Novel Self Healing Thermoplastic Elastomers

by

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This is to certify that I have examined this copy of a master's thesis by

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and have found that it is complete and satisfactory in all respects,
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ABSTRACT

Elastomeric copolymers based on acrylic acid and butyl acrylate and their ionomers were prepared and characterized. A large number of segmented polyurethane and polyurea elastomers were also synthesized, characterized and blended with acrylic elastomers. Self healing behaviors of these copolymers and their blends were investigated at room temperature. Self healing behavior was determined by the extent of the recovery of the tensile strength of the samples. Effect of the copolymer structure, blend composition and the healing time on the recovery of the tensile properties was studied. All copolymers with ultimate tensile strength values around or below 1 MPa showed complete self healing. Polymers with higher tensile strengths seem to heal well initially within a few hours, but the healing does not seem to go completion upon further aging. These results seem to indicate a competition between microphase separation due to hydrogen bonding in the hard segments of the copolymer within the cut surfaces versus self healing or cross-interaction between the groups at the two interfaces.

ÖZET

Akrilik asit ve butil akrilat içeren elastomerik kopolimerler ve bunların iyonomerleri hazırlanıp karakterize edildi. Aynı zamanda çok sayıda poliüretan ve poliüre sentezlenip karakterize edildi ve akrilik elastomerlerle karışımları (blend) hazırlandı. Bu kopolimerler ve blendlerin oda sıcaklığında kendini iyileştirme özellikleri kopma mukavemetlerini geri kazanabilme dereceleri incelenerek belirlendi. Kopolimer ve blend kompozisyonu ile iyileşim süresinin çekme-kopma özellikleri üzerindeki etkisi çalışıldı. Kopma anındaki mukavemetleri 1 MPa ya da daha düşük olan kopolimerler tamamen iyileşme gösterdiler. Daha yüksek mukavemete sahip polimerler ilk bir kaç saatte yüksek oranda iyileşme göstermesine rağmen daha sonraki zamanda iyileşme verimlerinde kayda değer bir artış gözlenmemiştir. Bu sonuçlar, kesilen yüzeyler arasındaki karşılıklı etkileşim (iyileşme) ile bu parçalardan her birinin kendi içerisindeki hidrojen bağıyla pekişen mikro faz ayrımına bağlı etkileşimin arasında rekabet olduğunu ve iyileşmenin bu iki farklı mekanizmaya bağlı olduğunu gösterir.

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NOMENCLATURE

δ	solubility parameter
AA	acrylic acid
ATR-FTIR	attenuated total reflection fourier transform infrared spectroscopy
ATRP	atom transfer radical polymerization
BA	n-butyl acrylate
BP	benzoyl peroxide
DA	Diels-Alder
DMA	dynamic mechanical analysis
DMF	dimethylformamide
DYTEK	2-methyl-1,5-diaminopentane
FTIR	Fourier transform infrared spectroscopy
H	Hydrogen atom
HE	healing efficiency
HMDA	hexamethylene diamine
HMDI	bis(4-isocyanatocyclohexyl)methane
HS	hard segment
IPA	isopropyl alcohol
kJ	kilojoule
MMA	methyl methacrylate
MW	molecular weight
MPa	megapascal
PAc	polyacylate
PBd	polybutadiene
PEO	poly(ethylene oxide),

PI	polyisoprene
PMMA	poly(methyl methacrylate)
PS	polystyrene
PTMO	poly(tetramethylene oxide)
PU	polyurea
PUU	poly(urethane urea)
r_A	reactivity ratios of monomer A in the copolymer
RT	room temperature
SS	soft segment
T	temperature
Tol	toluene
TS	tensile strength
T-12	dibutyltin dilaurate
tBA	tertiary butyl acrylate
T_g	glass transition temperature
THF	tetrahydrofuran
TPE	thermoplastic elastomer
TPU	thermoplastic polyurethane
w_x	weight fractions of monomer X

Chapter 1

INTRODUCTION

The major goal of this study was to investigate the preparation and characterization of novel self healing thermoplastic elastomers. To achieve effective self healing we mainly focused on two types of interactions in polymers; (i) hydrogen bonding and (ii) ionic interactions. For this purpose a series of polyurethanes, polyureas and acrylic ionomers were synthesized, characterized and their self healing behaviors were investigated. Self healing behaviors of the blends of polyurethane / polyurea and polyacrylates were also investigated.

Since a wide range of thermoplastic elastomers (TPE) with different structures, morphologies and intermolecular interactions were investigated, the introduction part of the dissertation was planned to cover; (i) the types, basic synthetic methods and structure-property behaviors of different thermoplastic elastomers, (ii) preparation and properties of self healing elastomers, and (iii) types and strengths of intermolecular interactions leading to self healing.

1.1. Thermoplastic Elastomers

Thermoplastic elastomers (TPE) are an interesting and important class of polymeric materials that combine the physical characteristics of elastomers with thermoplastic behavior or processability [1]. Since their discovery in 1960’s, there has been widespread interest in their synthesis, characterization and structure-property behavior, resulting in numerous studies by both academic and industrial research groups and leading to the rapid development of a wide range of novel products and their commercialization.

Elastomers are composed of long chains which have the capability to uncoil upon stretching and retract upon removal of the force [2]. The reason of transformation from stretched, oriented state under tension to a highly coiled state with the release is the high degree of disorder (entropy driven process). Since elastomers are lightly crosslinked through covalent bonds, these chemical links prevent macromolecules from slipping past each other and therefore prevent permanent elongation [3]. The crosslinking in elastomers is obtained by an irreversible heating process, which is generally termed as vulcanization or curing. Vulcanization is achieved by compounding rubbers with various chemical ingredients such as catalysts or accelerators and vulcanizing agents. Vulcanized rubbers display high tensile strengths, excellent elongation and resistance to heat and solvents [4].

TPEs display thermal and mechanical properties similar to those of crosslinked elastomers but they can be processed by the application of heat. Moreover, in contrast to vulcanized rubbers, TPEs are also soluble in organic solvents. These features allow processing methods such as injection molding, extrusion and solution processing.

In place of the covalent crosslinks in elastomers, TPEs which are usually based on two different polymeric groups, exhibit physical crosslinks based on various phenomena such as; hydrogen bonding, ionic interactions or crystallization. The unique properties of TPEs are strongly dependent on their molecular architecture. Most TPEs have multiphase structure, which consists of incompatible hard and soft segments. These segments are covalently bonded by graft or block polymerization. TPEs can be prepared by various approaches.

Most important approaches are:

1) Multiphase compositions in which one phase is a rigid and amorphous material with high (>100 ºC) glass transition temperature (T_g) and the other phase is a soft rubbery material.
2) Segmented architectures consisting of hard and soft segments, where the hard segments are either crystalline with a melting point well above room temperature or can make strong hydrogen bonding between themselves.
3) Incorporation of ionic groups that may form clusters in an elastomeric matrix, in a polymer blend, or in star polymers [5].

1.1.1. Triblock copolymers

Commercially most important TPEs are (A-B-A) type triblock copolymers, such as polystyrene-polyisoprene-polystyrene (PS-PI-PS) and polystyrene-polybutadiene-polystyrene (PS-PBd-PS) and their hydrogenated versions. PS-PI-PS and PS-PBd-PS triblock copolymers are synthesized by anionic polymerization and generally composed of high molecular weight (50,000-100,000) PBd or PI central block and lower molecular weight (20,000-40,000) PS end blocks. Here, PS is the hard phase, which is incompatible with the elastomeric central phase. At room temperature, PS domains act as physical crosslinks (through entanglements) as seen in Figure 1.1. These crosslinks resemble S-S crosslinks in vulcanized rubbers. However, as temperature increases, PS phase softens and entanglements are broken, so the material can be processed by conventional molding techniques. Cooling reestablishes the glassy domains of PS and the material again act as elastomers at ambient temperature [6].

