

According to Shinoda's concept of organized solutions there is no restriction on solvents and solute other than the requirement of amphiphilicity in solute–solvent interactions (Figure. 2.3) (Shinoda, 1991).

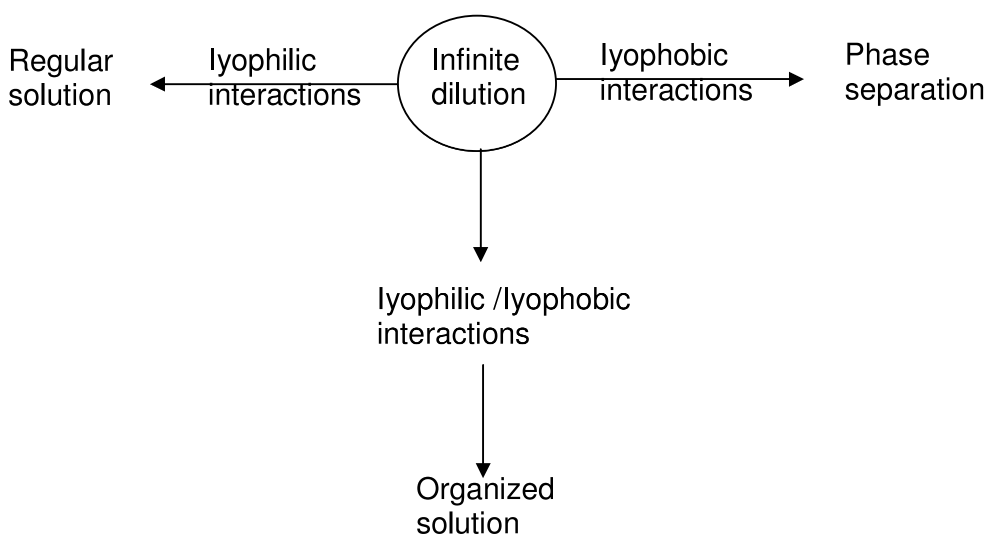


Figure 2.3. Scheme of solute-solvent interactions leading to three idealized solution types.

The conditions that define an organized solution according to Shinoda (Shinoda, 1991) are:

1. Low solute solubility.
2. Swelling of solvent by solute phase.
3. Solute in a liquid or liquid crystalline state.
4. High molecular or aggregate weight of solute species.

This knowledge allows for two routes to create self-assembled polyelectrolyte systems. In the first route the amphiphily comes directly from the polyelectrolyte. This requires that the polyelectrolyte is a semi-rigid one (this requires defined solvent concentrations) or it has to be modified hydrophobically. One possible way to accomplish this is to incorporate hydrophobic side-chains or hydrophobic blocks into the main chain. The first class of such modified polyelectrolytes is named associating polyelectrolytes or polysoaps and the second block polyelectrolytes. Well-defined supramolecular polyelectrolyte structures can be induced by hydrogen bonding. In the second route, the amphiphily is initiated predominantly by surfactant molecules. In those cases, we have to differentiate between self-assembled surfactant–polyelectrolyte systems and polyelectrolytes in self-assembled surfactant systems.

Polyelectrolytes carrying a low content of hydrophobic side chains are of increasing interest for a wide variety of industrial applications such as: flocculants, thickening agents in oil recovery, latex paints, cosmetics due to the advantage of both the polyelectrolyte and the hydrophobic group effects. The presence of both the charged and non-polar groups in the chain also makes from this kind of polymers convenient systems to explore the role of the electrostatic and hydrophobic interactions on the solution properties of polyelectrolytes which depend strongly on the conformational behavior of the individual chains.

Viscometry is the most widely used experimental method to examine the conformational transition of polyelectrolytes in solution. Viscosity depends very much on the chemical structure of the macroion, its size and charge density but also on the environment properties such as the ionic strength and the solvent polarity. Studies of the viscosity of several solution systems including polystyrene based cationic ionomers, have shown that the addition of an organic solvent leads to conformational changes of polyelectrolytes, with the change in the solvent composition. Reports of the conformational transition of cationic polyelectrolytes dissolved in mixed solvents are relatively scarce.

2.14. Dynamic Mechanical Analyzer (DMA)

When a material is subjected to a force, it deforms. If the material is an ideal elastic material the deformation disappears as soon as the force is removed. The elastic deformation is linear and proportional to the applied stress and occurs instantaneously. However, for some materials such as polymers the elastic deformation cannot be linear and instantaneous. The opposite of elastic behavior is viscous behavior. Viscous behavior is the way a liquid behaves. In ideal viscous behavior strain rate is proportional to stress. Although these basic laws exist theoretically and in some very simple materials, such as steel and water, most important industrial materials like synthetic polymers do not behave entirely as one of these two ideal classes of materials.

Most polymers possess properties of both elastic and viscous materials, and the contribution of each component varies with time, temperature, deformation, and rate of deformation. Polymers fit into a broad class of complex fluids and are characterized by the term viscoelastic (Colo et al., 1997).
Polymeric materials, because of their viscoelastic nature, exhibit behavior during deformation and flow that is both temperature and time (frequency) dependent. For example, if a polymer is subjected to a constant load, the deformation or strain (compliance) exhibited by the material will increase over a period of time. This occurs because the material under a load undergoes molecular rearrangement in an attempt to minimize localized stresses (Foreman, 1997).

DMA is a technique used to measure the mechanical properties of a wide range of materials. Many materials, including polymers, behave both like elastic solid and a viscous fluid, thus the term viscoelastic. Dynamic mechanical analysis (DMA) is a thermal analysis technique that measures the properties of materials as they are deformed under periodic stress. Specifically, in DMA a variable sinusoidal stress is applied, and the resultant sinusoidal strain is measured. If the material being evaluated is purely elastic, the phase difference between the stress and strain sine waves is 0° (i.e., they are in phase). If the material is purely viscous, the phase difference is 90° (Jones, 1999). However, most realworld materials including polymers are viscoelastic and exhibit a phase difference between those extremes. This phase difference, together with the amplitudes of the stress and strain waves, is used to determine a variety of fundamental material parameters, including storage, loss and flexural modulus, complex and dynamic viscosity, storage and loss compliance, transition temperatures, creep, and stress relaxation, as well as related performance attributes such as rate and degree of cure, sound absorption and impact resistance, and morphology (Radebaugh et al., 1983).

The Flexural test measures the force required to bend a beam under 3 point loading conditions. The data is often used to select materials for parts that will support loads without flexing. Flexural modulus is used as an indication of a material's stiffness when flexed. Since the physical properties of many materials (especially thermoplastics) can vary depending on ambient temperature, it is sometimes appropriate to test materials at temperatures that simulate the intended end use environment. The flexural strength of a material is defined as its ability to resist deformation under load (Moniruzzaman, et al., 2006).

Dynamic viscosity is the tangential force per unit area (shear or tangential stress) required to move one horizontal plane with respect to the other. It is also defined as the ratio of the shear stress to the strain rate, determined during forced harmonic oscillation (Mitusova et al., 1981).

DMA measures the viscoelastic properties using either transient or dynamic oscillatory tests. Transient tests include creep and stress relaxation. In creep, a stress is applied to the sample and held constant while deformation is measured vs. time.

After some time, the stress is removed and the recovery is measured. In stres relaxation, a deformation is applied to the sample and held constant, and the degradation of the stress required maintaining the deformation is measured versus time.

Dynamic Mechanical Analysis (DMA) is a sensitive technique that characterizes the mechanical responses of materials by monitoring property changes with respect to the temperature and/or frequency of oscillation. The technique separates the dynamic response of materials into two distinct parts: an elastic part (E') and a viscous or damping component (E"). The elastic process describes the energy stored in the system, while the viscous component describes the energy dissipated during the process. Mechanical loss factor (tan δ) is another useful parameter, which can be very useful in order to compare viscoelastic responses of different materials. The technique has gained a great amount of popularity thanks to its speed and high accuracy and the ability of scanning the materials over a wide range of temperatures and frequencies (Behzad et al., 2004).

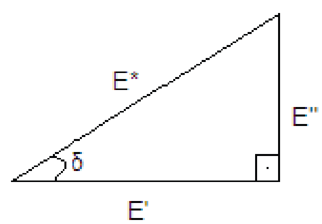


Figure 2.4. Relationship between modulus parameters

E* = stress / strain

E' = E* cos δ (the storage modulus)

E" = E* sin δ (the loss modulus)

tan δ = E" / E' (loss factor)

In a DMA experiment, the sample undergoes repeated small amplitude strains in a cyclic manner. The sample stores a portion of the imparted energy elastically and dissipates a portion in the form of heat. In this case, the modulus acquires a complex form, E*=E′+iE″, in which "i" represents the imaginary unit. The variable E′ (the storage modulus) is a measure of the energy stored elastically and represents the elastic or fully recoverable energy during deformation. Whereas E″ (the loss modulus) is a measure of the energy lost as heat and it represents the viscous or net energy dissipated. The loss factor is defined as tan delta (δ) =E″/E′, δ being the angle between the in phase and out of phase components in the cyclic motion and measures the damping capability of the material (Li et al., 2000; Picciochi et al., 2006).

The most common test is the dynamic oscillatory test, where a sinusoidal stress or strain) is applied to the material and a resultant sinusoidal strain (or stress) is measured. Due to the time-dependent properties of viscoelastic materials the resultant response is out-of-phase with the applied stimulus. It has been discussed that the observed complex modulus and its resolution into the recoverable stored energy (storage modulus) and dissipated energy in the form of loss modulus or phase lag (Bashaiwoldu et al., 2003).

Dynamic mechanical analysis (DMA) which measures the modulus (stiffness) and damping (energy dissipation) properties of a material as the material is deformed under periodic stress is one of the best thermal analysis techniques for using this time/temperature predictive approach. These measurements provide quantitative and qualitative information about the performance of materials. DMA is particularly useful for evaluating polymeric materials, which exhibit time, frequency, and temperature effects on mechanical properties because of their viscoelastic nature. The DMA is essentially able to detect all changes in the state of molecular motion in a viscoelastic solid as a function of temperature (Barral et al., 2000).

With sufficient heat supplied to the polymer, molecular motion is increased and molecules can slide against one another as the polymer becomes viscous, rubbery, and flexible. Such a physical change from an immobilized conformation to a flexible structure, which reflects an increase in motion of major segments of the polymer backbone, is called the glass transition. The glass transition is associated with the onset of large range cooperative segmental mobility in the amorphous phase, in either an amorphous or semi-crystalline polymer (Yang and Jia, 2004).

Glass transition in highly crystalline polymers is difficult to identify. This is true because in such cases Tg is a minor event, masked by crystallinity, and because crystalline polymers frequently have multiple transitions arising from relaxations associated with amorphous phase, the crystalline phase, or both (Behzad et al., 2004).

This method does not require any special sample (only stacking of coated supports or sample sandwiching) whilst it enables to characterize in situ polymer coating, even nano-coating. This characterization is of prime interest in technological coating developments such as paints, fiber sizing, glue, hair gel, etc. This possible measurement of thermal transitions peculiar to nano-coatings also opens more fundamental studies as the probing of interface influence on thermal transitions (Carlier et al., 2000).

Some main advantages of this technique are mentioned in Carlier et al.'s study, such as sensitivity, facility, repeatability and accuracy with a wide range of applications.

2.15. Differential Scanning Calorimeter (DSC)

Differential scanning calorimetry (DSC) is a technique for measuring the energy necessary to establish a nearly zero temperature difference between a substance and an inert reference material, as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate (Bhadeshia, 2003).

DSC is a thermo-analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Both the sample and reference are maintained at nearly the very same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned. The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more (or less) heat will need to flow to it than the reference to maintain both at the same temperature. Whether more or less heat must flow to the sample depends on whether the process is exothermic or endothermic (Dean, 1995).

By observing the difference in heat flow between the sample and reference, differential scanning calorimeters are able to measure the amount of heat absorbed or released during such transitions. DSC may also be used to observe more subtle phase changes, such as glass transitions (Pungor, 1995).

DSC is widely used in industrial settings as a quality control instrument due to its applicability in evaluating sample purity and for studying polymer curing. It can be used to measure a number of characteristic properties of a sample. Using this technique it is possible to observe fusion and crystallization events as well as glass transition temperatures (Tg). DSC can also be used to study oxidation, as well as other chemical reactions. This method is widely used in the pharmaceutical and polymer industries. For the polymer chemist, DSC is a handy tool for studying curing processes, which allows the fine tuning of polymer properties. The cross-linking of polymer molecules that occurs in the curing process is exothermic, resulting in a positive peak in the DSC curve that usually appears soon after the glass transition (Skoog et al., 1998).

2.16. Thermal Gravimetric Analysis (TGA)

Thermo-gravimetric analysis (TGA) is an analytical technique used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated. The measurement is normally carried out in air or in an inert atmosphere, such as Helium or Argon, and the weight is recorded as a function of increasing temperature. In addition to weight changes, some instruments also record the temperature difference between the specimen and one or more reference pans (differential thermal analysis, DTA). The latter can be used to monitor the energy released or absorbed via chemical reactions during the heating process (Riqueza et al., 2007).

A derivative weight loss curve can be used to tell the point at which weight loss is most apparent. TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, to determine degradation temperatures, absorbed by moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives and solvent residues (Chrissafis et al., 2007).

The basic principle in TGA is to measure the mass of a sample as a function of temperature. This, in principle, simple measurement is an important and powerful tool in solid-state chemistry and materials science. The method for example can be used to determine water of crystal, follow degradation of materials, determine reaction kinetics, study oxidation and reduction, or to teach the principles of stoichiometry, formulae and analysis. Drying, structural water release, structural decomposition, carbonate decomposition, gas evolution, sulfur oxidation, fluoride oxidation, and re-hydration are characteristic properties that can be measured by thermal gravimetric analysis (Meng et al., 2007; Kaczmarek et al., 2007).

2.17. X-Ray Diffraction (XRD)

The determination of the percentage crystallinity has always been of great importance for the understanding of the material properties of polymeric and fibrous materials. In the study of these types of materials many methods for the determination of the crystalline to amorphous ratio have been developed. One method that is unique in its ability to study the microstructure of materials is x-ray diffraction. X-ray diffraction will give very distinct patterns for crystalline and amorphous materials. The diffracting xrays interact with the variation of electron density inside the sample. X-ray diffraction can be used in a number of different ways to determine the amorphous to crystalline ratio. With the recent increase in the speed of development of new drugs and biotechnologies, the determination of the amorphous to crystalline ratio of an organic material has become increasingly important (Kratos, 1999).

X-ray crystallography, also known as single-crystal X-ray diffraction, is the oldest and most common crystallographic method for determining the structure of molecules. This method is widely used in chemistry and biochemistry (Scapin, 2006).

3. EXPERIMENTAL

3.1. Materials

Poly(methyl vinyl ether-alt-maleic anhydride) [Mn~485.000] and diglycidyl ether terminated- PDMS [Mn~980] were supplied by Aldrich Chemical Co.Ltd. Dioxane as a solvent for membrane preparation was obtained from Fluka at an analytical grade.

Poly(methyl vinyl ether-alt-maleic anhydride) [Mn~485.000] and hydroxy terminated- PDMS [Mn~550] were supplied by Aldrich Chemical Co.Ltd. Dioxane as a solvent for membrane preparation was obtained from Fluka at an analytical grade.

Poly(maleic anhydride-1,hexene-acrylic acid) terpolymer which was synthesis and diglycidyl ether terminated- PDMS [Mn~980] was supplied by Aldrich Chemical Co.Ltd. Dioxane as a solvent for membrane preparation was obtained from Fluka at an analytical grade.

3.2. Synthesis of Terpolymer

Terpolymerization reactions of monomer and complexing monomer pairs of the M.A – 1,H – A.A ternary system were carried out in 1,4 Dioxane in the presence of BP as an initiator at 70-75 ^{0}C around 8 hours under nitrogen atmosphere. Glass tube type of microreactors were used. The terpolymers synthesized using 1:1:2 mol ratios of initial monomers had 5.0 mol/L^{-1} total monomer concentration. There different initiator ratios were tried [(0.5 – 1.0 – 2.0 %)(per mole)] for the optimization of the initiator effect. Terpolymers were isolated from the reaction mixture by precipitation with n-hexene and dried under moderate vacuum at 40 ^{0}C.

3.3. Membrane Preparation

Poly(methyl vinyl ether-alt-maleic anhydride) and diglycidyl ether terminated PDMS were dissolved in dioxane at 25^0C at a percent of 40%(w/w)PDMS for the preparation of casting solution. Membrane was prepared by pouring the casting solution onto rimmed Teflon plates, and then allowing the solvent to evaporate completely at 25 ^{0}C.

Because of thermally self crosslinkable properties of the maleic anhydride and glycidyl ether groups, membranes were crosslinked thermally at 115 ^{0}C.

Poly (methyl vinyl ether-alt-maleic anhydride) and hydroxy terminated PDMS were dissolved in dioxane at 25 ^{0}C at a percent of 40% (w/w) PDMS for the preparation of casting solution. Membrane was prepared by pouring the casting solution onto rimmed Teflon plates, and then allowing the solvent to evaporate completely at 25 ^{0}C.

Because of thermally self crosslinkable properties of the maleic anhydride and hydroxy groups, membranes were crosslinked thermally at 115 ^{0}C.

Poly (maleic anhydride-1,hexene-acrylic acid) terpolymer and diglycidyl ether terminated PDMS and %0.1 (w/w) triethyl amin as a catalyst were dissolved in dioxane at 25 ^{0}C at a percent of 30% (w/w) PDMS for the preparation of casting solution. Membrane was prepared by pouring the casting solution onto rimmed Teflon plates, and then allowing the solvent to evaporate completely at 25 ^{0}C.

Because of thermally self crosslinkable properties of the maleic anhydride and glycidyl ether groups, membranes were crosslinked thermally at 115 ^{0}C.

3.4. Analysis

3.4.1. FTIR

The FTIR spectra of the membranes before and after thermal-treatment were recorded using a Nicolet 510 spectrometer in the 4000-400 cm^{-1} range. 30 scans were taken at a 4 cm^{-1} resolution.

3.4.2. DMA Measurements

DMA measurements were done by TA Instruments Q800 Dynamic Mechanic Analyzer. Different deformation modes were detected by Clamp system, which allows working with powder samples by mixing these samples with Al_2O_3 (50%w/w).Calibration is achieved for the Clamp system before the measurements.

3.4.3. DSC Measurements

DSC measurements were performed on a Shimadzu, TA-60WS Thermal Analyzer at a heating rate of 10 ºC/min, a temperature range of 25 to 400 ºC and sample mass of 10 mg. The reported glass transition temperatures were determined from the second heating run as the middle points of the characteristic enthalpy step.

3.4.4. TGA Measurements

TGA measurements were recorded on Shimadzu, TA-60WS Thermal Analyzer at a heating rate of 10 ºC/min, a temperature range of 25 to 800 ºC and sample mass of 7-10 mg.

3.4.5. XRD Measurements

X-ray diffraction patterns were taken at Hacettepe University, in Geology Department by using a Rigaku D/MAX 2200 PC X-ray Powder Diffractometer. The Cu anode Xray tube was operated at 40kV and 36mA in combination with a Ni filter to give monochromatic CuKα X-rays. Measurements were taken from 0º to

60º in the Bragg's angle 2θ scale. Diffractograms were taken at room temperature consecutively. Crystalline and amorphous regions have been found by Polynomial Regression method through Microsoft Office Excel 2003 program and subsequently, percentage crystallinities were evaluated.

3.4.6. Percent crosslinking

Percent crosslinking was determined gravimetrically using the following equation;

$$\text{Percent crosslinking}(\%) = W_2 \times 100 / W_1$$

where W_1 and W_2 are the dry weights of the sample before curing and after curing and dissolution,respectively.

3.4.7. Swelling

Swelling degree (S) of physically crosslinked polymers in DMF was determined gravimetrically using the following equation:

$$S(\%) = [(M_t - M_o) / M_o] \times 100$$

where M_o is the dry/initial weight of sol-gel, M_t is the weight of swollen sol-gel at given time (t) in DMF.