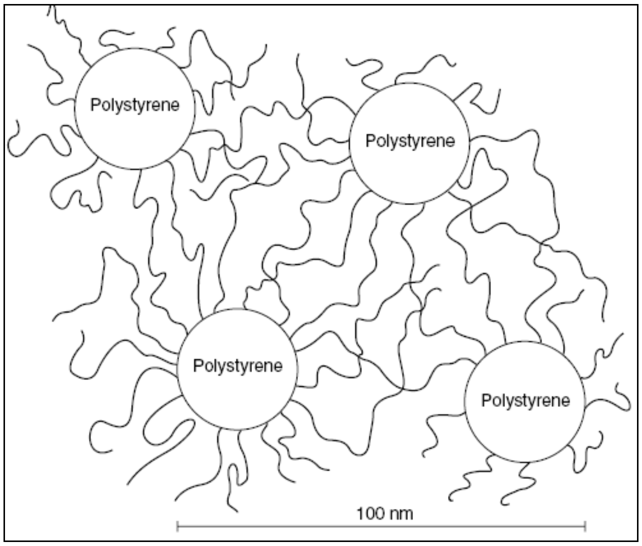


Figure 1.1. Microphase morphology of PS-PBd-PS triblock copolymer [2]

The morphology of styrenic triblock copolymers is reliant primarily on the relative composition of hard and soft segments. As the content of hard segment increases, the morphology changes from spherical to cylindrical domains of hard segments in the continuous soft matrix and subsequently to lamellar structure when relative amounts of each component reach to about 50% by weight [7].

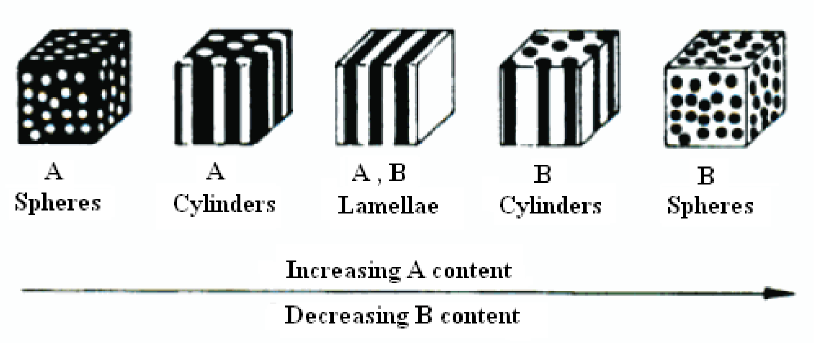


Figure 1.2. Changes in morphology of (A-B-A) triblock copolymer with composition [8]

B-A-B type block copolymers, where soft segments form the end blocks, do not exhibit TPE behavior since these systems can not form a network structure. For a continuous load bearing network to exist, the soft segments should be immobilized. This can only be achieved by anchoring both ends of the soft segment to hard domains [1].

1.1.2. Multiblock or segmented TPEs

Another class of TPEs consists of segmented or multiblock copolymers, where alternating hard and soft segments are chemically linked along a macromolecular backbone. Important segmented TPEs include polyurethanes, polyesters and polyamides. The microphase separation in multiblock or segmented copolymers may take place due to; (i) strong hydrogen bonding between hard segments (e. g. polyurethanes), (ii) crystallization of hard segments (e. g. polyesters), or (iii) both hydrogen bonding and crystallization (e. g. polyamides). The incompatibility of the hard and soft regions leads to microphase separation as given in Figure 1.3. In principle the microphase structure is similar to that of triblock copolymers, except in multiblock copolymers the hard segments are more closely packed and each chain has several alternating hard and soft segments along its backbone.

While the elastomeric phase provides flexibility, crystalline phase induces the thermal and mechanical strength in the material. Therefore, the properties depend on many parameters such as chemical structure, relative composition and molecular weight of the segments.

Segmented elastomers such as polyurethanes and polyesters are synthesized by step growth polymerization and generally through two step “prepolymer” method [9,10]. In the first part, a “prepolymer” is prepared from the reaction of soft segment oligomer with excess diisocyanate or diacid. Subsequently the hard segments are formed and the molecular weight of the polymer is increased by introducing quantitative amounts diamine or diol chain extenders.

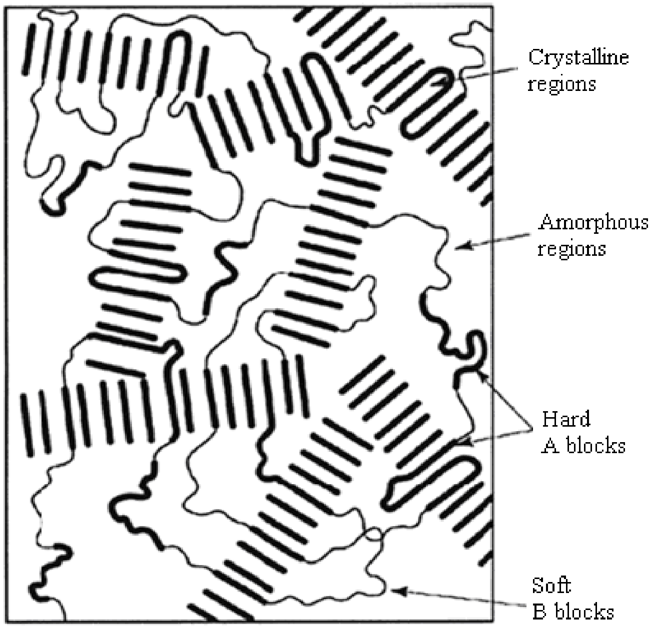


Figure 1.3. Microphase morphology of segmented copolymers [1]

1.1.2.1. Thermoplastic polyurethanes

Thermoplastic polyurethanes (TPU) are versatile materials which have applications ranging from films, coatings, adhesives to biocompatible polymers. The pioneering work on TPU was performed by Otto Bayer and his coworkers in Germany [11]. This work was followed by Du Pont [12] and ICI [13]. In the subsequent years, much effort was directed on a wide variety of starting materials and optimization of the reaction conditions (catalyst and method). The first commercial TPUs were on the market in 1960's under the trade names Lycra® by Du Pont and Ellastolan® by Bayer and Pellethane® by B. F.Goodrich. Today, due to extensive research and a much better understanding of the structure-property behavior, the properties of the polyurethanes can be tailored for the desired application.

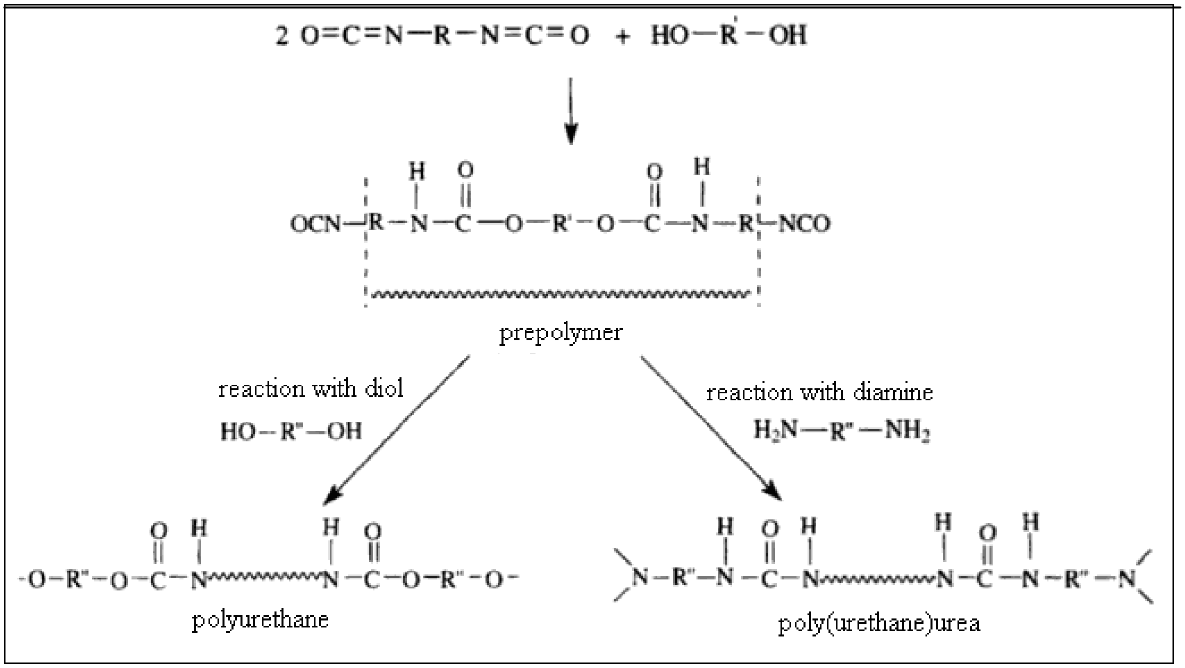


Figure 1.4. Reaction scheme for the preparation of segmented polyurethane and poly(urethane)urea by using the “prepolymer” method. Note that the difference relies on chain extension part [14]

Polyurethanes contain carbamate groups (–NHCOO-) in their backbone structure. Segmented TPUs are generally formed by the reaction of excess diisocyanate with a high molecular weight macroglycol (polyester or polyether based) and subsequently with stoichiometric amount of a short-chain diol called the “chain extender”. When the prepolymer is extended with a diamine, the final product is called a poly(urethane)urea. Figure 1.4 describes detailed reaction scheme for the preparation of segmented polyurethanes by prepolymer method.

Depending on the nature and structure of the diisocyanate (aromatic or aliphatic) urethane linkage formation reactions are performed at temperatures between 50 and 100 °C. When cycloaliphatic diisocyanates are used a catalyst is also employed. Thermoplastic properties are pronounced when difunctional reactants are used in stoichiometric ratios. The segmented structure of the resultant bulk material is shown in Figure 1.5.

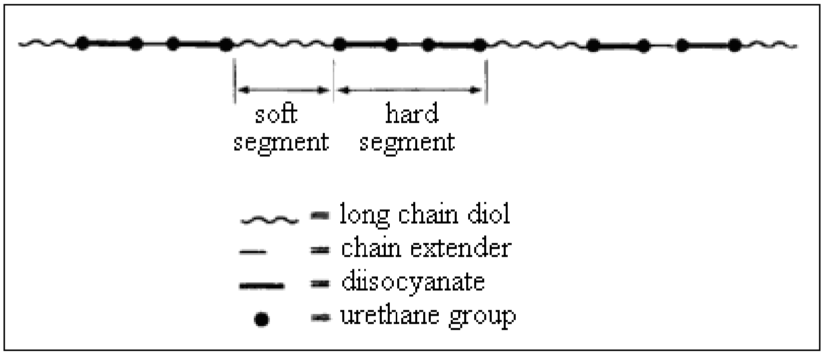


Figure 1.5. Schematical representation of TPU based on diisocyanate, long chain diol and low MW chain extender [8]

The hard segments and soft segments are incompatible in microscopic dimensions. The nature and degree of phase separation of TPUs depend on many parameters such as;

i) extent and strength of hydrogen bonding between hard-hard and hard-soft segments
ii) crystallinity and symmetry of hard segments
iii) chemical nature of soft segments
iv) molecular weight distribution of the segments
v) frequency of alternating segments
vi) interfacial adhesion between segments (segment compatibility)
vii) polymerization method (one or two stage) [10,15].

In segmented TPUs, hydrogen bonding between carbamate groups results in domain association and consequently regular packing of hard segments. As depicted in Figure 1.6, the primary intermolecular interaction in urethane is between C=O group of one chain and N-H group of another chain. In the case of poly(urethaneurea)s, in addition to monodentate interaction between carbamate groups, bidentate hydrogen bonding occurs between urea groups, which in turn affect the morphology and properties dramatically. H-bonding between -NH groups (proton donor) and polyether oxygen or polyester carbonyl groups is also of great importance since they lead to microphase mixing [14].

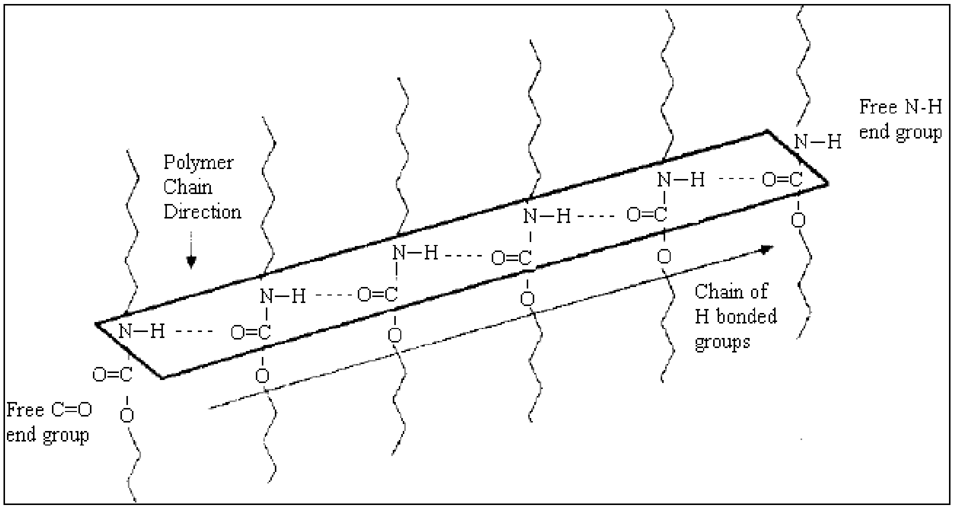
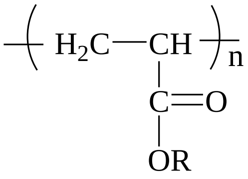


Figure 1.6. Chain arrangement induced by monodentate hydrogen bonding between carbamate groups in polyurethanes [16]

The choice of macrodiol influences many properties such as the low temperature performance and resistivity to solvents whereas the hardness, stiffness, and load-bearing properties, increases with increasing hard-segment content [17]. The hard segments are virtual crosslinks that can be altered by heating or dissolution. Subsequent cooling or desolvation makes the polymer regain its microphase morphology and the room temperature properties.

1.1.3. Acrylate based TPEs

Acrylate based or acrylic TPEs belong to a group of vinyl polymers, which have a hydrocarbon backbone with ester side groups as shown in Figure 1.7. Important monomers used in the preparation of acrylic elastomers are ethyl, n-butyl, 2-methoxyethyl and 2-ethoxyethyl acrylates. The saturated backbone provides heat and oxidative stability whereas ester group induces polarity into the material [18]. Pendant R group which can be a hydrogen atom, alkyl chain or alkyl chain with electronegative atoms, has also a dramatic effect on the performance of the resultant polymer.



$$\left(\mathrm{H_2C-CH(C{=}O)OR}\right)_n$$

Figure 1.7. Structure of an acrylic polymer

Poly(n-alkyl acrylates) have long alkyl chains as R constituents. Depending on the structure and length of the side chain, the properties such as low temperature flexibility, polarity and solubility parameter (δ) of the polymer can be altered [18].

Copolymers of acrylates are generally synthesized by radical polymerization techniques. The sequence of the monomers in the backbone is determined by the relative reactivities of radicals. For instance, the reactivity ratio r_{AB} reflects the affinity of radical A to react either with monomer A or monomer B. The reactivity ratios of monomers determine the type of the resultant polymer such as alternating, block or random copolymer regardless of the feed composition.

Similar to styrenic elastomers, (A-B-A) type triblock copolymers in which at least one constituent is based on an acrylic monomer has also been studied [19]. PS hard blocks in PS-PBd-PS is replaced by a higher T_g polymer which is poly(methyl methacrylate) (PMMA), therefore a higher service temperature could be obtained for the resultant macromolecule. Other examples of this type of triblock copolymers are poly(MMA-Butadiene-MMA) and poly(MMA-tBA-MMA), where tBA indicates tert-butyl acrylate backbone. These copolymers are generally synthesized by atom transfer radical polymerization (ATRP).

Copolymers of acrylates which contain acidic groups are categorized under a different class as ionomers and are discussed below.