4. RESULTS AND DISCUSSION

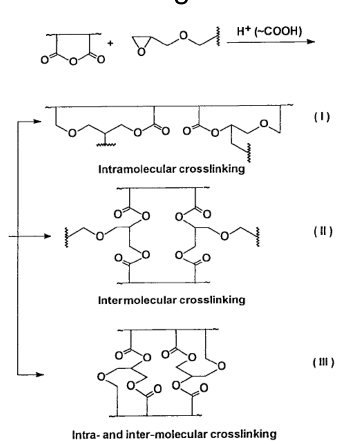
4.1. Synthesis of Membranes

Membranes were prepared from diglicidyl ether terminated PDMS and poly (methyl vinyl ether-alt-maleic anhydride) copolymer, hydroxy terminated PDMS and poly (methyl vinyl ether-alt-maleic anhydride) copolymer, diglicidyl ether terminated PDMS and poly (maleic anhydride-1,hexene-acrylic acid) terpolymer ; containing highly reactive free epoxide, hydroxy and anhydride groups in the side chain which easily undergo crosslinking by thermotreatment at 100 – 120 ^{0}C. As a result of crosslinking reaction, membranes become insoluble.

4.1.1. Crosslinking reaction of diglicidyl ether terminated PDMS and poly (methyl vinyl ether-alt-maleic anhydride) copolymer

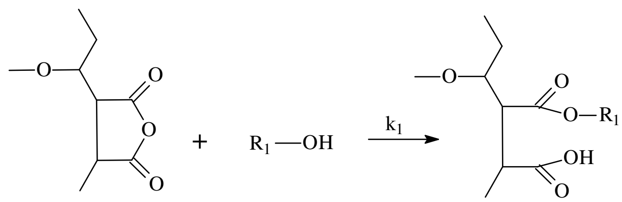
It is well known that anhydrides of organic dicarbonic acids are effective crosslinker for epoxy oligomers. The epoxy group is characterized by its reactivity towards nucleophilic and electrophilic species and thus it is reactive to a wide range of reagents.

The intermolecular epoxy-anhydride reaction is catalysed by free carboxyl groups, traces of which can be formed as a result of the opening reaction of the anhydride ring with atmospheric water in the film forming process. Crosslinking of macromolecules can proceed through intra- and inter-molecular reactions of anhydride and epoxy fragments according to the following scheme:

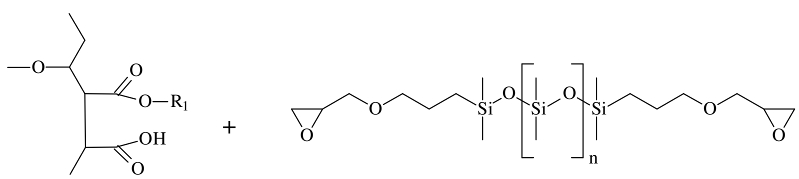


The generally accepted stepwise reaction mechanism is schematically shown in Figure 4.1.

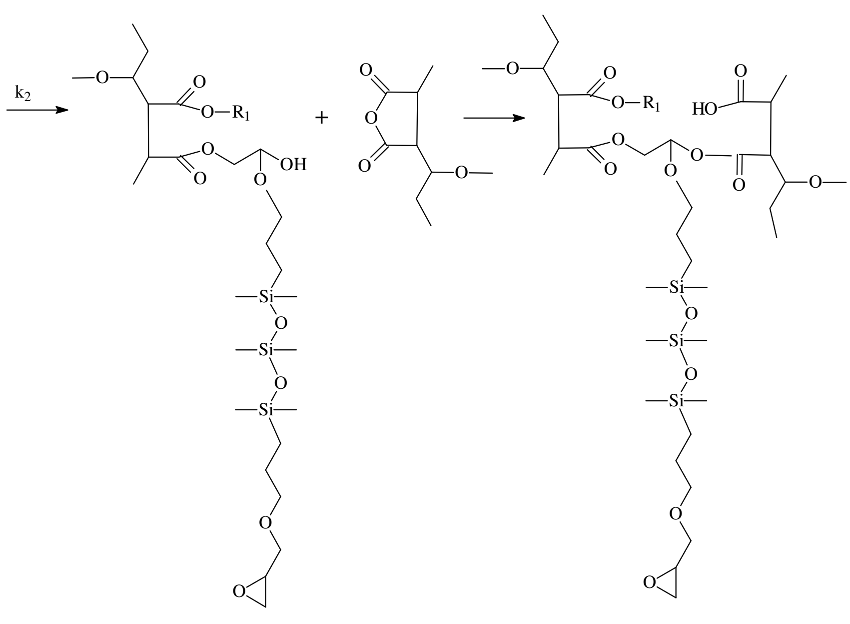
Step 1



Step 2



Step 3



Step 4

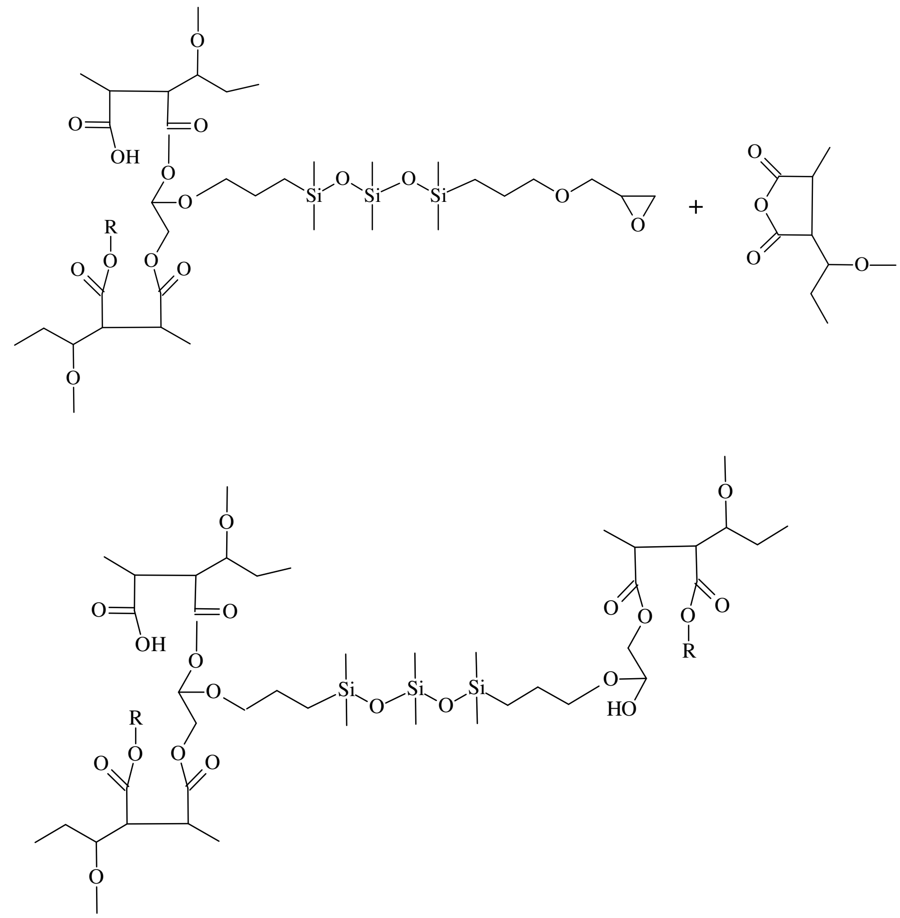


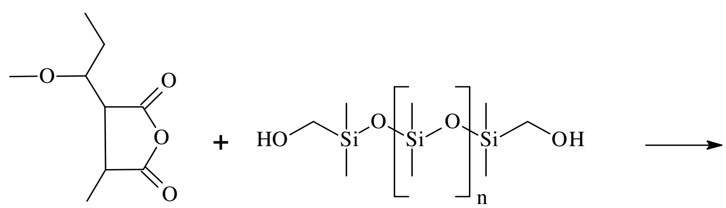
Figure 4.1. Schematic representation of crosslinking reaction of DGE terminated PDMS and poly (MVE-alt-MA) copolymer

During the hydroxy-anhydride initiation (step1), the OH-group donates its proton and thus opens the anhydride ring and generates an ester group and carboxylic acid group. The carboxylic acid then reacts with another epoxy group, forming a diester (step 2) yielding a secondary hydroxyl group. Ideally, this reaction proceeds now by the alternating addition of anhydride and epoxy until the sequence is terminated by condensation of one terminal carboxylic acid and alcohol to an ester linkage (step 3-4).

4.1.2. Crosslinking reaction of hydroxy terminated PDMS and poly (methyl vinyl ether-alt-maleic anhydride) copolymer

The reaction between a hydroxy compound and an anhydride proceeds in two steps.

Step 1



Step 2

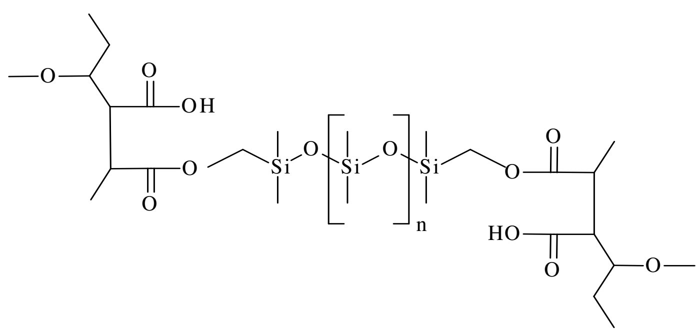


Figure 4.2. Schematic representation of crosslinking reaction of OH terminated PDMS and poly (MVE-alt-MA) copolymer

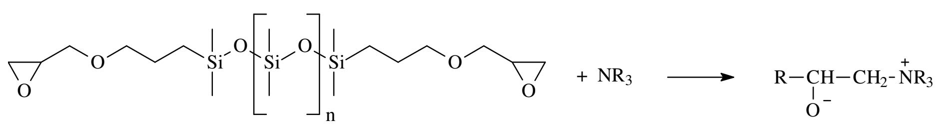
Esterification of the anhydride (step 1) to form an ester and a free acid group, followed by esterification of the remaining free acid groups.

An attact of hydroxyl groups on the anhydride molecules results in a monoester having a free carboxyl group (step 1). This free carboxyl group (monoester) then reacts with other hydroxy group to yield a diester (step 2).

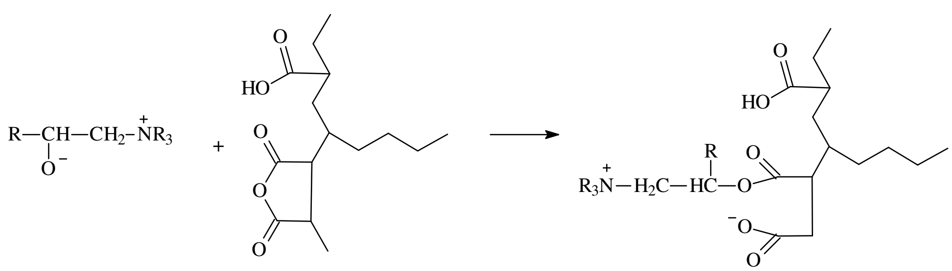
4.1.3. Crosslinking reaction of diglicidyl ether terminated PDMS and poly (maleic anhydride -1,hexene - acrylic acid) terpolymer

An essentially different mechanism occurs when strong Lewis bases, e.g. tertiary amine, imidazoles or ammonium salts, are used to catalyze the polymerization. In case of technical monomers, the curing reaction might be described as shown in Figure 4.3.

Step 1

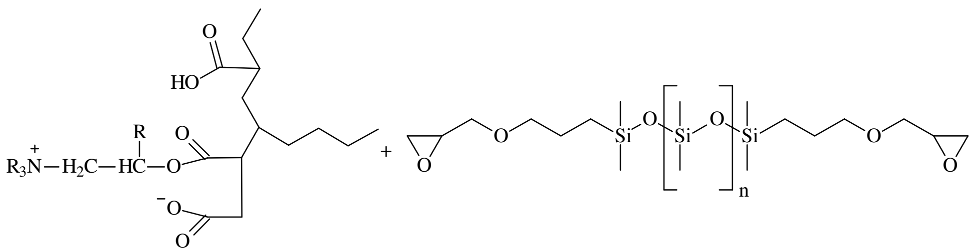


Step 2



It is proposed that the tertiary amine reacts with the epoxy monomer and forms a zwitterion that contains a quaternary nitrogen atom and an alkoxide as shown in step 1 reaction. The alkoxide rapidly reacts further with an anhydride group leading to a carboxylate anion as shown by reaction step 2. This carboxylate anion may be considered as active center for the chainwise alternating co-polymerization.

Step 3



Step 4

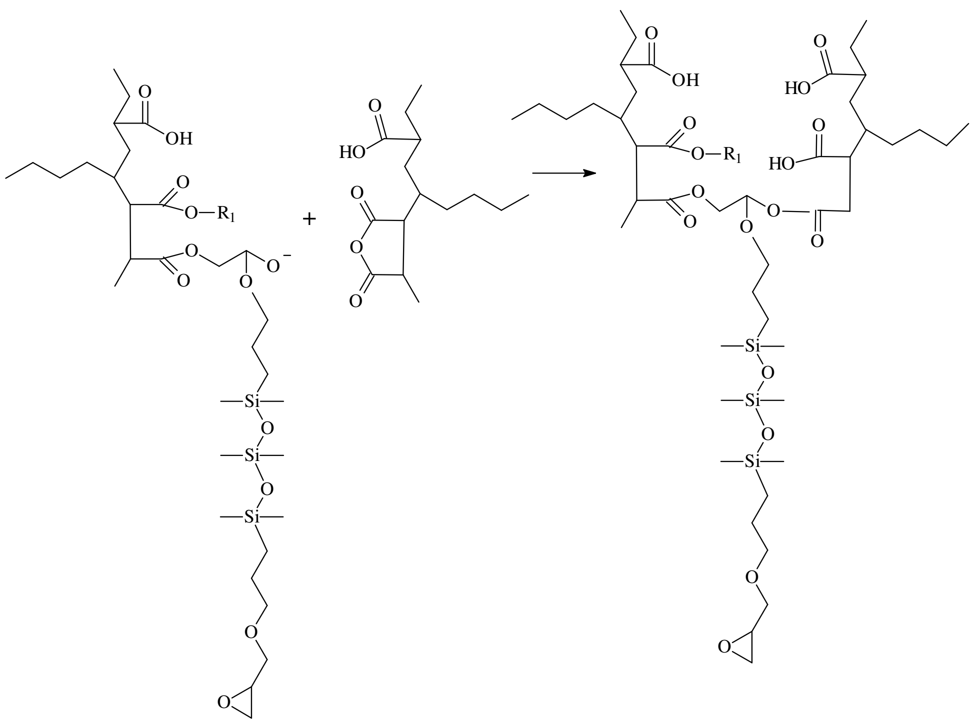


Figure 4.3. Schematic representation of crosslinking reaction of DGE terminated PDMS poly (MA -1,H - AA) terpolymer

Propagation occurs through the reaction of the generated carboxylate with an epoxy group and the accompanied formation of new alkoxide anion, (reaction step 3). This, in turn, reacts at a very fast rate with an anhydride group regenerating the carboxylate anion, (reaction step 4).

4.2. Characterization of Membranes

4.2.1. Determination of Percent Crosslinking

3 hours curing process at different PDMS contents was investigated for the optimization. Crosslinked polymer was submerged into 1,4 Dioxane with consistent stirring at room temperature for 24 hours to dissolved uncrosslinked polymers. The undissolvable part was washed again with 1,4 Dioxane to remove the unreacted polymers. It was dried in a vacuum oven for 24h. Percent crosslinking was calculated.

Table 4.1. comprises the relation between the PDMS content and % conversion for diglicidyl ether terminated PDMS and poly (methyl vinyl ether-alt-maleic anhydride) copolymer, hydroxy terminated PDMS and poly (methyl vinyl ether-alt-maleic anhydride) copolymer, diglicidyl ether terminated PDMS and poly(maleic anhydride -1,hexene – acrylic acid) terpolymer.

As shown in the table, %40(w/w) PDMS content was selected as an optimum value for poly (methyl vinyl ether-alt-maleic anhydride) and diglycidyl ether terminated PDMS, poly (methyl vinyl ether-alt-maleic anhydride) and hydroxy terminated PDMS. %30(w/w) PDMS content was selected for poly (maleic anhydride-1,hexene-acrylic acid) terpolymer and diglycidyl ether terminated PDMS.

Table 4.1. Conversion percents of crosslinked structures.

Poly(MVE-alt-MA)- DGE terminated PDMS	
% PDMS(w/w)	**% conversion**
70	45
60	59
50	76
40	91
30	72

Poly(MVE-alt-MA)- OH terminated PDMS	
% PDMS(w/w)	**% conversion**
70	46
60	58
50	74
40	90
30	70

Poly(MA -1,H - AA)- DGE terminated PDMS	
% PDMS(w/w)	**% conversion**
75	29
70	39
60	50
50	60
40	71
30	87
20	70

4.2.2. FTIR analysis

Vibrational spectroscopy plays an important role in the elucidiation of molecular structure. The vibrational spectrum of a polymer is determined by its conformational state and the nature of the force field. Thus a detailed analysis of its IR and Raman spectra provide an insight into intramolecular interactions. The study of vibrational spectra involve assignment of frequencies to vibrational modes which in turn leads to the distribution of potential energy in the internal/external coordinates.

It is quite well known that the relation of a related functional group may be followed much more clearly and precisely by FTIR measurements. These spectrometric behaviors of the studied systems have been investigated in detail and the stretching frequency shifts have brought a clear interpretation for the interaction dynamism.

Fourier transform infrared (FT-IR) spectroscopy has been widely used by many researches. FTIR spectrum provides information regarding intermolecular interaction via analysis of FTIR spectra corresponding to stretching or bending vibrations of particular bonds and the positions at which these peaks appear depends directly on the force constant or bond strength. Hydrogen bonding or other secondary interactions between chemical groups on the dissimilar polymers should theoretically cause a shift in peak position of the participating groups.

4.2.2.1. Membrane of poly(methyl vinyl ether-alt-maleic anhydride)-diglycidyl ether terminated PDMS

Figure 4.4 shows the FTIR spectra of poly (methyl vinyl ether-alt-maleic anhydride) before curing and crosslinked structure of poly(methyl vinyl ether-alt-maleic anhydride) and diglycidyl ether terminated PDMS after 3 hours, 115 ^{0}C curing conditions.

As shown in the Figure 4.4, the spectrum of poly(methyl vinyl ether-alt-maleic anhydride) copolymer before curing shows characteristic bands of stretching of C=O group in anhydride ring at 1856, 1781 cm^{-1} , and also at 1737 cm^{-1} for C=O stretching of carboxylic acid occurs. These bands are important for comperative analysis. In this spectrum 1070 cm^{-1} characterizes the stretching band for C-O-C groups of anhydride . Weak band at 736 cm^{-1} refers O-C=O bending of anhydride unit and also at 624 cm^{-1} C-H bending occurs for anhydride unit. 925 cm^{-1} corresponding to OH bending for carboxylic acid.

The comperative analysis of FTIR spectra between poly(methyl vinyl ether-alt-maleic anhydride) copolymer and the crosslinked membrane prepared from poly(methyl vinyl ether-alt-maleic anhydride) and diglycidyl ether terminated PDMS at 40%(w/w) PDMS content, has yielded interesting results with regard to the peaks appearing at 1737 cm^{-1}(carboxyl group), 1722 cm^{-1} (ester formation) which confirm a crosslinking reaction.

The intensity of the distinguishing symmetric and asymmetric stretching bands for C=O group and C-O-C bond of maleic anhydride unit appearing at 1856, 1781, 1070,and 736 cm^{-1} gradually decreased. All anhydride functional group peak intensities decrease progressively through out the entire cure. The total conversion of the functional anhydride groups can be gained using the typical anhydride ring vibrations at 1856 and 1781 cm^{-1}, respectively.

A new band appears for ester groups at 1722 cm^{-1} in the spectra of crosslinked poly(methyl vinyl ether-alt-maleic anhydride) and diglycidyl ether terminated PDMS which have been thermothreated. There are to many peaks appearing after thermo treatment which are the characteristics of siloxane groups.

The infrared spectra frequencies and the spectral characterizations of before and after curing reaction of poly(methyl vinyl ether-alt-maleic anhydride) and diglycidyl ether terminated PDMS are given in Table 4.2.