1.1.3.1. Ionomers as TPEs

Ionomers are polymeric materials which contain small amounts of ionic side groups (about 1-10 mole percent) in their hydrophobic backbone [20]. The ionic parts are generally carboxylic, sulfonic or phosphonic acid groups that are partially or completely neutralized.

Ionomers have received significant attention due to their interesting properties. The unique morphology of ionomers results from the introduction of metal cations, which can interact with ionizable side groups in the chain. The Coulombic attraction between side groups and metal cations form ion-counterion pairs. The aggregation of these ion pairs is called multiplets. Multiplets act as physical crosslinks and therefore provide excellent thermal and mechanical properties to the copolymer. They may also cause a slight increase in the T_g of the polymer [21].

Isolated multiplets restrict the mobility of the adjacent polymer chains so each of them is surrounded by a region of restricted mobility (Figure 1.8). As the ion content of the ionomer increases, the multiplets approach each other and the reduced mobility regions begin to overlap. After a critical point, the continuous region exhibits its own glass transition temperature other than that of the polymer matrix and termed as a cluster [22].

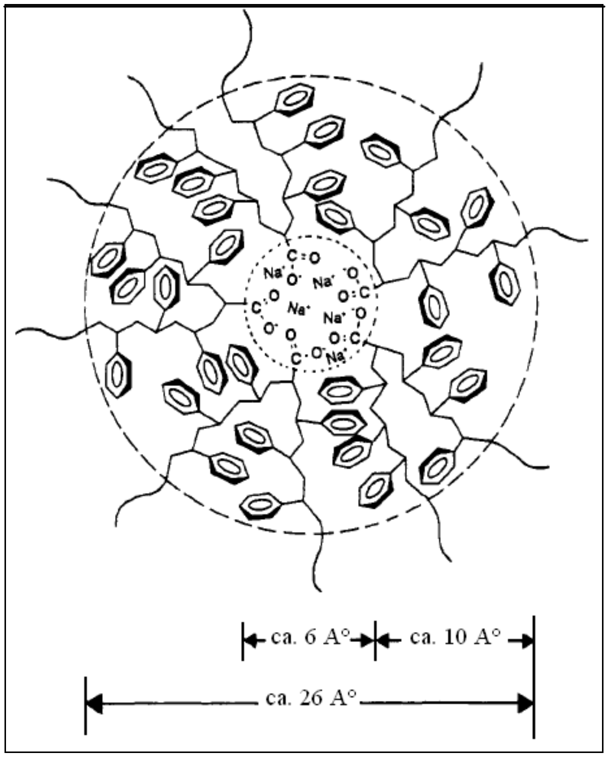


Figure 1.8. Schematic diagram of poly(styrene-co-sodium methacrylate) ionomer with ca. 10 A° restricted region surrounding ca. 6 A° multiplet [22]

The mechanical properties of ionomers depend on many factors such as the chemical structure of the non-ionic polymer backbone, type of the ionic groups (such as carboxylate or sulfonate), ion content, the degree of neutralization, the nature of the counterion and the preparation conditions [23]. One of the most important commercial ionomer is marketed under the trade name Surlyn by DuPont. It is a copolymer of ethylene and methacrylic acid and is available in different neutralization ratios.

1.1.4. TPEs through polymer blends

In addition to triblock copolymers, segmented elastomers and ionomers, polymer blends constitute an important class of TPE. By definition, polymer blending is mixing of two or more polymers to achieve a final material with desired properties. A blend can be miscible, partially miscible or immiscible. The miscibility of the constituent polymer chains is mainly governed by thermodynamic parameters. If mixing of two polymers has a negative Gibbs free energy of mixing, they form a homogeneous mixture in the molecular level and the properties of the final product are the averages of constituents [24].

Generally, an ideal blend can be made from nearly compatible polymer chains where the blend is visually homogeneous but phase separated in micro scale [25]. The components are mechanically mixed together and different polymer chains form an interdispersed multiphase morphology. This phase arrangement provides improved characteristics such as impact strength, processability, tensile strength, stiffness and heat resistance. Blends of ethylene-propylene copolymer or propylene homopolymer (as hard phase) with soft elastomers are commercially important TPE combinations of this type [18]. In some cases, the rubbery component can be produced in situ by a process called dynamic vulcanization. The morphologies for mechanical blends and dynamic vulcanizates are provided in Figure 1.9. Today, it is estimated that about one third of all commercially produced polymer materials are blends of two or more polymers [26].

Blends can also be prepared from immiscible polymers by a process termed as compatibilization. Here, the interface of the polymers is altered by introducing suitable compatibilization agents in order to decrease interfacial tension and improve adhesion [27].

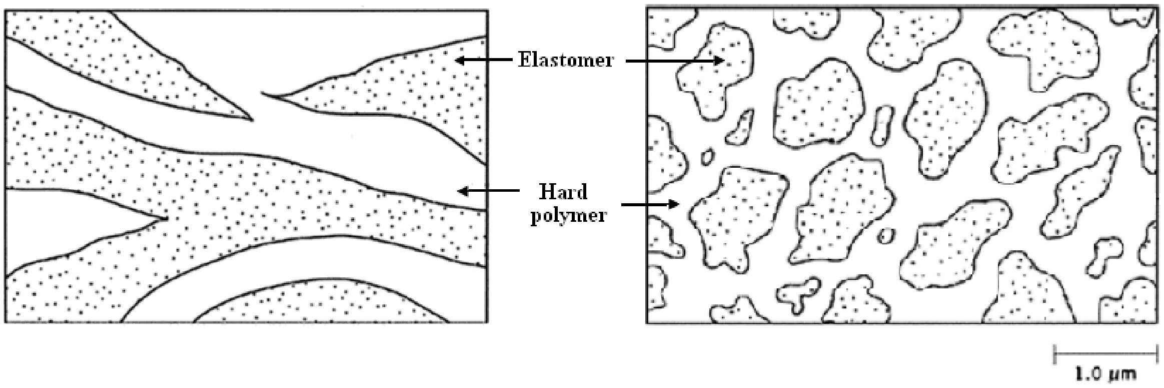


Figure 1.9. Microphase arrangement in hard polymer/elastomer combinations obtained by; (a) mechanical blending (left) (b) dynamic vulcanization (right) [1]

1.2. Self Healing Polymers

Self healing materials include polymers, metals, ceramics and their composites, which have the capability of heal when damaged by thermal, mechanical, ballistic impact or other means [27].

The idea of designing self healing materials is inspired by biological systems. There are a number of examples in nature such as wound healing of skin, healing of a fractured bone and strength recovery of mussel byssal threads after yielding [28]. Mimicking self healing ability of the nature during material design gives rise to production of safer and more durable materials. Therefore, healing of composites, concrete, fabrics and polymers has gathered significant attention over the last decades.

In this section, repair mechanisms and methods in polymers, mainly TPEs will be discussed.

1.2.1. Self Healing in TPEs

Although self healing behavior of polymeric materials differs considerably for thermoplastics and thermosets, the repair process can be either autonomous or nonautonomous. Autonomic self healing requires no stimulus whereas the latter can be achieved only by the aid of an external stimulus such as light or heat [29].

Several theories have been proposed to explain the self healing mechanism in thermoplastics. Among them, the one developed by Wool and O'Connor has been proven to be successful [30]. According to this model, as also shown schematically in Figure 1.10, self healing takes place in five stages; namely (1) surface rearrangement, (2) surface approach, (3) wetting, (4) diffusion and (5) randomization. In the first stages, two surfaces that are formed by cracking, fracture or cutting are brought into contact. Instantaneously, polymer chains on both surfaces begin to interact with each other and start diffusing. The interface gradually disappears and mechanical strength is regained. The crack healing is primarily due to chain diffusion or reptation[31] across the interface [32]. Chain mobility can be improved by application of external heat or evolution of heat as a result of impact. Otherwise, there should be reasonably strong interaction within the material such as electrostatic interaction between ionic groups or hydrogen bonding for effective repair.

1.2.1.1. Self Healing in Ionomers

In addition to their improved mechanical properties, ionomers are also known for their self healing ability. Two ionomers commercialized by DuPont, namely (i) ethylene-co-methacrylic acid copolymers which are marketed under the trade name Nucrel® and (ii) its neutralized forms based on sodium or zinc and known by the Surlyn® trade name have attracted much interest. A number of investigations on self healing behavior of these materials were performed by various research groups.