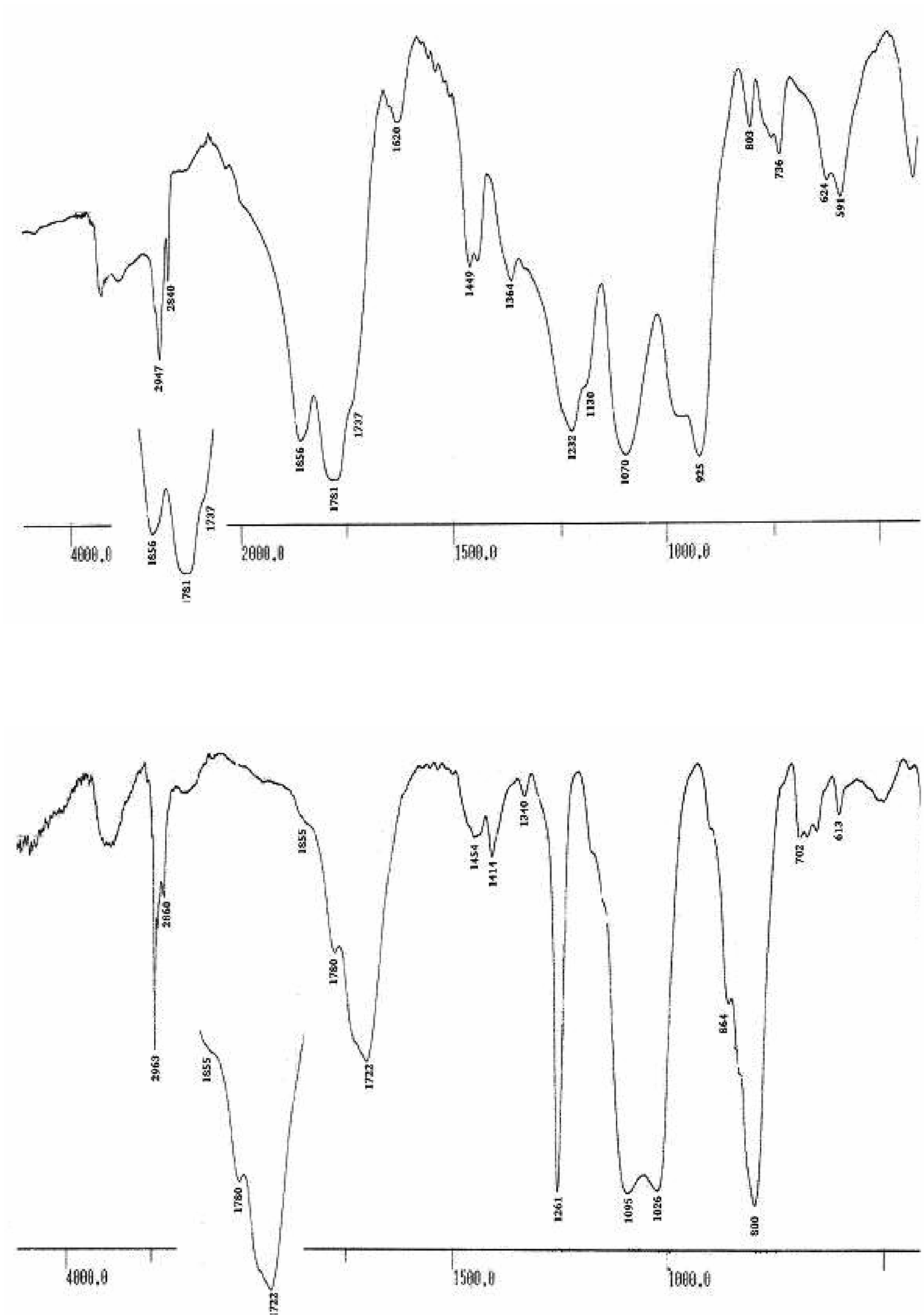


Figure 4.4. FTIR spectra of poly(MVE-alt-MA) before curing and crosslinked structure of poly(MVE-alt-MA) and DGE terminated PDMS after thermotreatment. (membrane 1)

Table 4.2. Characteristic FTIR bands before and after curing of membrane 1

CHARACTERISTIC FTIR BANDS BEFORE CURING OF COPOLYMER	
Frequency (cm^{-1})	***Assignment***
2947	C-H *stretching*
1856,1781	C=O *stretching for anhydride ring*
1737	C=O *stretching for carboxylic acid*
1458	CH_2 *bending*
1070	C-O-C *stretch of anhydride*
1364	*Symmetric* CH_2 *bending*
1232	C(=O)O *stretching of anhydride*
925	OH *bending for carboxylic acid*
736	O-C=O *bending of anhydride units*
624	C-H *bending of anhydride units*

CHARACTERISTIC FTIR BANDS AFTER CURING	
Frequency(cm^{-1})	***Assignment***
2963	$Si(CH_3)_2$-O- $Si(CH_3)_2$ *stretching*
1855,1780	C=O *stretching for anhydride ring*
1722	C=O *stretching for ester*
1454	CH_2 *bending*
1340	*Symmetric* CH_2 *bending*
1261	Si- CH_3 *stretch*
1095,1026	Si-O-Si *stretch*
868	Si- CH_3 *stretch*
802	Si- CH_3 *stretch*
702	O-C=O *bending of anhydride units*
613	C-H *bending of anhydride units*

4.2.2.2. Membrane of poly(methyl vinyl ether-alt-maleic anhydride)- hydroxy terminated PDMS

Figure 4.5 shows the FTIR spectra of poly (methyl vinyl ether-alt-maleic anhydride) before curing and crosslinked structure of poly(methyl vinyl ether-alt-maleic anhydride) and hydroxyl terminated PDMS after 3 hours, 115 ^{0}C curing conditions.

As shown in the Figure 4.5, the spectrum of poly(methyl vinyl ether-alt-maleic anhydride) copolymer before curing shows characteristic bands of stretching of C=O group in anhydride ring at 1856, 1781 cm^{-1} , and also at 1737 cm^{-1} for C=O stretching of carboxylic acid occurs. These bands are important for comperative analysis. In this spectrum 1070 cm^{-1} characterizes the stretching band for C-O-C groups of anhydride . Weak band at 736 cm^{1} refers to O-C=O bending of anhydride unit and also at 624 cm^{-1} C-H bending for anhydride unit occurs. 925 cm^{-1} corresponding to OH bending for carboxylic acid.

The comperative analysis of FTIR spectra between poly(methyl vinyl ether-alt-maleic anhydride) copolymer and the crosslinked membrane prepared from poly(methyl vinyl ether-alt-maleic anhydride) and hydroxy terminated PDMS at 40%(w/w) PDMS content disclose the important differences. The intensity of the distinguishing symmetric and a symmetric stretching bands for C=O group and C-O-C bond of maleic anhydride unit appearing at 1856, 1781, 1070,736 cm^{-1} gradually decrease. All anhydride functional group peak intensities decrease progressively through out the entire cure. The total conversion of the functional anhydride groups can be gained using the typical anhydride ring vibrations at 1856 and 1781 cm^{-1}, respectively.

A new band appears for ester groups at 1720 cm^{-1} in the spectra of crosslinked poly(methyl vinyl ether-alt-maleic anhydride) and hydroxy terminated PDMS which have been thermothreated. There are to many peaks appearing after thermo treatment which are the characteristics of siloxane groups at 1260,1093,1028,868 and 802 cm^{-1}, respectively. These bands are definitely the evidence of PDMS addition for the crosslinking reaction.

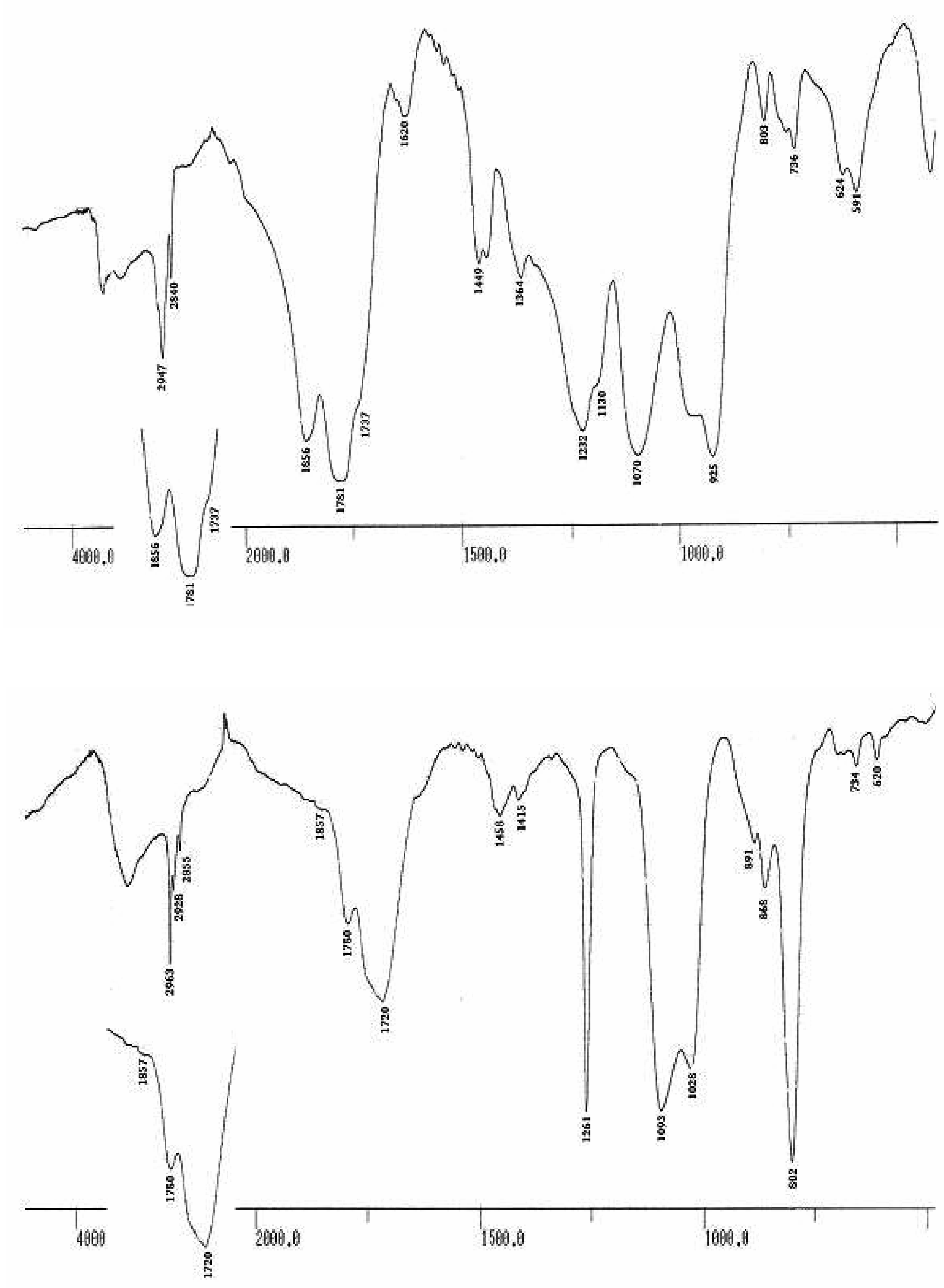


Figure 4.5. FTIR spectra of poly(MVE-alt-MA) before curing and crosslinked structure of poly(MVE-alt-MA) and OH terminated PDMS after thermotreatment (membrane 2)

The infrared spectra frequencies and the spectral characterizations of before and after curing reaction of Poly(methyl vinyl ether-alt-maleic anhydride) and hydroxy terminated PDMS are given in Table 4.3

Table 4.3. Characteristic FTIR bands before and after curing of membrane 2.

CHARACTERISTIC FTIR BANDS BEFORE CURING OF COPOLYMER	
Frequency(cm^{-1})	***Assignment***
2947	C-H *stretching*
1856,1781	C=O *stretching for anhydride ring*
1737	C=O *stretching for carboxylic acid*
1458	CH_2 *bending*
1070	C-O-C *stretch of anhydride*
1364	*Symmetric* CH_2 *bending*
1232	C(=O)O *stretching of anhydride*
925	OH *bending for carboxylic acid*
736	O-C=O *bending of anhydride units*
624	C-H *bending of anhydride units*

CHARACTERISTIC FTIR BANDS AFTER CURING	
Frequency(cm^{-1})	***Assignment***
2963	$Si(CH_3)_2$-O- $Si(CH_3)_2$ *stretching*
1857,1780	C=O *stretching for anhydride ring*
1720	C=O *stretching for ester*
1458	CH_2 *bending*
1415	*Symmetric* CH_2 *bending*
1261	Si- CH_3 *stretch*
1093,1028	Si-O-Si *stretch*
868	Si- CH_3 *stretch*
802	Si- CH_3 *stretch*
702	O-C=O *bending of anhydride units*
613	C-H *bending of anhydride units*

4.2.2.3. Membrane of poly(maleic anhydride-1,hexane-acrylic acid)-diglycidyl ether terminated PDMS

Figure 4.6 refers to the FTIR spectra of poly(maleic anhydride -1,hexene - acrylic acid) terpolymer before curing and crosslinked structure of poly(maleic anhydride -1,hexene - acrylic acid) terpolymer and diglycidyl ether terminated PDMS after 3 hours, 115 ^{0}C curing conditions.

FTIR spectrum of terpolymer are characterized by the typical absorption bands of stretching of C=O group in anhydride ring at 1854, 1779 cm^{-1} , and also at 1732 cm^{-1} for C=O stretching of carboxylic acid for acrylic acid occurs. At 1072 cm^{-1} (for MA) and 1454 cm^{-1} (for H-1) characteristic absorption bands appeared. In this spectrum 1072 cm^{-1} characterizes the stretching band for C-O-C groups of anhydride . Weak band at 738 cm^{-1} refers to the O-C=O bending of anhydride unit. 920 cm^{-1} corresponds to OH bending for carboxylic acid.

As a result of curing reaction, new bands appear for ester groups at 1722 cm^{-1} and for siloxane groups at 1262, 1096, 1024, 870, 800 cm^{-1}, respectively, in the spectra of crosslinked poly(maleic anhydride -1,hexene – acrylic acid) terpolymer and diglycidyl ether terminated PDMS .

The infrared spectra frequencies and the spectral characterizations of before and after curing reaction of poly(maleic anhydride -1,hexene – acrylic acid) terpolymer and diglycidyl ether terminated PDMS are given in Table 4.4.

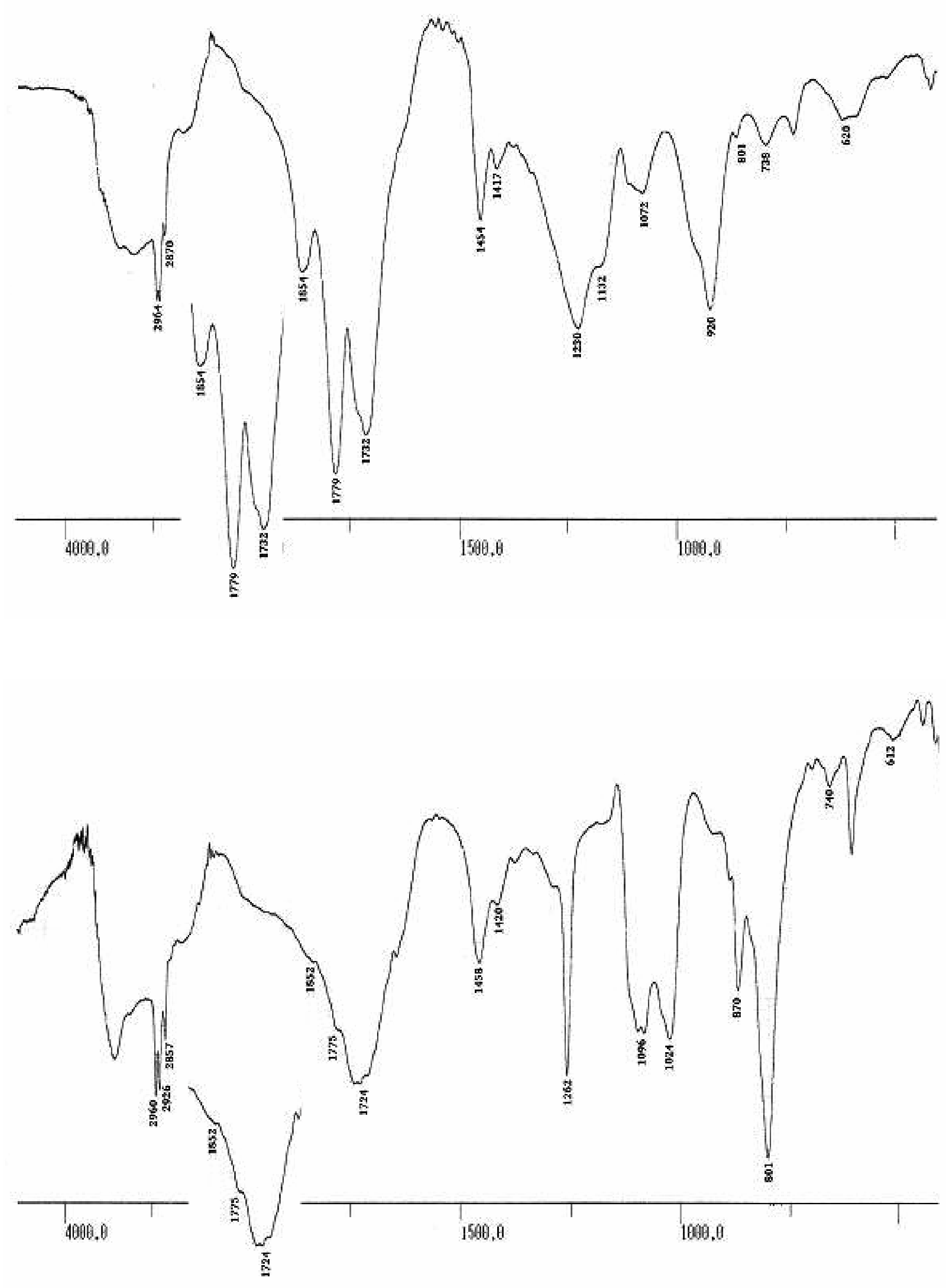


Figure 4.6. FTIR spectra of poly(MA-1,H-AA) before curing and crosslinked structure of poly(MA-1,H-AA) and DGE terminated PDMS after thermotreatment. (membrane 3)

Table 4.4. Characteristic FTIR bands before and after curing of membrane 3.

CHARACTERISTIC FTIR BANDS BEFORE CURING OF TERPOLYMER	
Frequency(cm^{-1})	***Assignment***
2964	C-H *stretching*
1854,1779	C=O *stretching for anhydride ring*
1732	C=O *stretching for carboxylic acid*
1454	CH_2 *bending*
1072	C-O-C *stretch of anhydride*
1417	*Symmetric* CH_2 *bending*
1230	C(=O)O *stretching of anhydride*
920	OH *bending for carboxylic acid*
738	O-C=O *bending of anhydride units*
620	C-H *bending of anhydride units*

CHARACTERISTIC FTIR BANDS AFTER CURING	
Frequency(cm^{-1})	***Assignment***
2960	$Si(CH_3)_2$-O- $Si(CH_3)_2$ *stretching*
1852,1775	C=O *stretching for anhydride ring*
1724	C=O *stretching for ester*
1458	CH_2 *bending*
1420	*Symmetric* CH_2 *bending*
1262	Si- CH_3 *stretch*
1096,1024	Si-O-Si *stretch*
870	Si- CH_3 *stretch*
800	Si- CH_3 *stretch*
740	O-C=O *bending of anhydride units*
613	C-H *bending of anhydride units*

4.2.3. NMR analysis

The investigation of microstructure of the copolymer is very effective in establishing the structure-property relationships (Bruce et al., 1998). High resolution NMR spectroscopy has been a powerful tool for the determination of the microstructure (Aerds et al., 1991). The copolymer structures were investigated on the basis of high resolution ^{1}H NMR and ^{13}C NMR.

4.2.3.1. ^{1}H NMR analysis

^{1}H-NMR spectrum for after thermo-treatment diglycidyl ether terminated PDMS and poly(methyl viniyl ether-alt-maleic anhydride) copolymer mixture is presented in Figure 4.7.

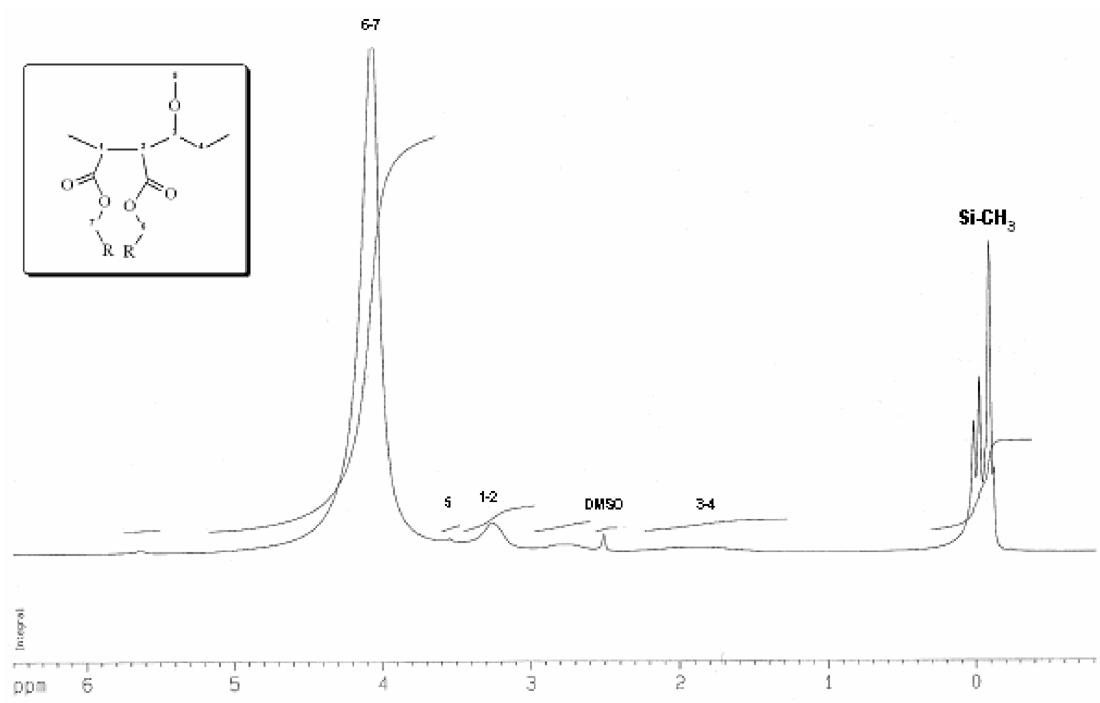


Figure 4.7. ^{1}H-NMR spectrum for crosslinked structure of DGE terminated PDMS and poly(MVE-alt-MA) copolymer

Due to the ring opening at epoxide group, ester formation occurs after the reaction between maleic anhydride and epoxy groups as a result of thermo-treatment.

As can be seen from the Figure 4.8, the characteristic peaks in the ^1H NMR spectrum of the crosslinked structure of diglycidyl ether terminated PDMS and poly(methyl viniyl ether-alt-maleic anhydride) copolymer can be identified as: methyl groups of Si-CH_3 at 0.01-0.014 ppm, (1,2) 2H, CH for MA unit at 3.3 ppm; (7,6) 2H, CH_2 in –CH_2-OOC- at 4.1ppm. The peaks at 2.5 ppm belong to DMSO, respectively.

Figure 4.8 refers to the crosslinked structure of hydroxy terminated PDMS and poly(methyl viniyl ether-alt-maleic anhydride) copolymer.

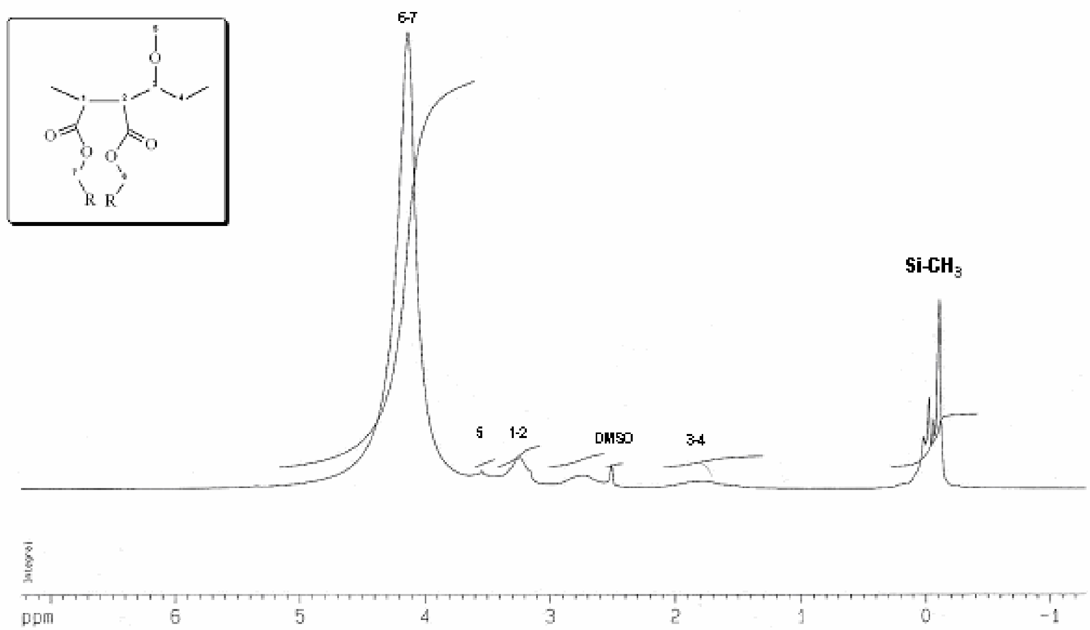


Figure 4.8. ^1H-NMR spectrum for crosslinked structure of OH terminated PDMS and poly(MVE-alt-MA) copolymer

As shown in the figure after thermotreatment new characteristic peaks for siloxane at 0.01-0.02 ppm and ester groups at 4.14 ppm appear. ^1H NMR spectrum of the crosslinked structure can be identified as: methyl gorups of Si-CH_3 at 0.01-0.02 ppm, (1,2) 2H, CH for MA unit at 3.2-3.3 ppm; (7,6) 2H, CH_2 in –CH_2-OOC- at 4.14 ppm. The peaks at 2.5 ppm belong to DMSO, respectively.

Figure 4.9 refers to the ¹H-NMR spectrum of poly(maleic anhydride -1,hexene – acrylic acid) terpolymer which was synthesized.

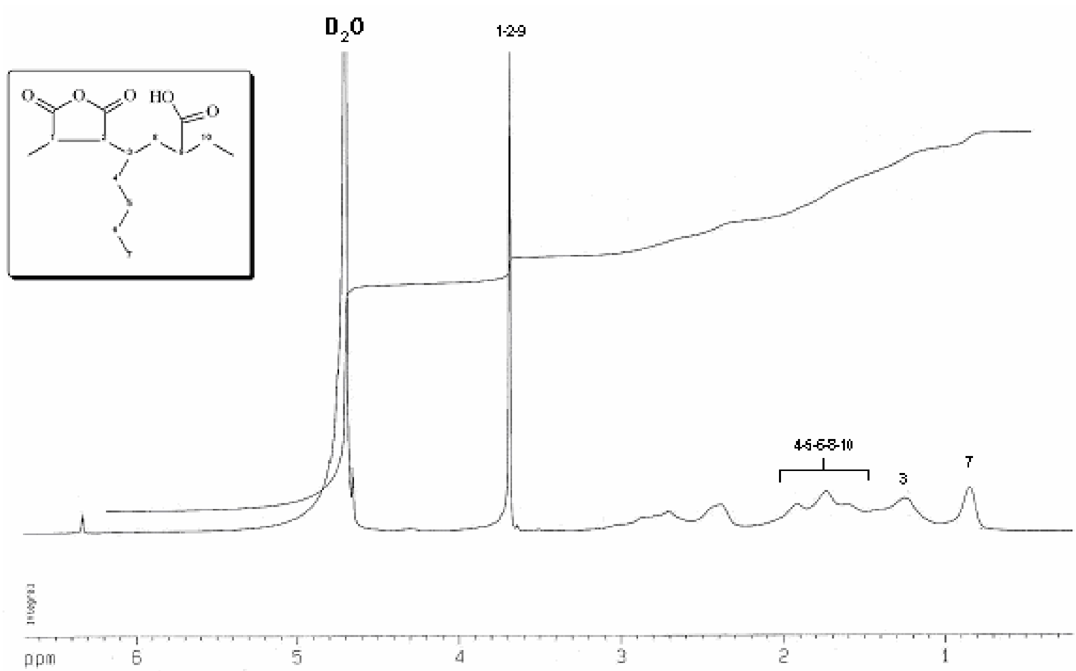


Figure 4.9. ¹H-NMR spectrum of poly(MA -1,H - AA)

The characteristic peaks in the ¹H NMR spectrum of the terpolymer of poly(maleic anhydride -1,hexene – acrylic acid) which is synthesized can be identified as (7) CH_3 of 1, Hexene at 0.84 ppm ; (3) CH of 1, Hexene and acrylic acid at 1.24 ppm ; (4,5,6,8,10) CH_2 of 1, Hexene and acrylic acid at 1.9-1.7 ppm ; (1,2,9) CH of MA and AA at 3.7-3.6 ppm . The peaks at 4.7 ppm belong to D_2O, respectively.

The signals obtained from the ¹H NMR spectrum of synthesized terpolymer of poly(maleic anhydride -1,hexene - acrylic acid) verify the formation of terpolymer.

[1]H-NMR spectrum of the crosslinked structure of diglycidyl ether terminated PDMS and poly(maleic anhydride -1,hexene – acrylic acid) terpolymer is presented in Fig.4.10.

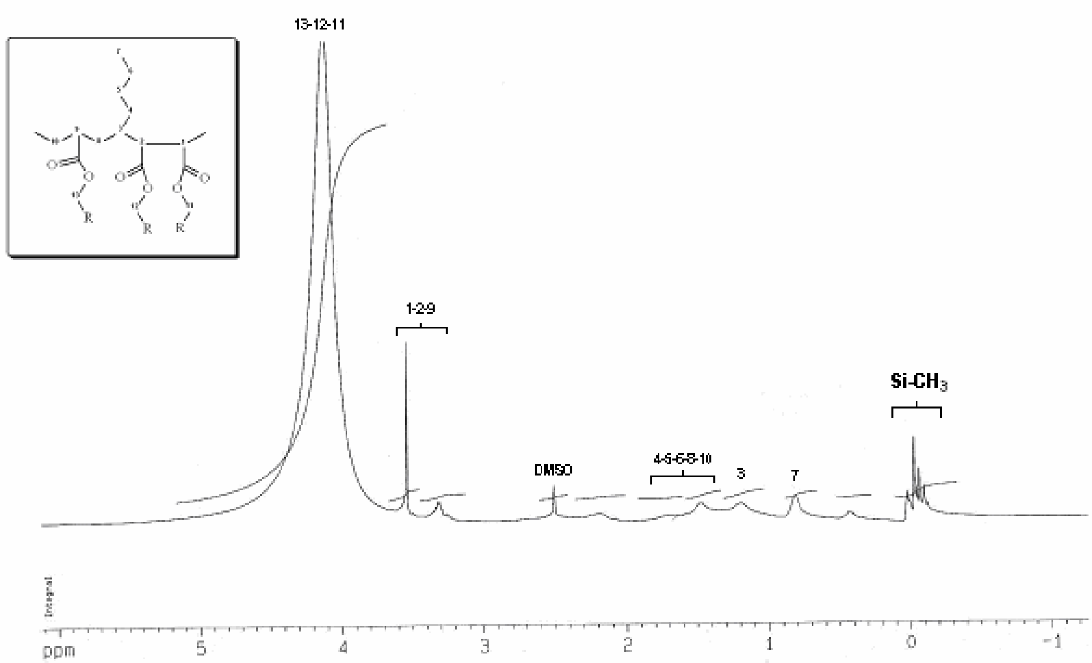


Figure 4.10. [1]H-NMR spectrum for crosslinked structure of DGE terminated PDMS and poly(MA -1,H – AA) terpolymer

As shown in Figure 4.10, there are some difference between the terpolymer and crosslinked structure after crossinking reaction of diglycidyl ether terminated PDMS and poly(maleic anhydride -1,hexene – acrylic acid) terpolymer.

Methyl groups of Si-CH_3 at 0.01-0.014 ppm, (1,2,9)CH of MA and AA at 3.6-3.5 ppm ;(11,12,13) CH_2 in –CH_2-OOC- at 4.1ppm, (7) CH_3 of 1,hexene at 0.81 ppm ; (3) CH of 1,hexene and acrylic acid at 1.19 ppm; (4,5,6,8,10)CH_2 of 1,hexene and acrylic acid at 1.6-1.5 ppm. The peaks at 2.5 ppm belong to DMSO, respectively.

4.2.3.2. ^{13}C NMR analysis

The structure of terpolymer was also confirmed by using ^{13}C NMR analysis . ^{13}C NMR spectrum of terpolymer is given in Figure 4.11.

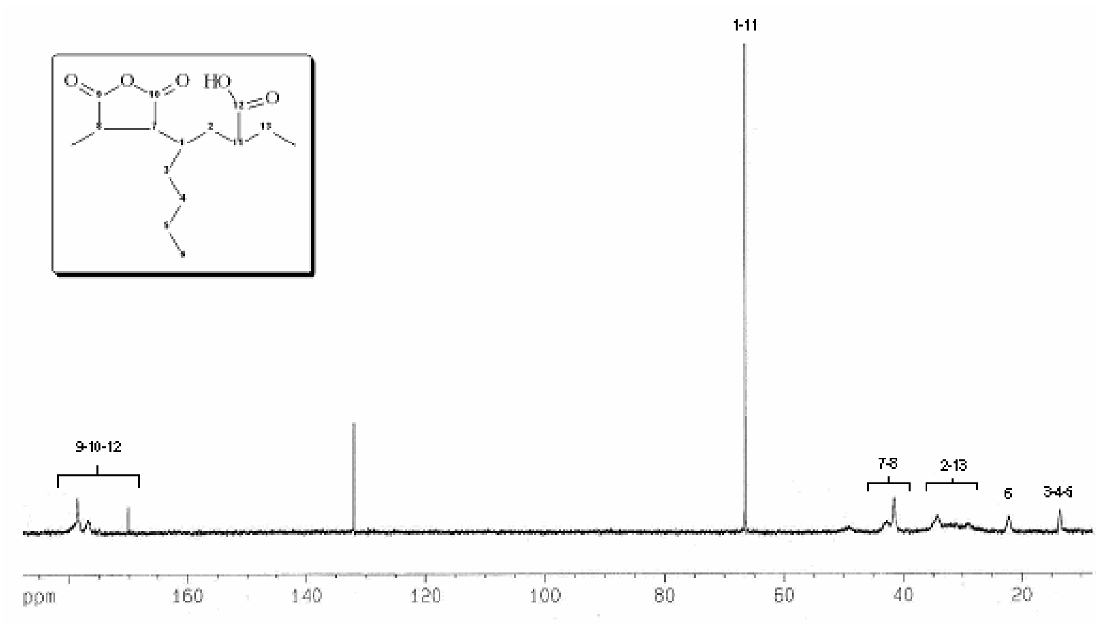


Figure 4.11. ^{13}C NMR spectrum of poly(MA -1,H – AA)

^{13}C NMR spectrum of terpolymer can be characterized by : the appearance of the characteristic signals of carbon atoms (peaks for backbone CH groups) at 31.2 (H-1 unit), 41.60 and 42.02 ppm CH groups of MA and AA. Peaks which occur at 13.60 and 22.37 ppm refer CH_2 and CH_3 groups of 1,hexene.

Characteristic signals of acrylic acid and maleic anhydride which are coming from carbon atoms of C=O groups in both acrylic acid and maleic anhydride appear in the range of 178.67 - 170.10 ppm.

4.2.4. SWELLING BEHAVIOUR

A fundamental relationship exists between the swelling of cross-linked polymer in a solvent and the nature of the polymer and solvent. Swelling of the cross-linked polymers in the chosen and/or suitable solvent is the most important parameter (especially since one of the most important parameters is mass swelling) for swelling studies.

Crosslinking and swelling ratios were investigated for different temperatures. This investigation showed that our hydrogels have temperature sensitivity. Swellings were observed in DMF at 25 ^{0}C and 40 ^{0}C.

When a xerogel is brought into contact with solvent, the solvent diffuses into the network and a volume phase transition occurs, resulting in the expansion of the gel. Diffusion involves the migration of fluid into pre-existing or dynamically formed spaces between the gel chains. Swelling of the hydrogel involves large segmental motion resulting, ultimately, in the increased separation of the gel chains. The swelling behavior was followed by the degree of swelling, until thermodynamic equilibrium, qe, was reached. The swelling equilibrium occurs when the values of the osmotic force driving the solvent into the network and of the elastic force of the stretched sub-chains become equal.

To analyze the fluid transport in swellable polymers, the fluid sorption data were determined by gravimetric studies.

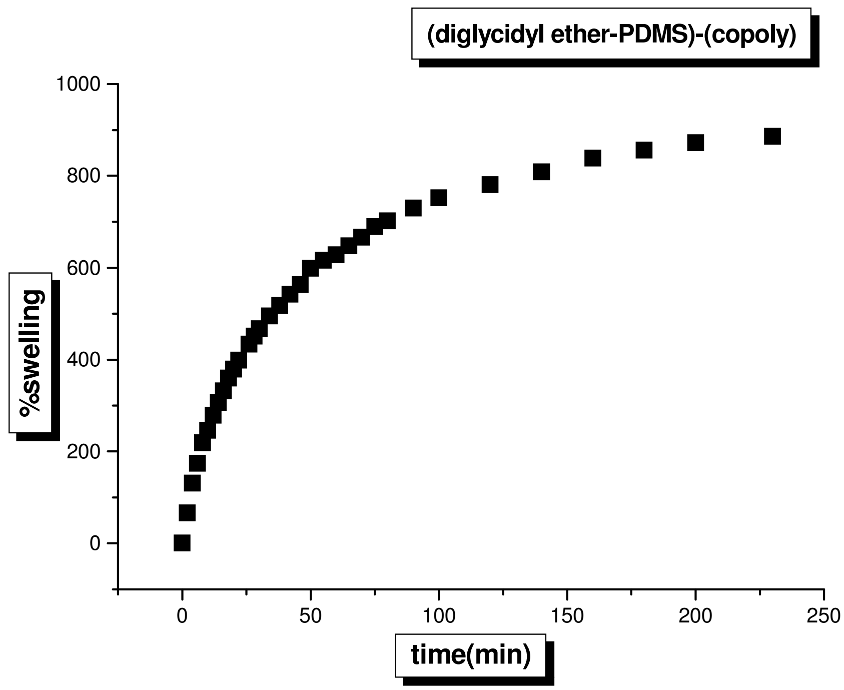
The swelling process was analysed by fitting the first 60% of the sorption data to the following simple empirical equation.

The following equation was used to determine the nature of diffusion of DMF into hydogels:

$$F = M_t / M_\infty = k.t^{\,n} \qquad (4.1)$$

where, $\mathbf{M_t}$ and $\mathbf{M_\infty}$ denote the amount of DMF diffused into the gel at time **, t,** and infinite time (at equilibrium), respectively, **k** is a constant related to the structure of the network, and the exponent **n** is a numerical value to determine the type of diffusion. For a cylindirical shapes, $n \leq 0{,}50$ corresponds to Fickian diffusion, whereas $0{,}50 < n < 1{,}00$ indicates that diffusion is non-Fickian. Equation was applied to various stages of swelling and plots of ln *F* against ln *t* yielded straight lines from which the exponents *n* and *k* were calculated from the slope and intercept of the lines.

Fickian diffusion (n = 0.5), also known as Case I diffusion(a), occurs when the rate of diffusion is significantly slower than the rate of relaxation of the polymer chains. (b) Case II transport (n = 1) arises when the rate of diffusion is greater than the rate of the relaxation of the polymer chains. The main feature of this second limiting model is the establishment of a sharp boundary between the glassy core and the swollen shell, which advances at a constant velocity. (c) Non-Fickian or anomalous diffusion (0.5 < n < 1) occurs when the rates of diffusion and polymer relaxation are comparable and is connected with the transition region between the two limiting cases of Case I and Case II.