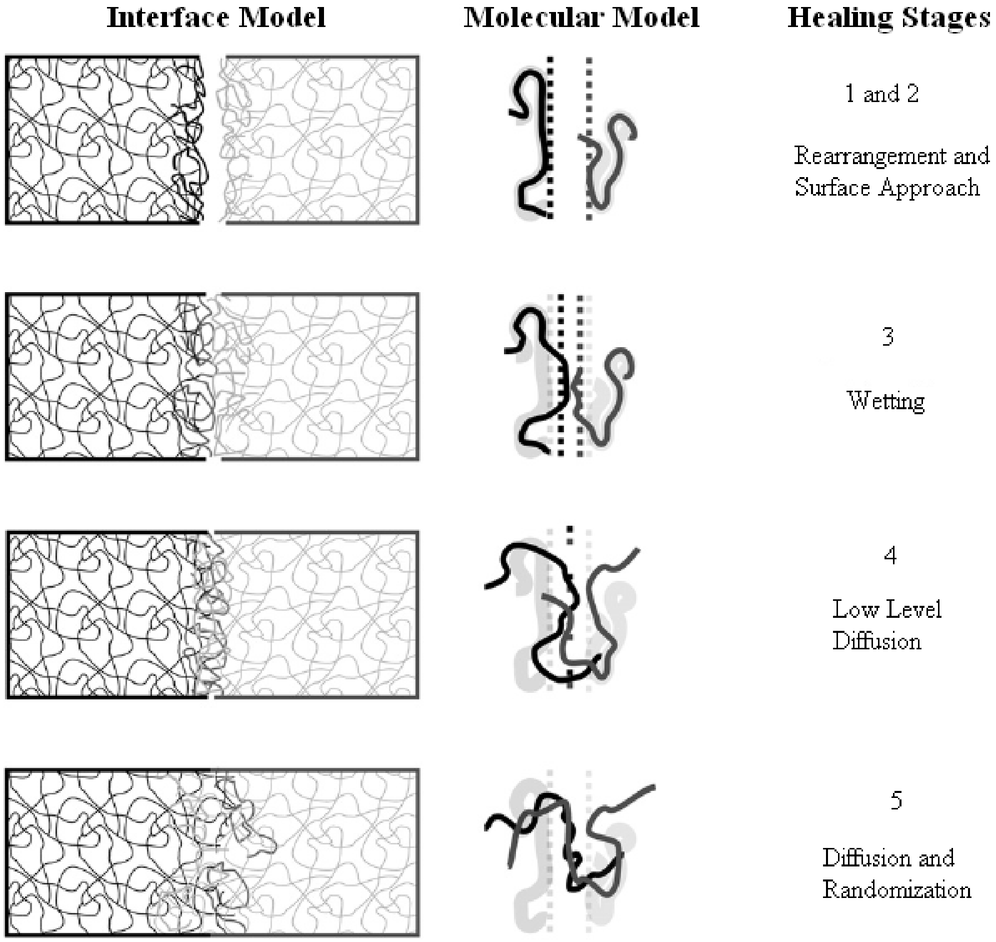


Figure 1.10. Theoretical stages in crack healing [33]

The self healing behavior of these ionomers was studied by puncturing them with high speed bullet shots from a rifle and observing the sealing of the holes. The energy transferred into the material via impact led to a local increase in the temperature, which in turn resulted in healing. Initially, self healing behavior of these ionomers was attributed to their ionic content [34]. Fall proposed that ionic aggregation and melt flow in the material are the key factors for healing. However, observed healing of Nucrel® with unneutralized acid groups could not be explained. Recent studies on the healing behavior of these materials performed by Ward and co-workers [35-37] provided valuable information. In their work, polyethylene, Nucrel® and Surlyn® polymers were subjected to projectile and peel tests and comparison of the materials led to interesting conclusions. First of all, it was realized that the healing ability of the samples depended primarily on the carboxylic groups instead of the ionic content. The thermally controlled hydrogen bonding between these groups was responsible for puncture reversal and/ or self healing in Nucrel®.

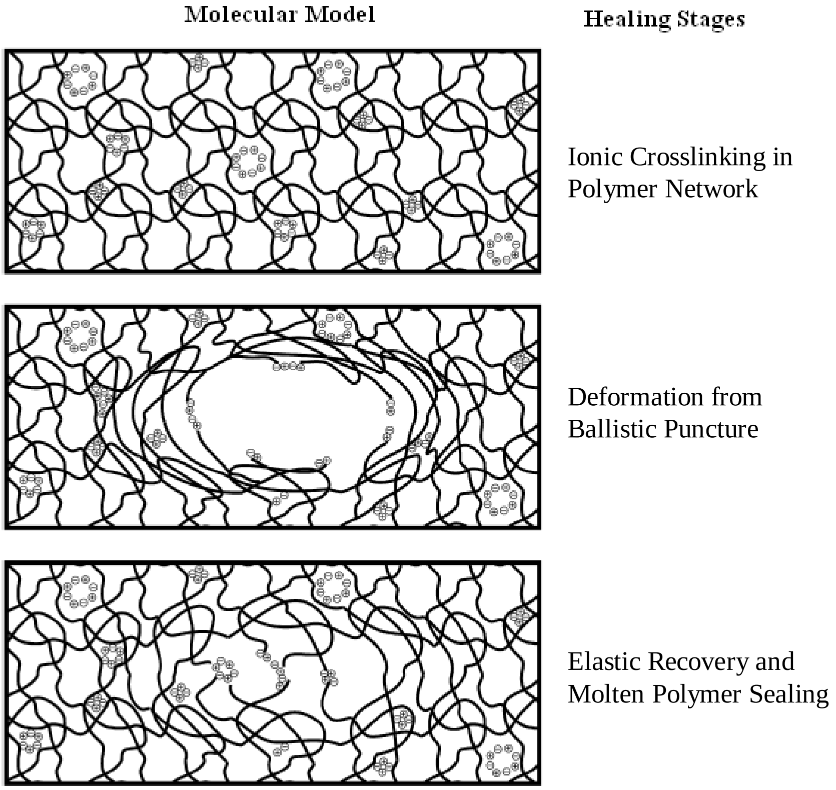


Figure 1.11. Healing Mechanism in Ionomers [33]

The self healing after impact was explained by a two stage mechanism, which consisted of; (i) the elastic recovery and (ii) subsequent inter-diffusion of chains as shown in Figure 1.11.

Projectile puncture resulted in local melt, which retracted after bullet has passed through. If the materials were heated prior to the projectile test, permanent deformation was likely to occur and the material exhibited viscous response. Hence, elevated temperatures inhibited healing as seen in Figure 1.12.

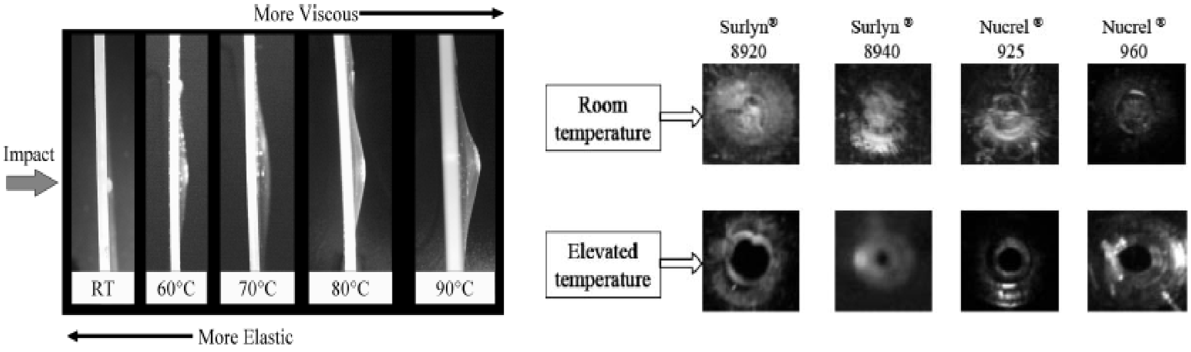


Figure 1.12. Temperature effect on elastic recovery and healing

Since chain mobility and diffusion were triggered by temperature increase via projectile impact, same effect was also observed during the sawing tests. The healing was achieved by the heat evolved because of friction. Moreover, the projectile shape has an influence on healing for instance blunt ended cylindrical bullet impacts were irreversible.