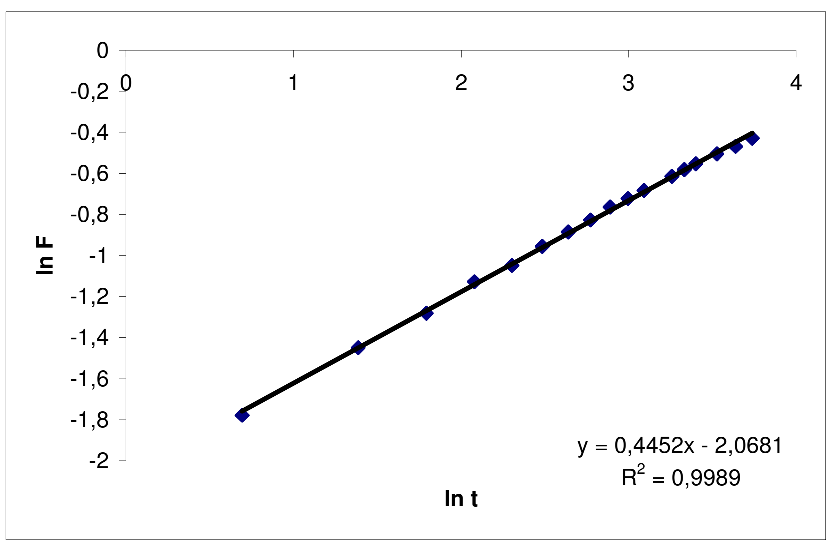
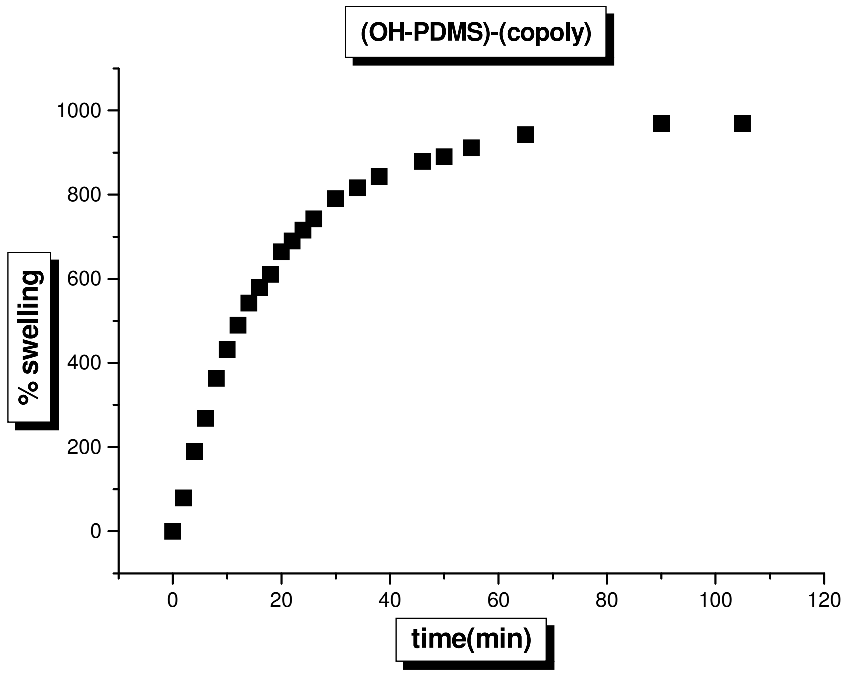


Figure 4.12. Swelling behaviour of crosslinked poly(MVE-alt-MA) and DGE terminated – PDMS in DMF at 25 ^{0}C. (membrane 1)



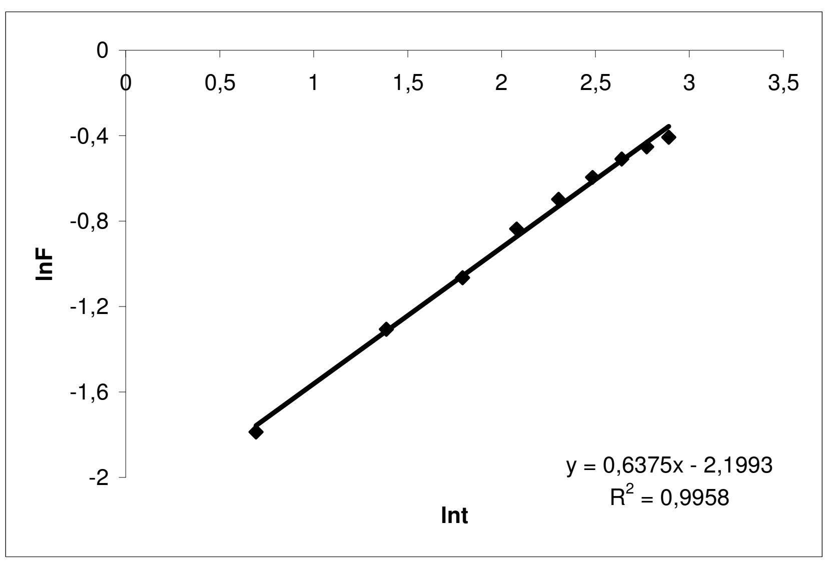
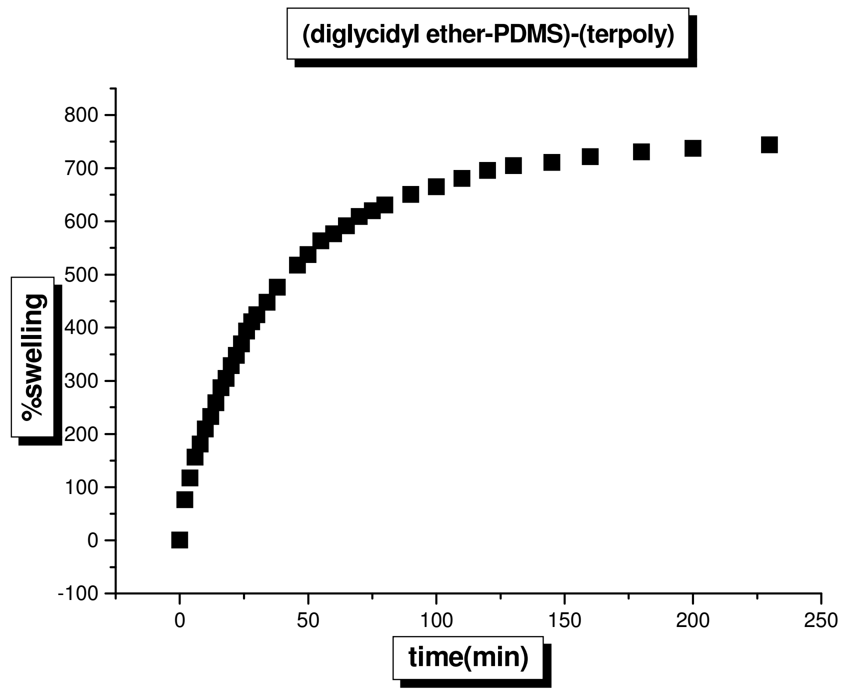


Figure 4.13. Swelling behaviour of crosslinked poly(MVE-alt-MA) and OH terminated - PDMS in DMF at 25 ^{0}C. (membrane 2)



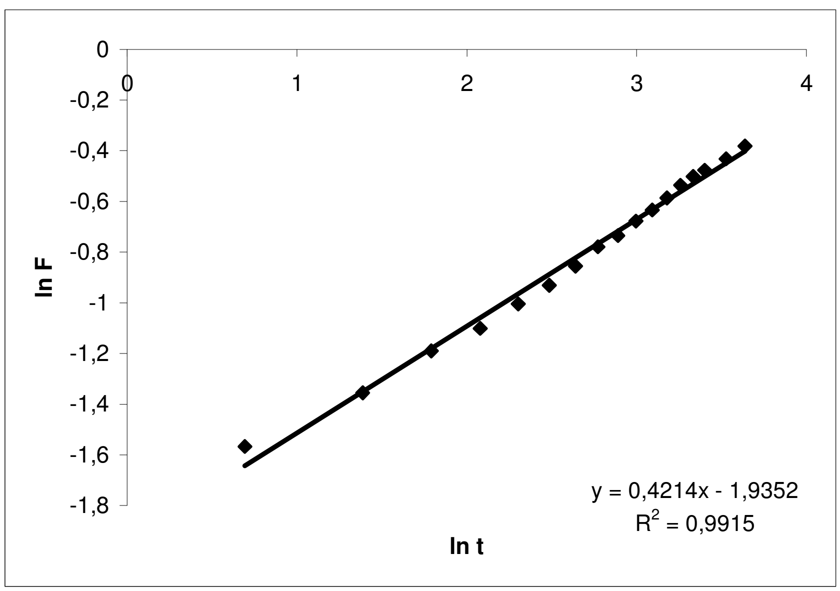
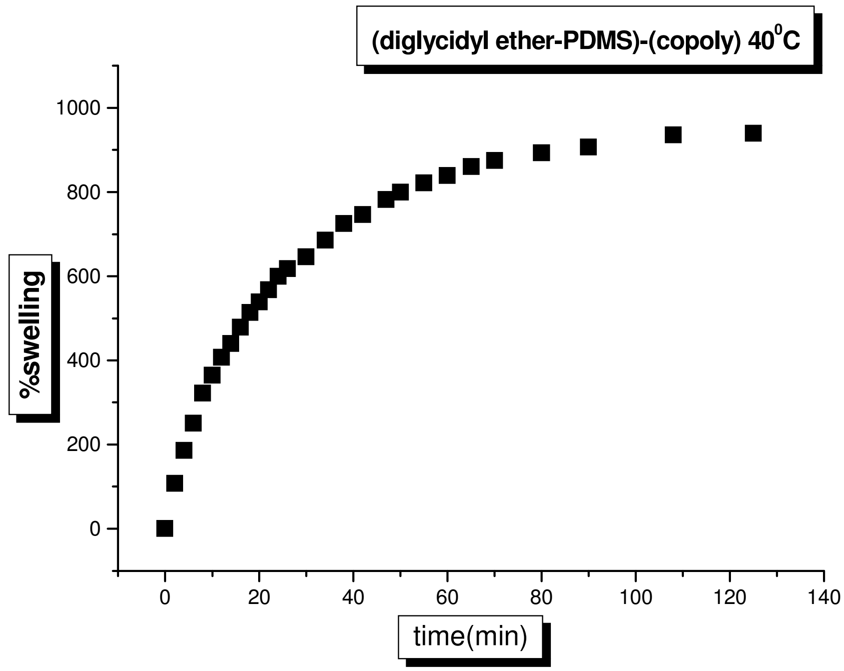


Figure 4.14. Swelling behaviour of crosslinked terpolymer and DGE terminated – PDMS in DMF at 25 ^{0}C. (membrane 3)



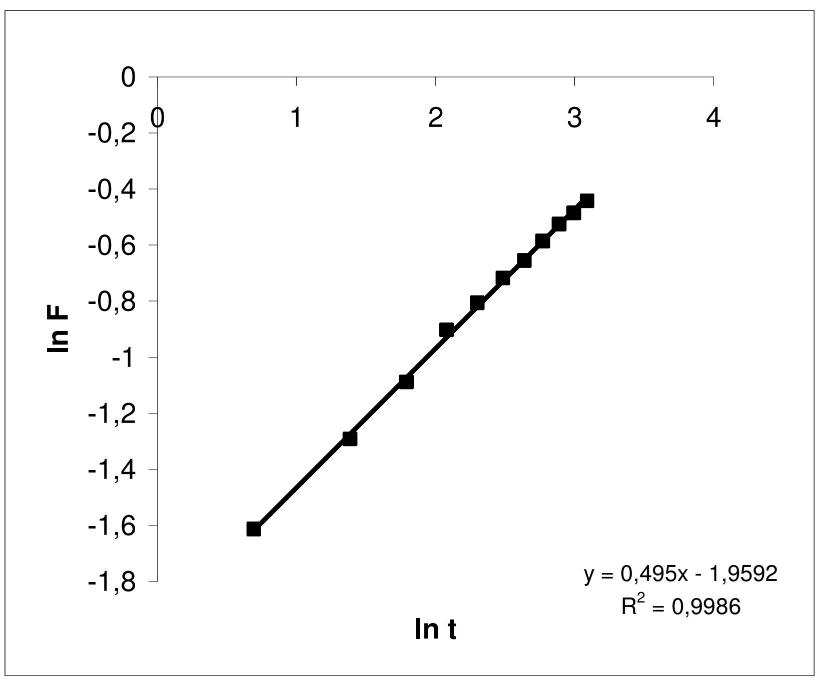
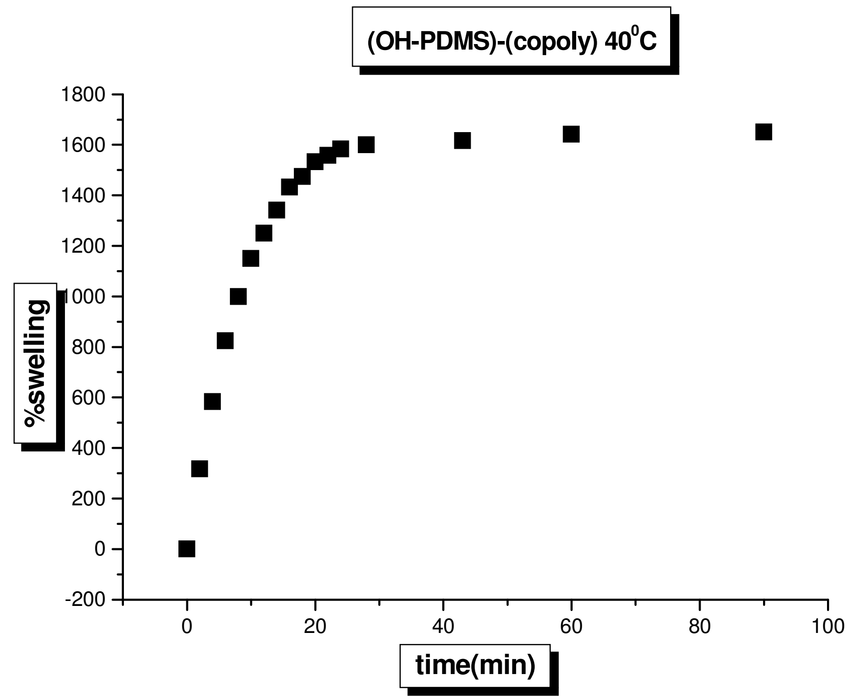


Figure 4.15. Swelling behaviour of crosslinked poly(MVE-alt-MA) and DGE terminated –PDMS in DMF at 40 ^{0}C. (membrane 1)



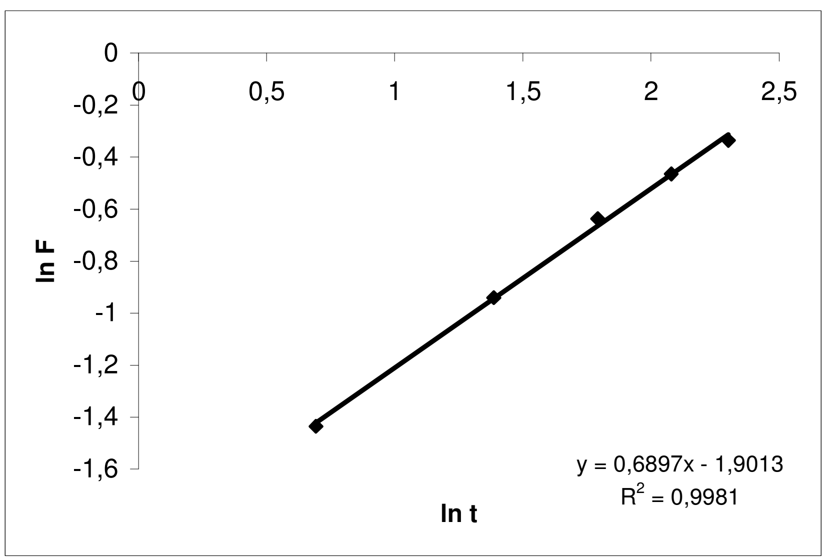
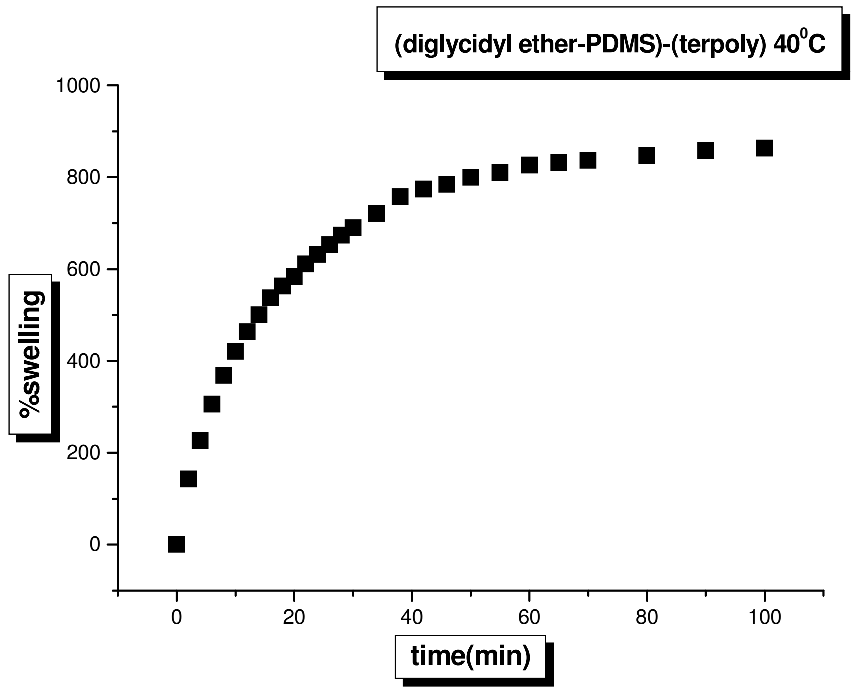


Figure 4.16. Swelling behaviour of crosslinked poly(MVE-alt-MA) and OH terminated- PDMS in DMF at 40 ^{0}C. (membrane 2)



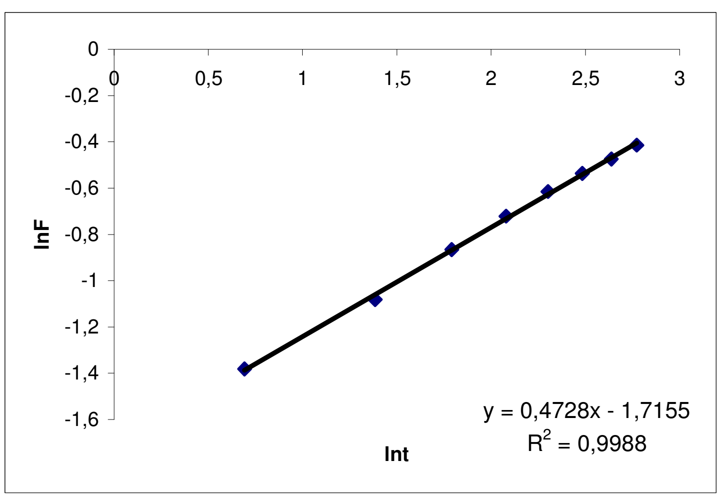


Figure 4.17. Swelling behaviour of crosslinked terpolymer and DGE terminated – PDMS in DMF at 40 ^{0}C. (membrane 3)

Table 4.5. Swelling parameters as refer in Equation 4.1

membrane number	temperature	k	n	R^2
1	25	0,1264	0,4452	0,9989
	40	0,1410	0,4950	0,9986
2	25	0,1109	0,6375	0,9958
	40	0,1494	0,6897	0,9981
3	25	0,1444	0,4214	0,9915
	40	0,1799	0,4728	0,9988

Dynamic swelling behaviour of crosslinked poly(methyl vinyl ether-alt-maleic anhydride) and diglycidyl ether terminated – PDMS and crosslinked terpolymer and diglycidyl ether terminated – PDMS in DMF indicates that the swelling process follows Fickian behaviour.

For crosslinked poly(methyl vinyl ether-alt-maleic anhydride) and hydroxy terminated-PDMS in DMF swelling process follows non-Fickian behaviour.

Table 4.6. Equilibrium swelling ratios

membrane number	Q(equilibrium swelling ratio)	
	25 ^{0}C	40^{0}C
1	8,86	9,39
2	9,68	16,50
3	7,43	8,63

Equilibrium swelling ratios of all hydrogels are listed in table at two temperatures. It is interesting to note that the equilibrium swelling ratios of the other hydrogels increase with increasing temperature from 25 to 40 ^{0}C .

The crosslinked structures containing both hydrophilic and hydrophobic groups should exhibit thermosensitivity owing to the strengthening of the hydrophobic interactions with increasing temperature.

The thermosensitivity of swelling can be attributed to the delicate hydrophilic / hydrophobic balance of polymer chains and is affected by size, configuration, and mobility of alkyl side groups.

4.2.5. THERMAL PROPERTIES

4.2.5.1. TGA-DTA

TGA-DTA curves of crosslinked structure of diglicidyl ether terminated PDMS and poly (methyl vinyl ether-alt-maleic anhydride) copolymer are shown in Figure 4.18.