It was concluded that ionic and/or secondary interactions are responsible for healing but an optimization should be made between two competing mechanisms: recovery enhancement and decline in the mobility by physical crosslinks.

1.2.1.2. Self healing by Secondary Interactions / Supramolecular assembly

Recently Leibler and co-workers demonstrated self healing by supramolecular assembly [38]. Supramolecular polymers are macromolecules in which noncovalent bonds hold the monomers together [39]. In this study, a mixture of fatty diacid and triacid is allowed to react with diethylene triamine and subsequently with the urea as depicted in Figure 1.13. Since one type of the monomer is multifunctional, it can associate with more than two molecules, thus resulting in a network. The network is physically crosslinked by the high density of hydrogen bonding among associating groups. The variety of these associating groups prevents close packing of chains in other words crystallization of the supramolecular polymer structure formed but it is not sufficient to induce a microphase separated morphology.

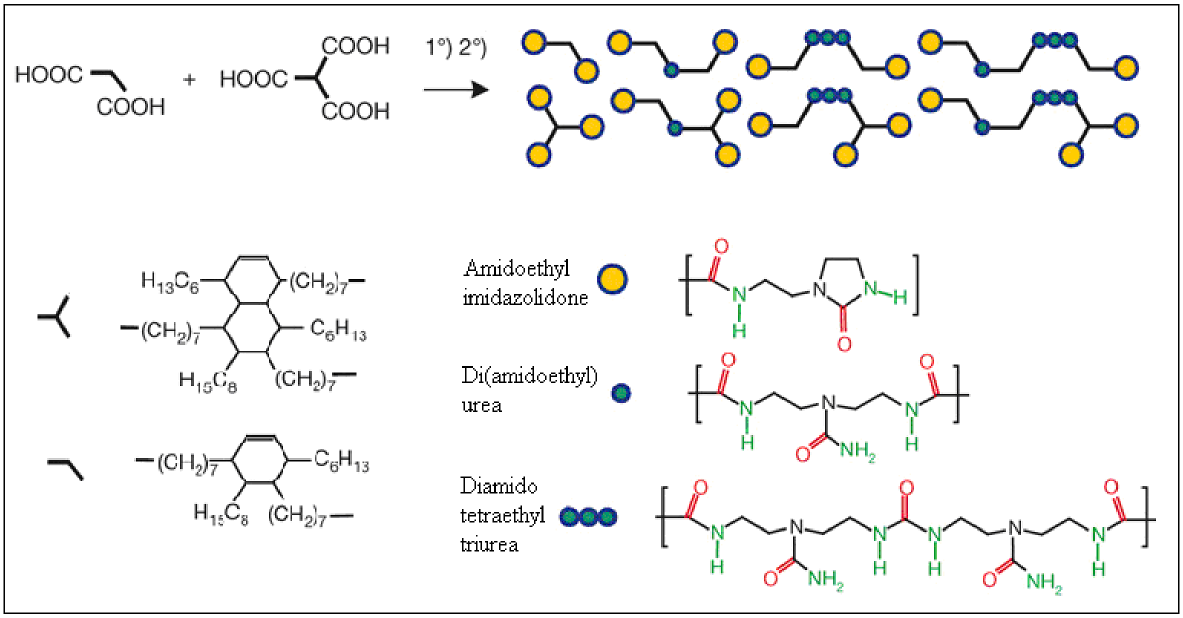


Figure 1.13. Reaction scheme of supramolecular network from fatty diacid and triacid reacted with 1°) triamine 2°) urea to give H bonding groups: amidoethyl imidazolidone, di(amidoethyl)urea and diamido tetraethyl triurea.[38]

Leibler and co-workers also showed the self healing ability of the self-assembled polymer by following free and bound N-H bond peaks in time resolved FTIR spectroscopy. Sample was first heated to 125°C and then quench-cooled. Time dependent IR experiments revealed that reassociation time for free N-H bonds is longer than the relaxation time of rubber network. This confirmed that free H-bonds had sufficient time to self mend.

Self healing tests which are basically ‘cut and join type’ demonstrated that healing is reliant on the elapsed time between severing and combining the ends of the fractured parts. Upon cutting, the H-bonding groups on each surface are free and tend to seek for partners. If fractured parts are kept away for long hours, H-bonds in the cut face interact within the same piece. The time effect was also observed by comparing stress strain behavior of mend samples and original polymer.

1.2.2. Self Healing in thermosets

Self healing in thermosets is mainly achieved either by using reversible crosslinking or storing healing agents in material. Wudl and coworkers studied mendable polymers by using Diels-Alder reactions [39]. Since these reactions are thermally reversible, the covalent bonds of the polymer backbone or pendant groups can be easily reverted by heat. The fractured parts of crosslinked polymer are clamped together and heated to reform DA adducts which exhibit retro DA across the crack surface. The difficulty of the method is that the repair process can occur only in the presence of an external stimulus.

White and coworkers have achieved autonomous self mending by using microcapsules of monomer embedded in polymer matrix [40]. Upon cracking, the monomers are released from the capsules and fill the crack via capillary action, and subsequently react with the catalyst in the polymer matrix as schematically shown on Figure 1.14.

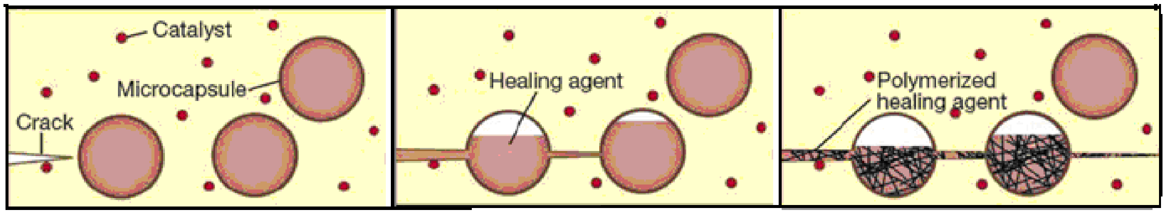


Figure 1.14. The autonomic self healing. From left to right; a. Crack forms upon damage of the material, b. The crack ruptures the microcapsules, monomers are released into crack, c. Polymerization starts as monomers coincide with catalyst

Braun and coworkers studied same concept with a different approach [41]. In this case, the healing agent is not encapsulated but exists as phase separated droplets whereas the catalyst is encapsulated in the matrix. When damage occurs, the capsules rupture and the catalyst is released into the crack. As catalyst comes into contact with the silicone based macromer droplets, it triggers polymerization of the healing agent and therefore healing of the crack is achieved.

The main disadvantage of encapsulated systems is inefficient mending if cracks occur at the same place many times. This problem could be overcome to some extent by constructing channels to deliver the liquid healing agents through the network.

1.3. Intermolecular Interactions in Self Healing Elastomers

Polymers are macromolecules in which small repeating units are joined by chemical linkages. The term ‘macromolecule’ was first coined by Staudinger in 1922 [42]. It was his pioneering work which emphasized that polymeric properties result from the macromolecular nature. He explained that a large number of repeating units are linked by covalent bonds to form long chains and entanglements of those affect the properties of macromolecule [43].

Later on, it was realized that the properties of polymers were determined not only by covalent bonds between individual atoms but also by the secondary inter- and intramolecular interactions. The intermolecular forces are namely electrostatic or ionic attraction, hydrogen bonding, dipole-dipole and Van der Waals interactions. These non-covalent interactions are weak and reversible, however may be strong enough to affect the molecular architecture. The bond energy and relative strengths of different intermolecular forces are given in Table 1.1.

Table 1.1. Bond Energy and Relative Strength of Different Intermolecular Forces [44]

Type of interaction	Bond energy (kJ/mol)	Relative strength
Ionic attraction	850 - 1700	1000
Hydrogen bonding	15 - 170	100
Dipole-dipole interaction	2 – 8	10
Van der Waals interaction	~1	1

In order to understand self healing phenomena observed in TPEs, the nature of the favorable secondary interactions such as hydrogen bonding and ionic interactions which are responsible for healing behavior should be studied.

1.3.1. Hydrogen Bonding

Hydrogen bonding can be defined as the interaction between a hydrogen (H) atom linked to a more electronegative atom (X) such as N, O and F and the more electronegative atom on a neighboring or on the same molecule as shown by the dotted line below.

X─H·······X─A

Depending on the magnitude of the interaction energy, hydrogen bonding is usually divided in three different categories, which are; (i) weak (< 15 kJ/mol), (ii) moderate (15-60 kJ/mol) and (iii) strong (60-170 kJ/mol) hydrogen bonding [45].

The importance of hydrogen bonding (H-bonding) relies on its strength and responsiveness to an external stimulus such as temperature, solvent and pH. Most of the highly complex natural systems take advantage of H-bonding for instance, two strands of DNA molecule are held by H-bonding between base pairs.

In 1980's, a new research field emerged called supramolecular chemistry. Supramolecular chemistry aims at developing complex chemical systems from components interacting through noncovalent intermolecular forces [46]. It is known that all polymers possess at least one type of secondary interaction, but here repeating units are held together by other bonds than covalent bonds.

One of the main categories of supramolecular polymers is based on hydrogen bonding. These polymers are good candidates for self healing since H-bonding interactions are strong, directional and reversible, which not only give integrity to the structure but also flexibility to tune the strength when exposed to external stimuli. Combining several H-bonding units in one repeat unit and building an arrangement in a particular direction enhances the bond strength and specificity. This effect was observed when quadruple H-bonding units based on ureidopyrimidinone (UPy) were employed by Meijer and Sijbesma [47]. UPy units have high association constants therefore it is possible to produce supramolecular networks with significant degree of polymerization. The H-bonding pattern between two UPy units is schematically shown in Figure 1.15. Although supramolecular polymers based on UPy units behave as conventional polymers at room temperature, they display liquid-like properties at elevated temperatures [48].

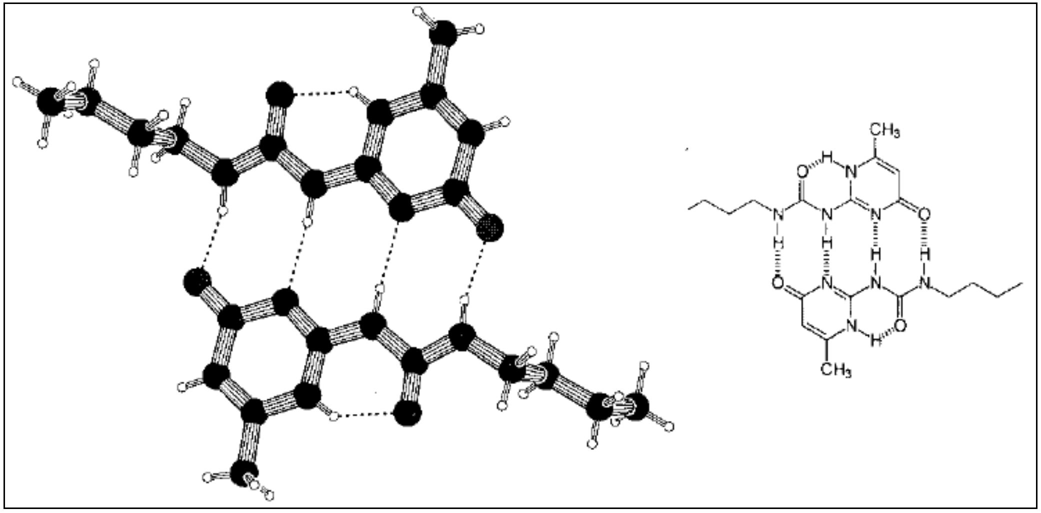


Figure 1.15.The X-ray structure indicating H bonding pattern between two UPy units [48]

The flexibility of the H-bonds paved the way to design self mending polymers. As already explained above, Leibler and coworkers studied the synthesis of supramolecular self healing elastomers from fatty acid derivatives, diethylene triamine and urea. Owing to high concentrations of associating moieties, mending was achieved when cut samples are brought together at room temperature [38].

Self healing in ionomers was also found to be related with thermally controlled hydrogen bonds as depicted in Figure 1.16. The carboxylic acid groups in Nucrel® (unneutralized ethylene-co-methacrylic acid copolymer) were responsible for rapid puncture reversal during projectile tests. Although the healing was provoked by local increase in the temperature via the bullet impact, elevated temperatures did not lead to healing of the damaged sample as already explained in section 1.2.1.1 [36].

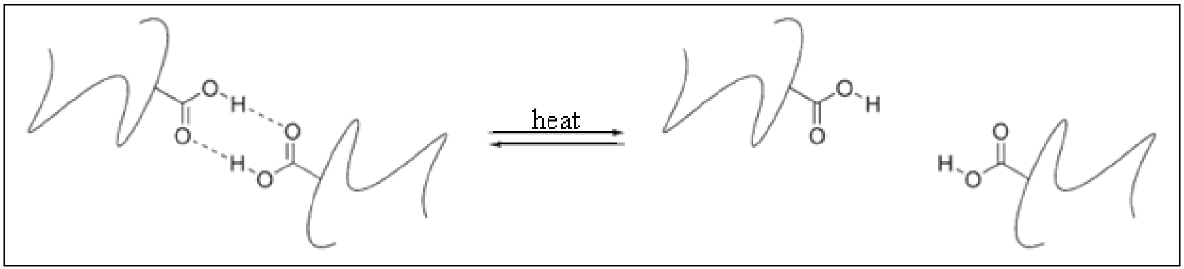


Figure 1.16. Thermally responsive H bonds in Nucrel ionomer [49]

1.3.2. Ionic Interactions

Ion containing polymers have been of great interest for many years because of numerous possible applications ranging from process modifiers, additives to membranes and cosmetics. These applications are due to dramatic effect imparted by presence of ions on the polymer properties.

Ion containing polymers are usually divided in two categories according to their ionic content, which are (i) ionomers (polymers with low ion content), and (ii) polyelectrolytes [20]. The amount of ionic groups in the non-ionic backbone determines the final characteristics such as modulus, tensile strength, impact resistance and melt viscosity. Ionomers contain up to 10% ionic side groups which can be partially or completely neutralized by metal cations. As a result of Coulombic attraction, ionic multiplets form and behave as physical crosslinks. This is beneficial up to a certain value in terms of glass-transition temperature, mechanical properties, transport properties, melt viscosities and self healing ability.

Self healing ionomers were studied by Ward and co-workers [36,37]. The work included projectile tests on several unneutralized and neutralized ionomer samples. It was concluded that in addition to the positive effect of H-bonding on self healing phenomena, there were two competing mechanisms, (i) recovery enhancement due to increase of ionic interaction, and (ii) the loss due to rigidity of ionic crosslinks. Therefore an optimization should be made on the ion content and degree of neutralization for optimum healing behavior.

1.4. Polymer Blends Through Specific Interactions

Blending of polymers is achieved by many ways such as melt mixing, solution blending and dynamic vulcanization. However, the key point during preparation is to obtain significant molecular mixing between different polymer chains by the use of favorable interactions. These specific intermolecular interactions in blends are classified as hydrogen bonding, ionic interactions, strong dipolar interactions and charge transfer complexes [50].

In order for two polymers to form a miscible blend, there should be a balance in terms of intermolecular interactions between the like and unlike polymers. For instance, if one of the polymers is strongly self associated, then the other polymer should be relatively weakly self associated and/or it should contain sites able to interact with the unlike polymer chains [16]. Self association becomes evident in the case of strong interactions such as H-bonding. For instance, polymers containing amide and urethane groups can self associate in the form of linear chains whereas carboxylic groups form cyclic structures such as dimers [50].