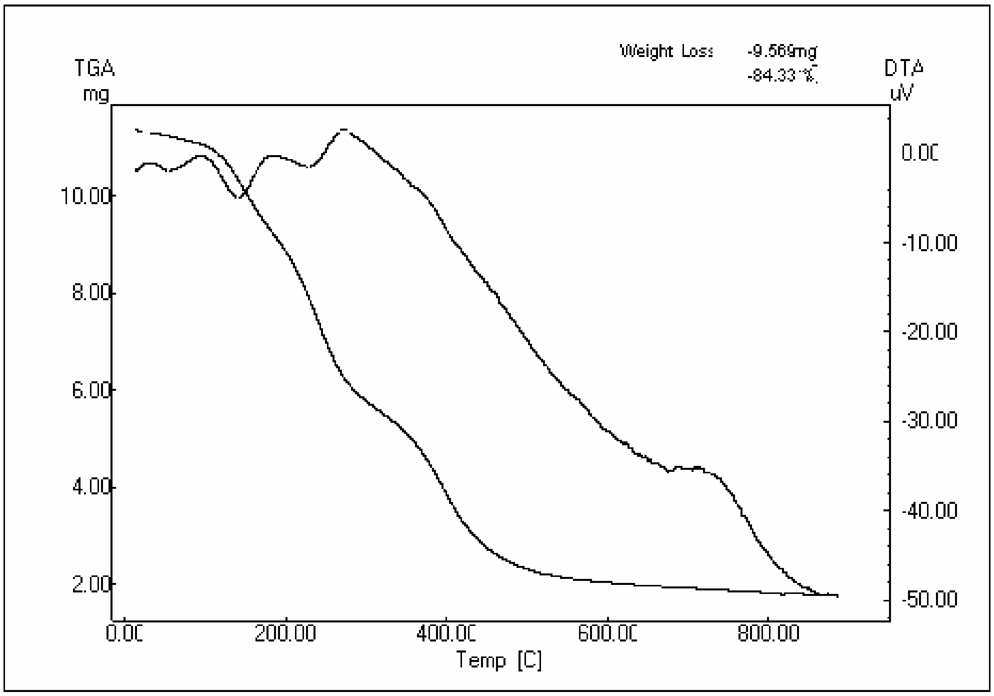


Figure 4.18. TGA-DTA curves of crosslinked structure of DGE terminated PDMS and poly (MVE-alt-MA) copolymer

The first weak exo-effect around 100 ^{0}C on the DTA curves might be related to a ‘physical aging’ of H-bonded structure which is accompanied by the breaking of inter- and intramolecular OH ….O=C- bonds of the macromolecules. The strong endo-effects on the curves are related to Tg as on the DSC curves.

From the DTA-TGA analysis for the crosslinked structure two step degradation is displayed around ~200 ^{0}C (T_{1d}) and ~300 ^{0}C (T_{2d}). The first step of degradation appears in the form of broad exo-effect peaks. It can be related to thermal decarboxylation reaction of anhydride linkages. The (T_{2d}) values are associated with thermal chain-degradation reactions of the studied system.

Thermal stability of the crosslinked structure was measured by TGA. The onset degredation is about ~110 ^{0}C. Crosslinked structure of diglicidyl ether terminated PDMS and poly (methyl vinyl ether-alt-maleic anhydride) copolymer leads to the thermal degradation in a wide temperature range between 110 ^{0}C and 600 ^{0}C. The thermograms also show that the residual weight percent of the crosslinked network is 15.7 % at 800 ^{0}C.

TGA-DTA curves of crosslinked structure of hydroxy terminated PDMS and poly (methyl vinyl ether-alt-maleic anhydride) copolymer are shown in Figure 4.19.

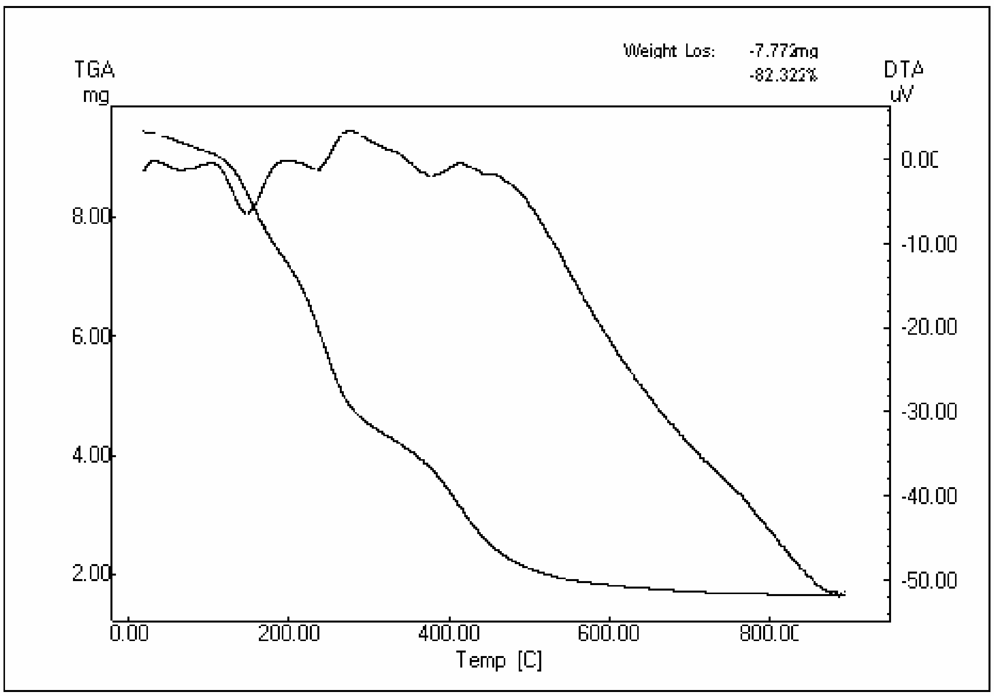


Figure 4.19. TGA-DTA curves of crosslinked structure of OH terminated PDMS and poly (MVE-alt-MA) copolymer

The first weak exo-effect around 105 ^{0}C on the DTA curves might be related to a 'physical aging' of H-bonded structure which is accompanied by the breaking of inter- and intramolecular OH ….O=C- bonds of the macromolecules. The strong endo-effects on the curves are related to Tg as on the DSC curves.

From the DTA-TGA analysis for the crosslinked structure two step degradation is displayed around ~200 ^{0}C (T_{1d}) and ~280 ^{0}C (T_{2d}). The first step of degradation appears in the form of broad exo-effect peaks. It can be related to thermal decarboxylation reaction of anhydride linkages. The (T_{2d}) values are associated with thermal chain-degradation reactions of the studied system.

Thermal stability of the crosslinked structure was measured by TGA. The onset degradation is about ~120 ^{0}C. Crosslinked structure of diglicidyl ether terminated PDMS and poly (methyl vinyl ether-alt-maleic anhydride) copolymer leads to the thermal degradation in a wide temperature range between 120 ^{0}C and 600 ^{0}C.

The thermograms also show that the residual weight percent of the crosslinked network is 17.7 % at 800 ^{0}C.

TGA-DTA curves of crosslinked structure of diglicidyl ether terminated PDMS and poly(maleic anhydride-1,hexene-acrylic acid) terpolymer are shown in Figure 4.20.

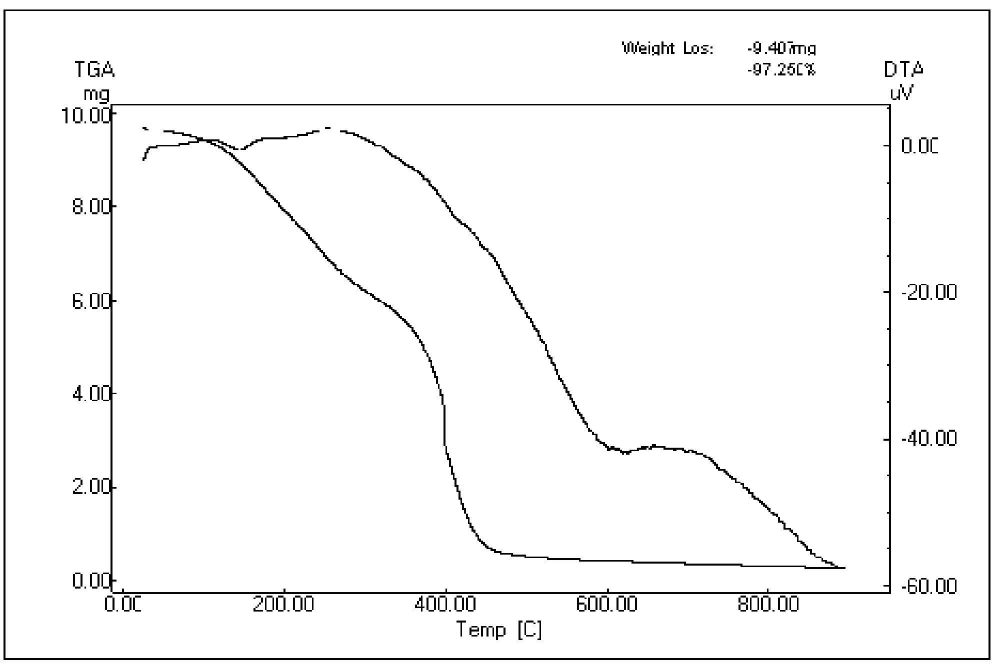


Figure 4.20. TGA-DTA curves of crosslinked structure of DGE terminated PDMS and poly(MA -1,H - AA) terpolymer

The first weak exo-effect around 100 ^{0}C on the DTA curves might be related to a 'physical aging' of H-bonded structure which is accompanied by the breaking of inter- and intramolecular OH ….O = C-- bonds of the macromolecules. The strong endo-effects on the curves are related to Tg as on the DSC curves.

From the DTA-TGA analysis for the crosslinked structure two step degradation is displayed around ~180 ^{0}C (T_{1d}) and ~270 °C (T_{2d}). The first step of degradation appears in the form of broad exo-effect peaks. It can be related to thermal decarboxylation reaction of anhydride linkages. The (T_{2d}) values are associated with thermal chain-degradation reactions of the studied system.

Thermal stability of the crosslinked structure was measured by TGA. The onset degredation is about ~110 ^{0}C. crosslinked structure of diglicidyl ether terminated PDMS and poly (methyl vinyl ether-alt-maleic anhydride) copolymer leads to the thermal degradation in a wide temperature range between 110 ^{0}C and 600 ^{0}C.

The thermograms also show that the residual weight percent of the crosslinked network is 2.75 % at 800 ^{0}C.

4.2.5.2. DSC

For polymers, thermal analysis is most commonly performed by differential scanning calorimetry (DSC) which provides information concerning the macroscopic properties of a polymer system. These properties are in turn determined by the microstructure of the polymer chain. Although it is not possible to deduce molecular details using calorimetry, some details of the chain behaviour can be inferred, especially with respect to analysis of the glass transition. The fundamental importance of thermal analysis as a polymer characterization tool is emphasized by an admirable project in which Wunderlich is in the vanguard.

The Tg is a transition commonly monitored using calorimetry since it arises due to a change in heat capacity or heat flow of the polymer system. The glassy phase has no long range order and as the glass is heated there occurs a temperature where the molecules acquire concerted motions along the chain backbone, i.e., translations and rotations within various conformations, primarily involving the chain ends or larger pendent groups. This added motional freedom brings the polymer into a more liquid-like state. This is (reversible) pseudo-second order transition, and as the polymer is cooled towards a glassy state the sample will again cross the temperature at which these motions case.

Figure 4.21 shows DSC trace for the crosslinked structure of diglicidyl ether terminated PDMS and poly (methyl vinyl ether-alt-maleic anhydride) copolymer.

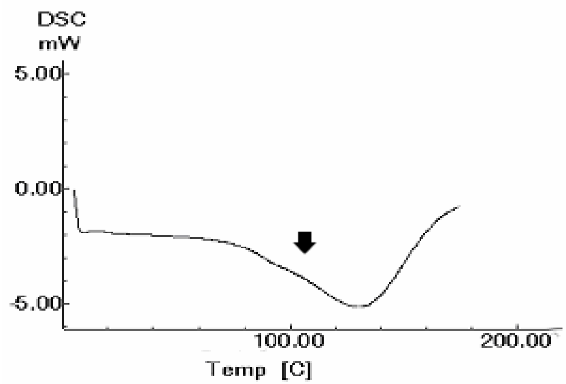


Figure 4.21. DSC trace for the crosslinked structure of DGE terminated PDMS and poly (MVE-alt-MA) copolymer. (structure 1)

The temperature endo effects on the DSC curve are associated with the glass transition temperature.

Figure 4.22 shows DSC trace for the of crosslinked structure of hydroxy terminated PDMS and poly (methyl vinyl ether-alt-maleic anhydride) copolymer.

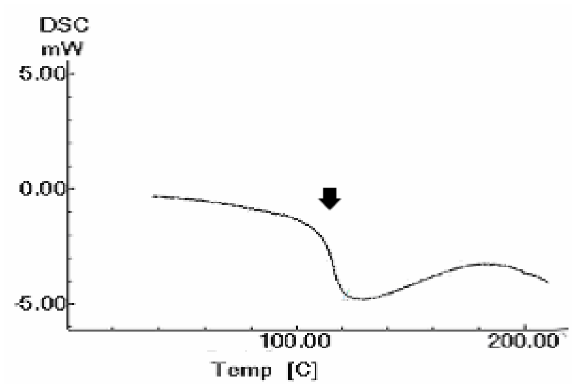


Figure 4.22. DSC trace for the of crosslinked structure of OH terminated PDMS and poly (MVE-alt-MA) copolymer. (structure 2)

The temperature endo effects on the DSC curve are associated with the glass transition temperature.

DSC curve of crosslinked structure of diglicidyl ether terminated PDMS and poly(maleic anhydride -1,hexene – acrylic acid) terpolymer are shown in Figure 4.23.

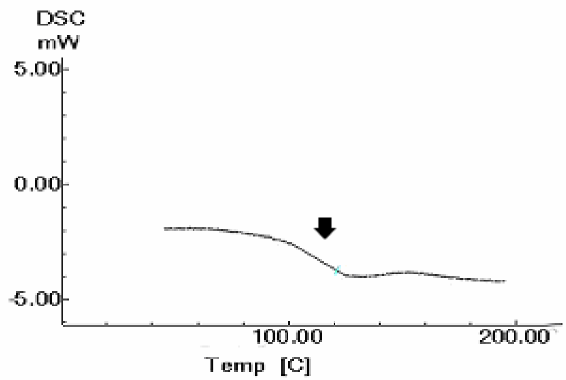


Figure 4.23. DSC trace for the of crosslinked structure of DGE terminated PDMS and poly(MA -1,H - AA) terpolymer (structure 3)

Table 4.7. Thermal behaviour of crosslinked structures.

structure	DSC Analysis $T_g(^0C)$	TGA-DTA analysis			
		$Td_1(^0C)$	$Td_2(^0C)$	150	200
1	105	200	300	6.96	17.75
2	110	200	280	9.21	23.68
3	115	180	270	7.35	17.64

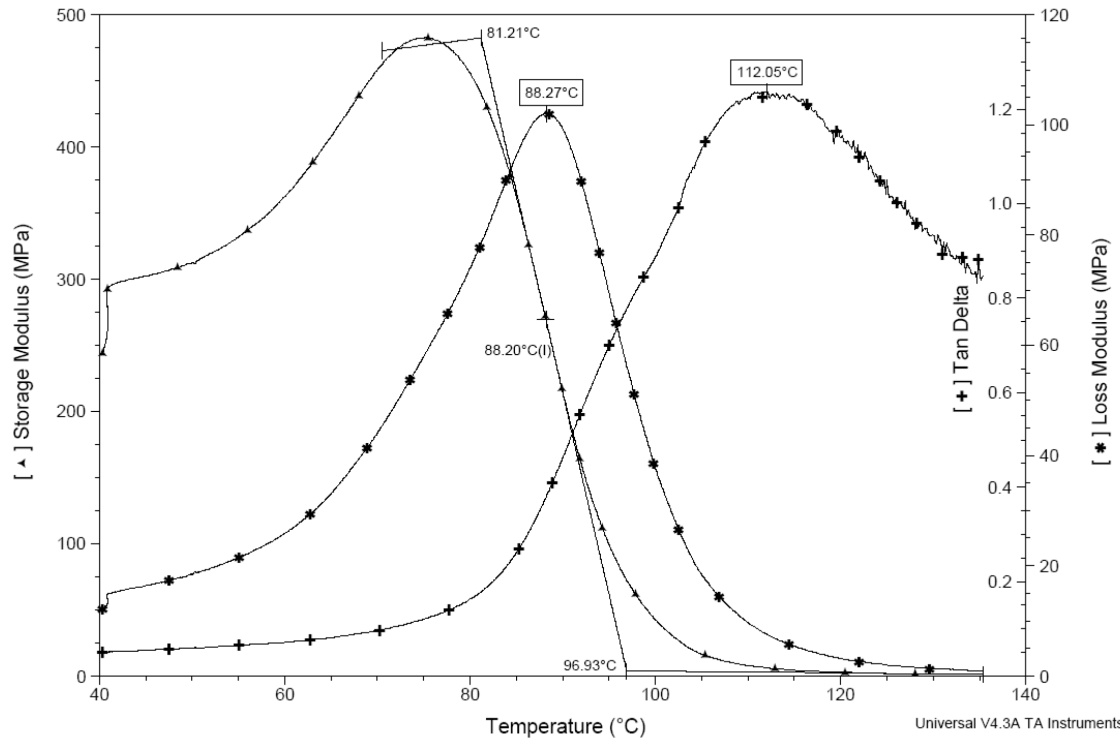
4.2.6. DYNAMIC MECHANICAL ANALYSIS (DMA)

Dynamic Mechanical Analysis (DMA) is a technique used to measure the viscoelastic properties of a wide range of materials using either transient or dynamic oscilatory tests. This method does not require any special sample (only stacking of coated supports or sample sandwiching) whilst it enables to characterize in situ polymer coating, even nanocoating. This characterization is of prime interest in technological coating developments such as paints, fiber sizings, glues, etc. This possible measurement of thermal transitions peculiar to nanocoatings also opens more fundamental studies as the probing of interface influence on thermal transitions (Carlier et al., 2000).

On the most fundamental measurements made on polymeric materials is the measurement of the glass transition temperature, Tg. In general, transitions in materials are associated with different localized or medium to long-range cooperative motions of molecular segments. The glass transition is associated with cooperative motion among a large number of chain segments, including those from neighboring polymer chains. Although there are several thermal techniques available to make Tg measurements, so far the most sensitive technique is dynamic mechanical analysis, DMA. DMA measures the viscoelastic moduli, storage and loss modulus, damping properties, and tan delta of materials, as they are deformed under a period (sinusoidal) deformation (stress or strain) (Turi, 1997).

The modulus measured in DMA is, however, not exactly the same as the Young's modulus of the classic stress–strain curve. Young's modulus is the slope of a stress–strain curve in the initial linear region. In DMA, a complex modulus (E^*), an elastic modulus (E'), and an imaginary (loss) modulus (E'') are calculated from the material response to the sine wave. These different moduli allow better characterization of the material, because we can now examine the ability of the material to return or store energy (E'), to its ability to lose energy (E''), and the ratio of these effects (tan delta), which is called damping.

The dynamic mechanical analyses of crosslinked membranes are shown in following figures and the data observed from the figures are given in Table 4.8.



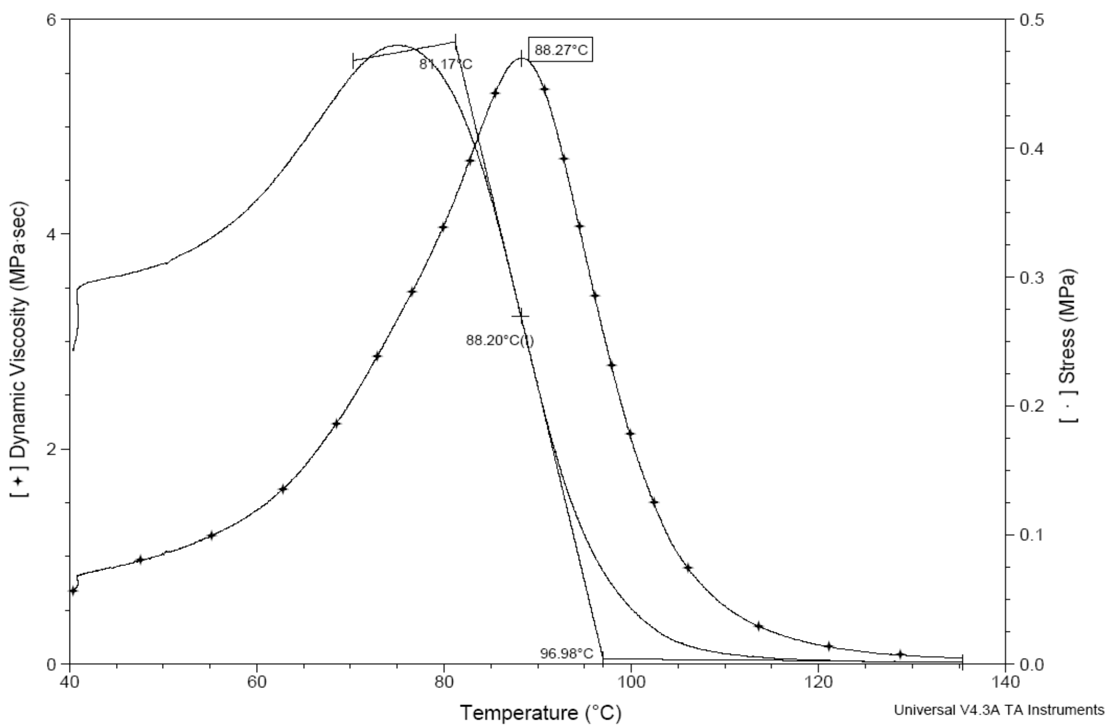
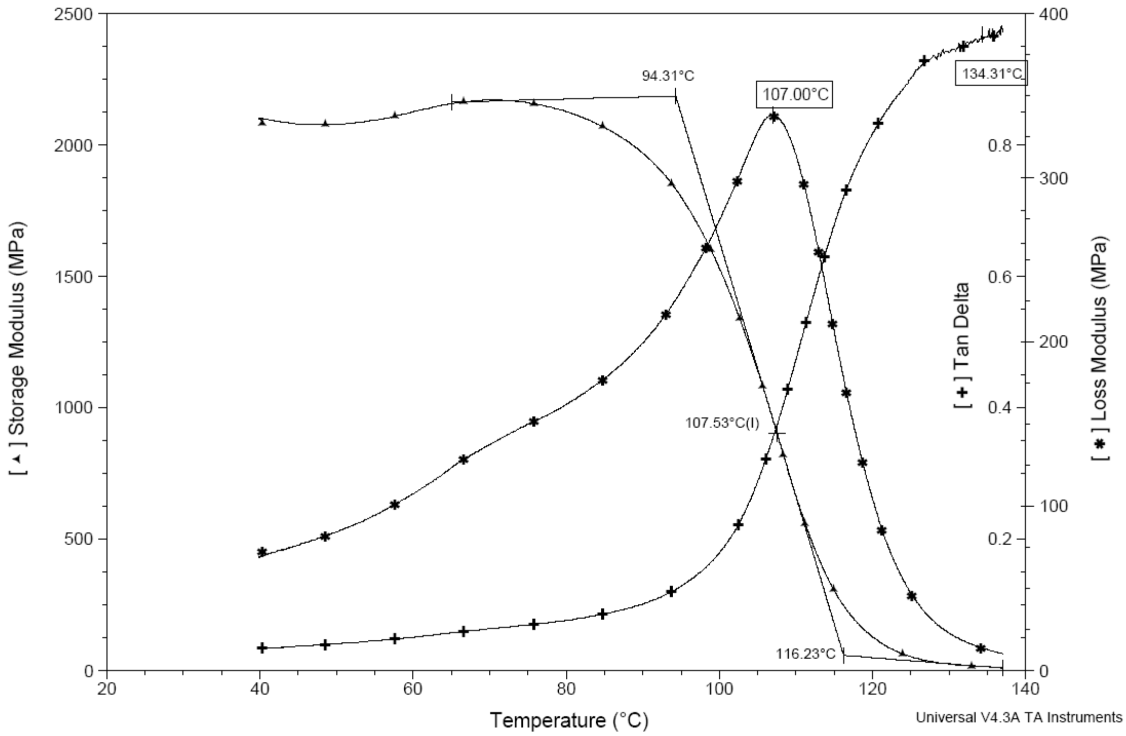


Figure 4.24. The dynamic mechanical analyses of crosslinked poly(MVE-alt-MA) and DGE terminated –PDMS



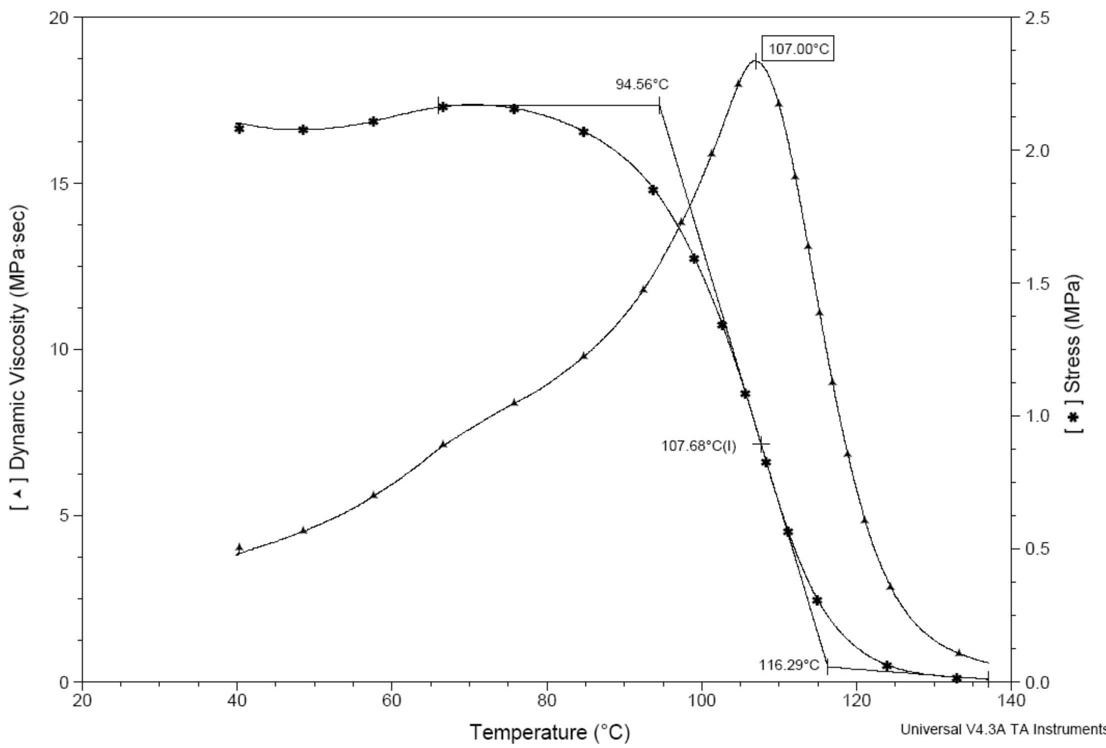
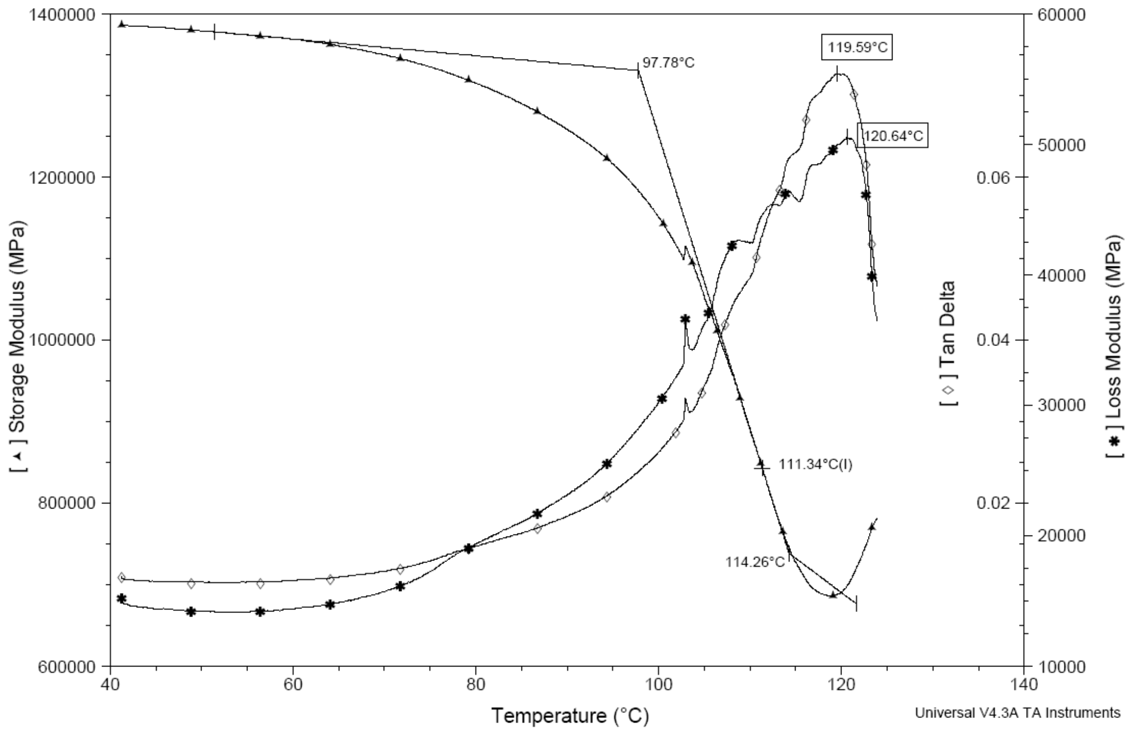


Figure 4.25. The dynamic mechanical analyses of crosslinked poly(MVE-alt-MA) and OH terminated –PDMS



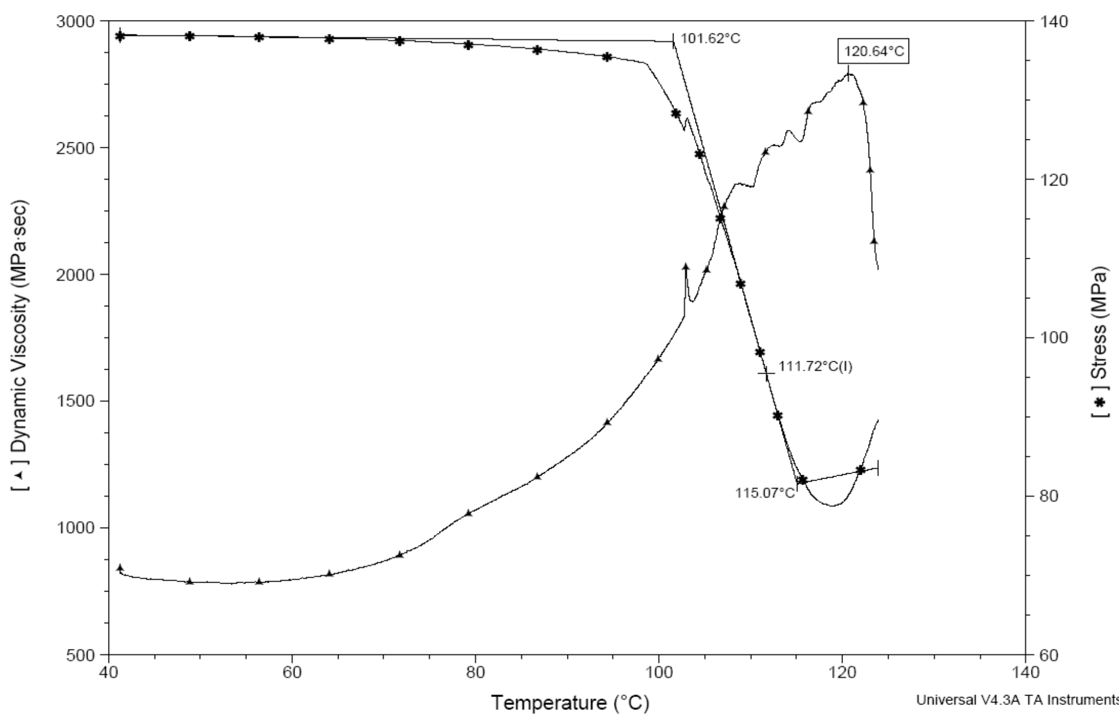


Figure 4.26. The dynamic mechanical analyses of crosslinked poly(MA-1,H-AA) terpolymer and DGE terminated PDMS.

After scanning the sample under test, any of these three viscoelastic parameters can be used to define the Tg values. This figure shows the Tg labeled for sample using the following parameters:

E' Onset : Relates to mechanical failure.

E" Peak : More closely related to the physical property changes attributed to the glass transition. It reflects molecular processes and agrees with the idea of Tg as the temperature at the onset of segmental motion.

Tan Delta Peak : It is a good measure of the 'leather like' midpoint between the glassy and rubbery states of a polymer. The height and shape of the tan delta peak change systematically with amorphous content (Turi, 1997).

Tan delta (Damping factor) is defined as the loss of energy in the system by deformation. It is usually related with the imperfection in the system and is used to define the molecular motions by the phase changes.

The tan delta curve peaks clearly present an ascending behavior at low temperatures, but after reaching the peak temperature, tan delta stabilizes to a value that is larger than the initial value, rather than descending to the value close to the one found below *T*g. High damping capability above *T*g may affect the properties of the materials and can be relevant for their processing. This behavior can be detected by the DMA in different materials during the occurrence of the glass transition phenomenon (Chen et al., 2007).

Depending on the industry standards or background of the operator, the peak or onset of the tan delta curve, the onset of the E' drop, or the onset or peak of the E" curve may be used. The values obtained from these methods can differ up to 25 °C from each other on the same run. In addition, a 10 - 20 °C difference from the DSC is also seen in many materials (Menard, 1999).

Stress/strain measurements are widely used to characterize films and fibers over a broad range of viscoelastic behavior. Although conventional physical testing devices can accommodate thin films and single filament fibers, the results are difficult to obtain, and the accuracy is doubtful since the mass and inertia of the grips are much greater than the tensile strength of the material being evaluated. The clamping arrangements and force range of DMA are more suitable for examining these materials (Foreman, 1997).

Table 4.8 refers to the data which are provided from the DMA graphics.

Table 4.8. Dynamic mechanical behaviour of crosslinked structures

DMA data of crosslinked poly(MVE-alt-MA) and DGE terminated –PDMS	
Tg (℃)	**f (x) – x**
88,20	Storage modulus – T (E' onset)
88,27	Loss modulus – T (E" onset)
112,05	Tan delta – T (E" / E')
88,27	Dynamic viscosity – T
88,20	Stress – T

DMA data of crosslinked poly(MVE-alt-MA) and OH terminated –PDMS	
Tg (℃)	**f (x) – x**
107,53	Storage modulus – T (E' onset)
107,00	Loss modulus – T (E" onset)
134,31	Tan delta – T (E" / E ')
107,00	Dynamic viscosity – T
107,68	Stress – T

DMA data of crosslinked poly(MA-1,H-AA) terpolymer and DGE terminated PDMS	
Tg (℃)	**f (x) – x**
111,34	Storage modulus – T (E' onset)
120,64	Loss modulus – T (E" onset)
119,59	Tan delta – T (E" / E')
120,64	Dynamic viscosity – T
111,72	Stress – T

The glass transition temperatures of crosslinked structures can be found by different f(x) – x functions. As expected, the loss modulus dispersion shows a maximum in the environment of Tg value and it is compatible with both tan delta and dynamic viscosity behavior.

Tg values can as well be determined from the mid-point of the S-shaped curves which are in excellent agreement with each other as given in Table 4.8.

4.2.7. HYDROPHILICITY

A contact angle (θ) is a quantitative measure of the wetting of a solid by a liquid. It is geometrically defined as the angle formed by a liquid at the three phase boundary where a liquid, gas, and solid meet.

Hydrophilicity of the crosslinked membranes of diglicidyl ether terminated PDMS and poly (methyl vinyl ether-alt-maleic anhydride) copolymer, hydroxy terminated PDMS and poly (methyl vinyl ether-alt-maleic anhydride) copolymer, diglicidyl ether terminated PDMS and poly(maleic anhydride -1,hexene – acrylic acid) terpolymer analysed with water contact angle.

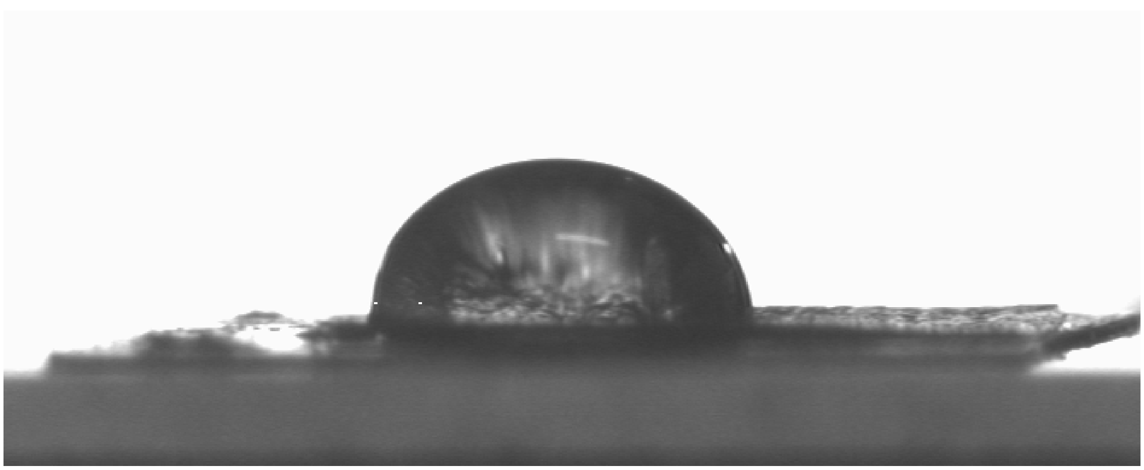


Figure 4.27. Membrane of poly(MVE-alt-MA)-DGE terminated PDMS(membrane1)

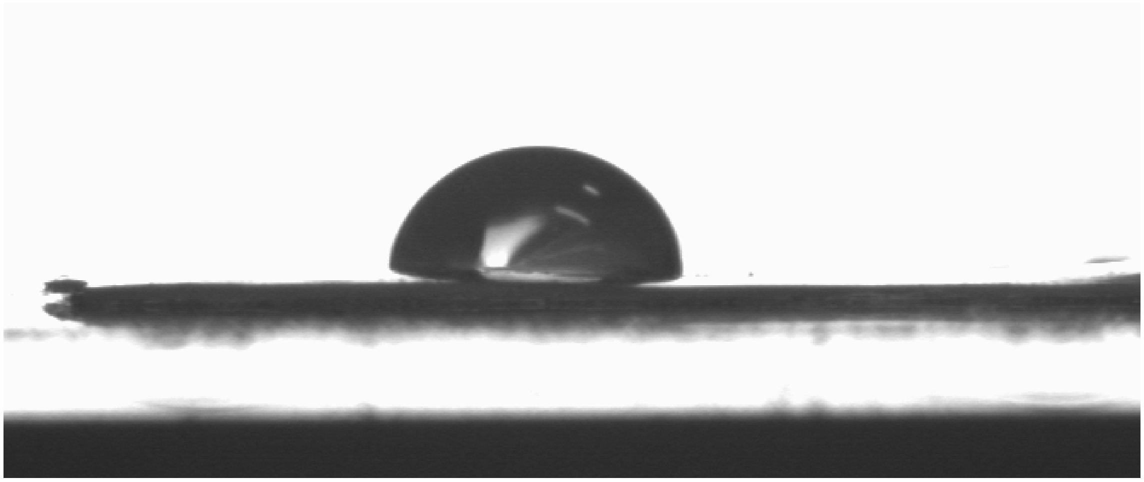


Figure 4.28. Membrane of poly(MVE-alt-MA)- OH terminated PDMS (membrane2)

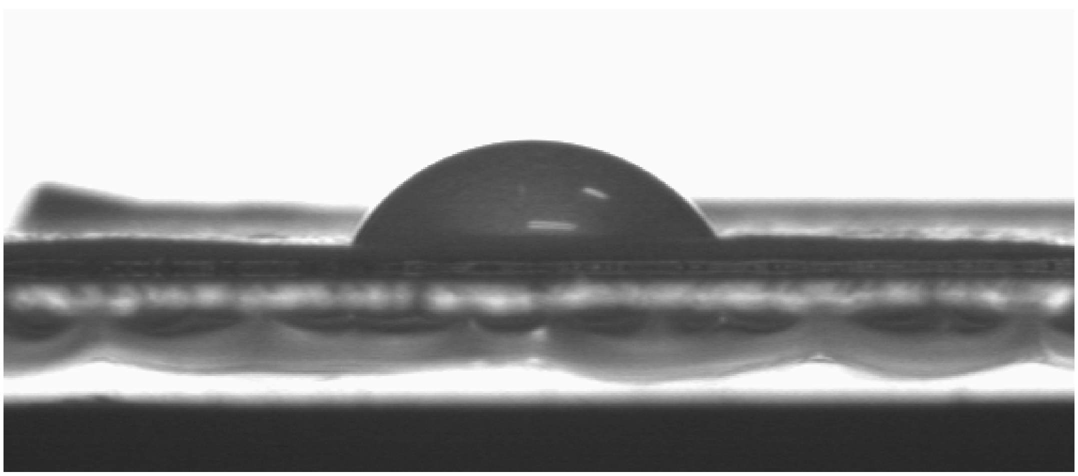


Figure 4.29. Membrane of poly(MA-1,H-AA)-DGE terminated PDMS (membrane3)

Table 4.9. The contact angle (θ) values of crosslinked structures

Membrane	Water Contact Angle (θ)
1	79.6
2	78.5
3	54.4

Crosslinked PDMS exhibits exceptional hydrophobicity. Its hydrophobicity is a result of (1) the methyl groups, having low intermolecular forces between themselves, providing hydrophobic characteristics to the polymer and (2) the flexibility of the siloxane backbone (Si-O-Si) which allows orientation of the methyl groups to the surface. In addition to that, maleic anhydride and acrylic acid show hydrophilic character. So that, the hydrophilicity of the crosslinked structure depends on the crosslinking ratio and uncrosslinked groups.

As shown in Table 4.9 diglicidyl ether terminated PDMS and poly(maleic anhydride -1,hexene – acrylic acid) terpolymer has a more hydrophilic character than the others. It can occur because of unreacted hydroxyl groups and lower crosslinking ratio.

4.2.8. XRD ANALYSES

The X-ray diffraction analysis of cross-linked structures are given in Figures 4.30, 4.31 and 4.32. The diffraction angle (2θ) values against the selected scattering intensities.

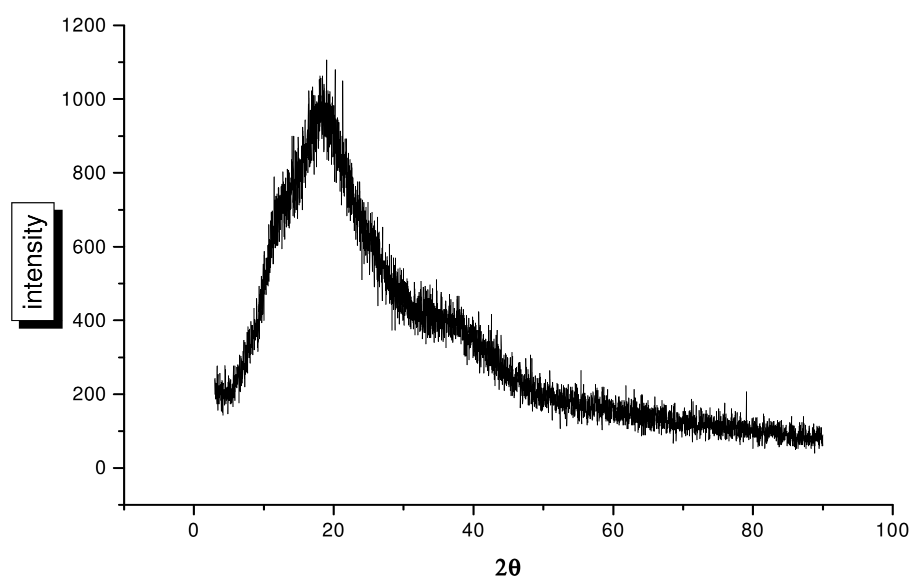


Figure 4.30. Crosslinked structures of DGE terminated PDMS and poly(MVE-alt-MA) copolymer

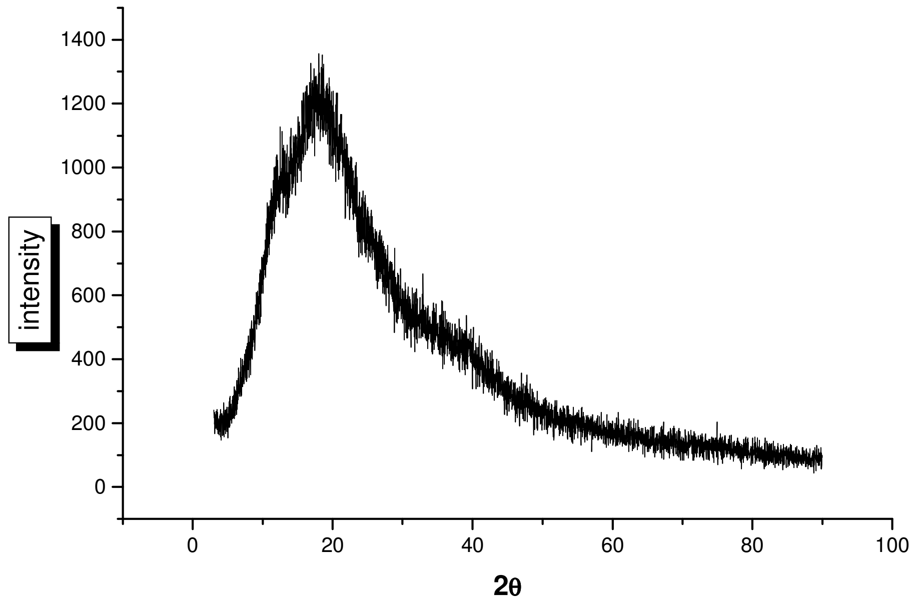


Figure 4.31. Crosslinked structures OH terminated PDMS and poly(MVE-alt-MA) copolymer

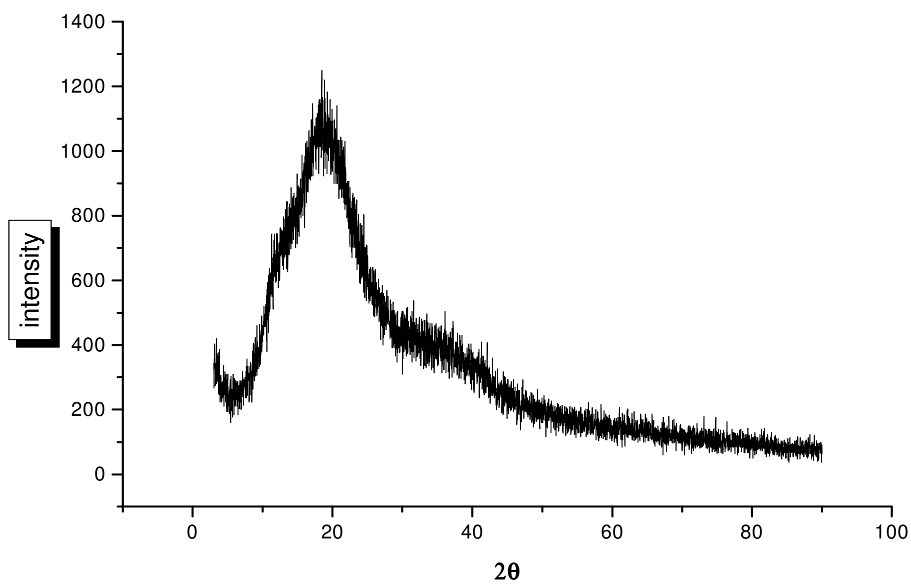


Figure 4.32. Crosslinked structures of DGE terminated PDMS and poly(MA -1,H -AA) terpolymer

And from figures, it can be easily implied that the cross-linked structures are completely amorphous.

4.2.9. VISCOSITY MEASUREMENTS AND CHARACTERISTIC PARAMETERS OF TERPOLYMER

During the recent years the polyelectrolyte behavior of MA containing copolymers in various solvents have been of great interest. In dilute polymer solutions the reduced and inherent viscosities are proportional to concentration as indicated by Huggins and Kraemer equations. However, in extremely dilute polymer solutions, the linear relationship between $\frac{\eta_{sp}}{C}$ vs C and $\frac{\ln \eta_r}{C}$ vs C has resulted with the polyelectrolyte behavior of the polymer deviating from the linearity.

In the alternating terpolymerization process of MA the monomer feed ratios were selected as 25:25:50 for MA/1,Hx/AA, respectively, according to the literature data (Mazı et al 2005).

In our study, viscosity measurements have been carried out with the purposes of characterization of terpolymer which were synthesized by different initiator ratios.

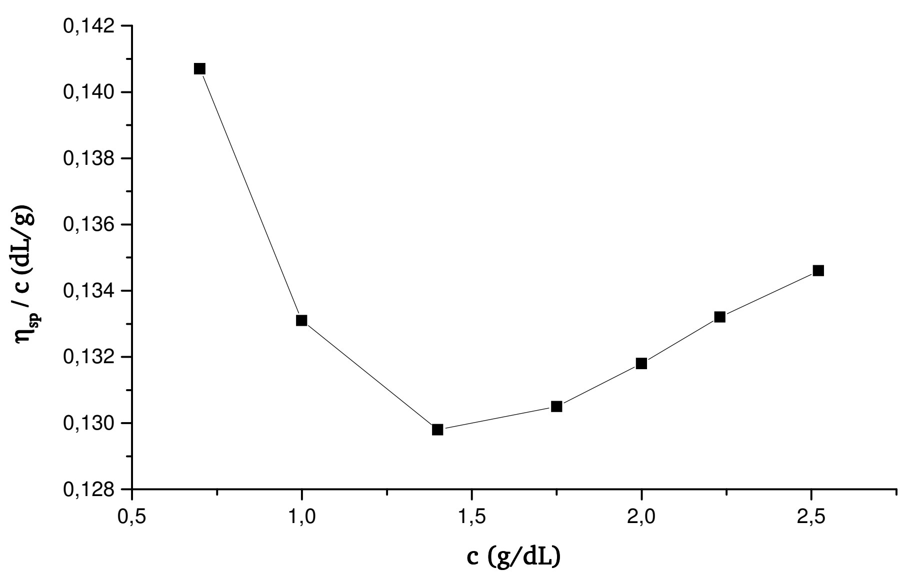


Figure 4.33. Variation of μ_{sp} /c vs c (polymer concentration) for poly(MA-1,H-AA) terpolymer with 0.5 % BPO as an initiator.

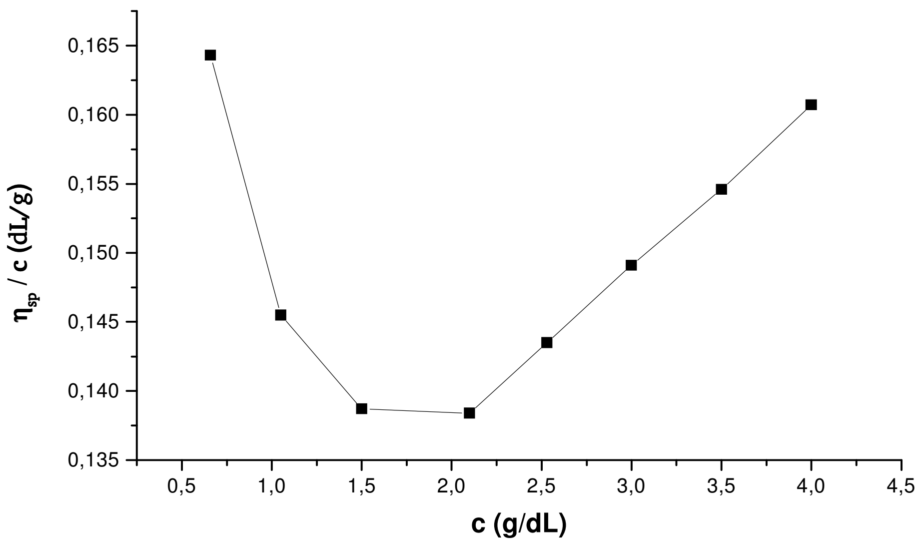


Figure 4.34. Variation of μ_{sp} /c vs c (polymer concentration) for poly(MA-1,H-AA) terpolymer with 1.0 % BPO as an initiator.

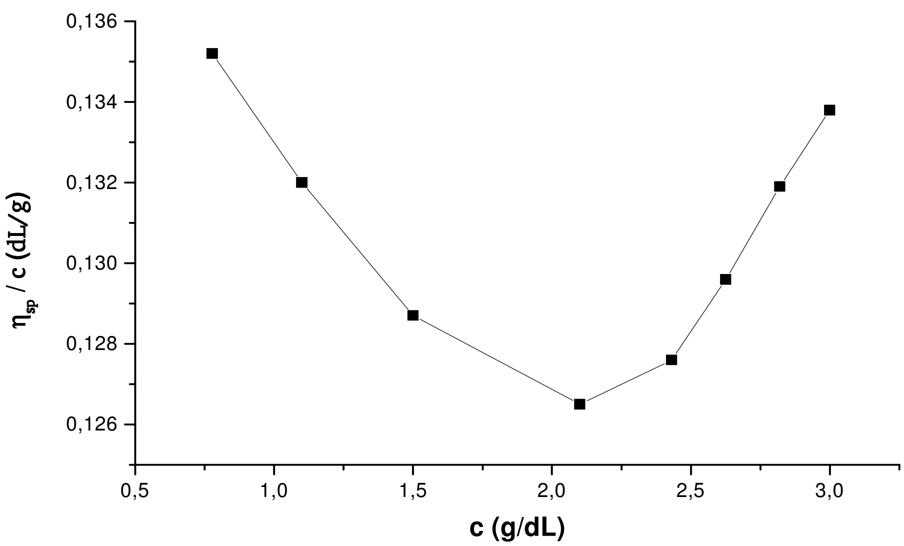


Figure 4.35. Variation of μ_{sp} /c vs c (polymer concentration) for poly(MA-1,H–AA) terpolymer with 2.0 % BPO as an initiator.

As shown in the figures the viscosity of the terpolymer in water system exhibit polyelectrolyte behaviour at lower polymer concentrations.

Table 4.10. Characteristic parameters of terpolymer with different initiator ratios.

initiator ratio (%)	**yield (%)**	**acid number (mg KOH/g)**	**[μ] at 25 ^{0}C ($dL.g^{-1}$)**
0,5	58	681	0,1211
1,0	84	692	0,1139
2,0	95	687	0,1009

Differences are expected to occur between the [μ] values at different initiator ratios. At higher initiator ratios, [μ] values decrease because of the short polymer chains. If the initiator ratio is increased, molecular weight of the polymer decreased and short polymer chains occur.

5. CONCLUSION

✓ Membranes were prepared from diglicidyl ether terminated PDMS and poly (methyl vinyl ether-alt-maleic anhydride) copolymer, hydroxy terminated PDMS and poly (methyl vinyl ether-alt-maleic anhydride) copolymer, diglicidyl ether terminated PDMS and poly (maleic anhydride-1,hexene-acrylic acid) terpolymer ; containing highly reactive free epoxide, hydroxy and anhydride groups in the side chain. As a result of crosslinking upon thermotreatment membranes become insoluble.

✓ Percent crosslinking has been determined for each synthesized membrane and the results show that 40 % (w/w) PDMS content is selected as an optimum value for poly (methyl vinyl ether-alt-maleic anhydride) and diglycidyl ether terminated PDMS, poly (methyl vinyl ether-alt-maleic anhydride) and hydroxy terminated PDMS, whereas, 30 % (w/w) PDMS content is optimum for poly (maleic anhydride-1,hexene-acrylic acid) terpolymer and diglycidyl ether terminated PDMS.

✓ The comparative analysis of FTIR spectra between poly(methyl vinyl ether-alt-maleic anhydride) copolymer and the crosslinked membrane prepared from poly(methyl vinyl ether-alt-maleic anhydride) and diglycidyl ether terminated PDMS at 40 %(w/w) PDMS content has yielded interesting results with regard to the peaks appearing at 1737 cm^{-1}(carboxyl group), 1722 cm^{-1} (ester formation) which confirm a crosslinking reaction. All anhydride functional group peak intensities decrease progressively throughout the entire cure. There are too many peaks appearing after thermotreatment which are the characteristics of siloxane groups which are definitely the evidence of PDMS addition for the crosslinking reaction.

✓ The copolymer structures were investigated on the basis of high resolution ^{1}H NMR analysis. ^{1}H-NMR spectrum for diglycidyl ether terminated PDMS and poly(methyl vinyl ether-alt-maleic anhydride) copolymer displays the ring opening at epoxide group, ester formation occuring after the reaction between maleic anhydride and epoxy groups as a result of thermotreatment. The crosslinked structure of hydroxy terminated PDMS and poly(methyl vinyl ether-alt-maleic anhydride) copolymer displays new characteristic peaks for siloxane at 0.01-0.02 ppm and ester groups at 4.14 ppm. The ^{1}H-NMR spectrum of poly(maleic anhydride -1,hexene – acrylic acid) terpolymer, on the other hand, displays some differences between the terpolymer and previous crosslinked structures.

✓ The structure of terpolymer was also confirmed by using ^{13}C NMR analysis from the characterized peaks.

✓ Dynamic swelling behaviour of crosslinked poly(methyl vinyl ether-alt-maleic anhydride) and diglycidyl ether terminated –PDMS and crosslinked terpolymer and diglycidyl ether terminated –PDMS in DMF indicates that the swelling process follows Fickian behaviour. For crosslinked poly(methyl vinyl ether-alt-maleic anhydride) and hydroxy terminated-PDMS in DMF swelling process follows non-Fickian behaviour. The crosslinked structures containing both hydrophilic and hydrophobic groups should exhibit thermosensitivity owing to the strengthening of the hydrophobic interactions with increasing temperature.

✓ From the DTA-TGA analysis for the crosslinked structure, two step degradation is displayed around 200 ^{0}C (T_{1d}) and 300 ^{0}C (T_{2d}). Crosslinked structure of diglicidyl ether terminated PDMS and poly (methyl vinyl ether-alt-maleic anhydride) copolymer leads to thermal degradation in a wide temperature range between 110 ^{0}C and 600 ^{0}C. The thermograms also show that the residual weight percent of the crosslinked network is 15.7 %. at 800 ^{0}C. Crosslinked structure of diglicidyl ether terminated PDMS and poly (methyl vinyl ether-alt-maleic anhydride) copolymer leads to thermal degradation in a wide temperature range between 120 ^{0}C and 600 ^{0}C.The thermograms also show that the residual weight percent of the crosslinked network is 17.7 % at 800 ^{0}C. Finally, crosslinked structure of diglicidyl ether terminated PDMS and poly (methyl vinyl ether-alt-maleic anhydride) copolymer leads to thermal degradation in a wide temperature range between 110 ^{0}C and 600 ^{0}C where the thermograms also show that the residual weight percent of the crosslinked network at 800 ^{0}C is 2.75 %. DSC trace for the crosslinked structure of each membrane result with the temperature endo effects on the DSC curve associated with the glass transition temperatures appearing at 105, 110, and 115 ^{0}C, respectively.

✓ Dynamic mechanical behaviour of crosslinked structures for each membrane were studied and the glass transition temperature was found by different f(x) – x functions. As expected, the loss modulus dispersion shows a maximum in the environment of Tg value and it is compatible with both tan delta and dynamic viscosity behavior. Tg values were also determined from the mid-point of the s-shaped curves which are in excellent agreement with each other.

✓ Hydrophilicity of the crosslinked membranes of diglicidyl ether terminated PDMS and poly (methyl vinyl ether-alt-maleic anhydride) copolymer, hydroxy terminated PDMS and poly (methyl vinyl ether-alt-maleic anhydride) copolymer, diglicidyl ether terminated PDMS and poly(maleic anhydride -1,hexene – acrylic acid) terpolymer were analyzed with water contact angle. Crosslinked PDMS exhibits exceptional hydrophobicity due to the methyl groups. The terpolymer, however, has a more hydrophilic character than the others which can occur as a consequence of unreacted hydroxyl groups and lower crosslinking ratio.

✓ XRD studies of the three individual membranes have yielded that the cross-linked structures are completely amorphous.

✓ The viscosity of the terpolymer in water system exhibits polyelectrolyte behaviour at lower polymer concentrations. At higher initiator ratios, [μ] values decrease and thus the molecular weight decreases due to the occurence of short polymer chains.

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