In this study, compatible polymer blends are prepared from two strongly self associated systems: polyureas and polyacrylates and the self healing behavior of resultant materials were studied.

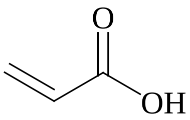
Chapter 2

EXPERIMENTAL

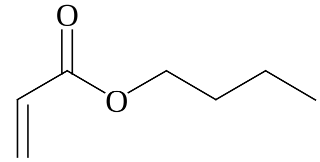
2.1. Materials

Acrylic acid (AA) and n-butyl acrylate (BA) were purchased from Aldrich. Benzoyl peroxide (BP) was obtained from Merck. Bis(4-isocyanatocyclohexyl)methane (HMDI) was kindly supported by Bayer, Germany. Purity of diisocyanate was determined as higher than 99.5% by dibutylamine back titration method. Poly(tetramethylene oxide) glycol (PTMO) with $<M_n>$ = 2040 g/mol (DuPont), α,ω-aminopropyl terminated poly(tetramethylene oxide) (PTMO-NH_2) with $<M_n>$ = 1100 g/mol (Aldrich) and amine terminated poly(ethylene oxide), Jeffamine ED2003, with $<M_n>$ = 2000 g/mol (Huntsman) oligomers and 2-Methyl-1,5-diaminopentane (Dytek) (DuPont) and hexamethylene diamine (Merck) were used as received. Dibutyltin dilaurate (T-12) was obtained from Air Products. All chemicals were of reagent grade and were used without further purification. Reagent grade isopropyl alcohol (IPA) (Merck), tetrahydrofuran (THF) (Merck), methanol (Merck), toluene (Merck) and technical grade n-hexane were all used as received. Methanolic NaOH was prepared and standardized against potassium hydrogen phthalate (KHP) solution. Number average molecular weights of amine terminated oligomers were determined by end group titration using standard hydrochloric acid and bromophenol blue indicator in methanol. Chemical structures of the reactants used during synthesis are provided in Table 2.1.

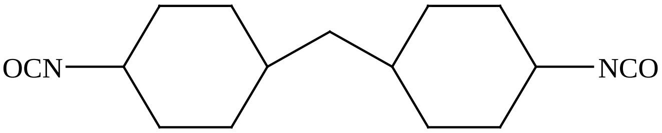
Table 2.1. Chemical structures of the reactants used



Acrylic acid
(AA)



n-butyl acrylate
(BA)



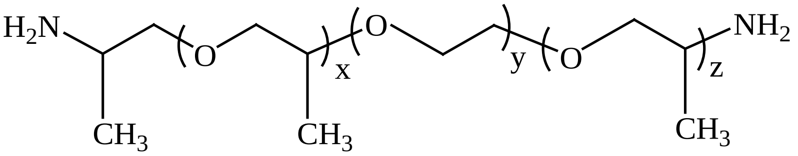
Bis(4-isocyanatocyclohexyl)methane (HMDI)

$$HO\!\left(CH_2CH_2CH_2CH_2-O\right)_x\!H \qquad x=27$$

Poly(tetramethylene oxide) glycol (PTMO)

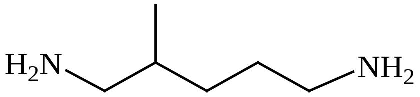
$$H_2N\!\left(H_2C\right)_3\!O\!\left(CH_2CH_2CH_2CH_2O\right)_x\!\left(CH_2\right)_3\!NH_2$$

α, ω-aminopropyl terminated poly(tetramethylene oxide) (PTMO-NH_2)

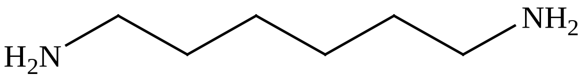


y≈39, (x+z)≈6

Jeffamine ED2003 (polyether amine, PEO-NH_2)



2-Methyl-1,5-diaminopentane (Dytek A)



Hexametylene diamine (HMDA)

2.2.Reaction procedures and sample preparation

2.2.1. Synthesis of acrylic elastomers

Free radical polymerization reactions were conducted in 500 mL, 3-neck, round bottom, Pyrex flasks equipped with an overhead stirrer, reflux condenser and a thermometer. Calculated amounts of n-butyl acrylate, acrylic acid, benzoyl peroxide and toluene were introduced into the flask. The homogeneous solution was heated slowly to 85 ± 5ºC and kept at this temperature for about 24 hours. Highly viscous polymer solution obtained was diluted with toluene / methanol (5/1) mixture. The polymer was coagulated in n-hexane, washed 3 times with n-hexane to remove any residual contaminants and dried in a vacuum oven at 50ºC until constant weight. The polymer was then re-dissolved in methanol/toluene (1/1) mixture to determine its acid content by titration or for the preparation of ionomers through controlled neutralization.

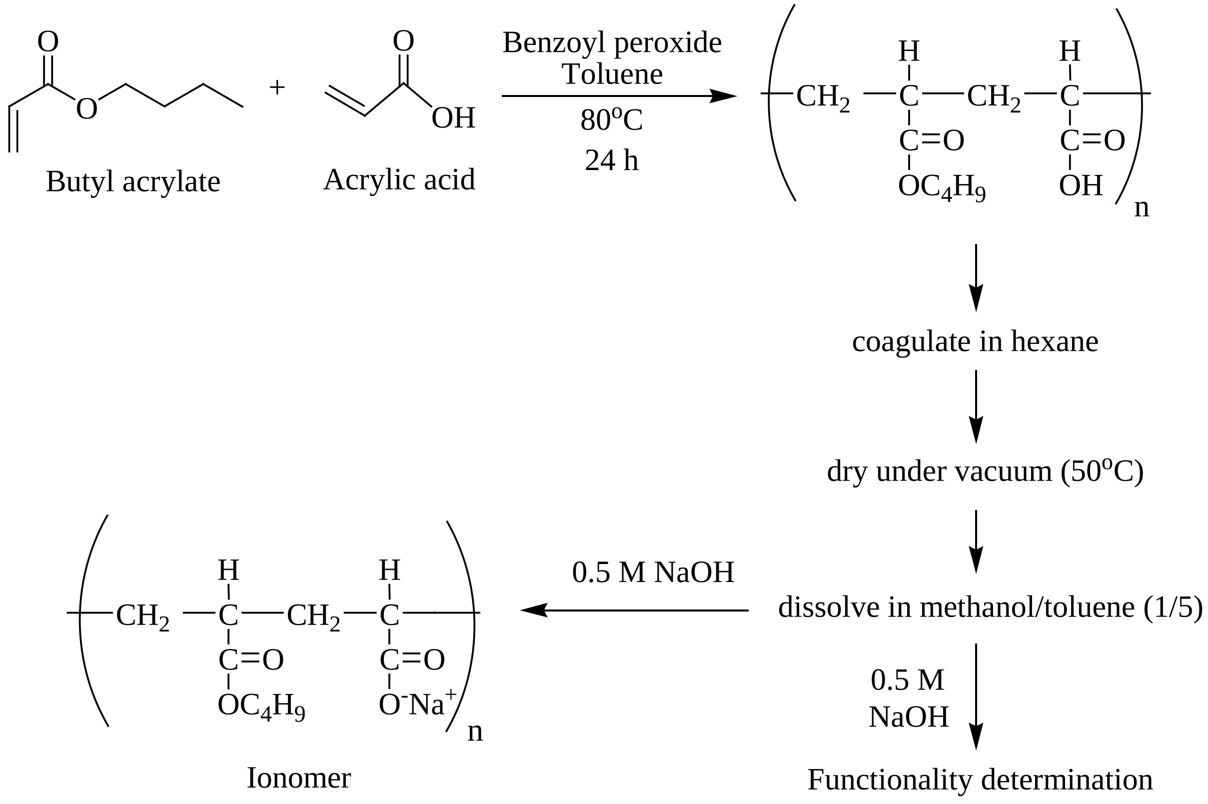


Figure 2.1. Reaction scheme for the synthesis and neutralization of BA/AA copolymers

2.2.2. Polyurea synthesis

All reactions were carried out in 250 mL, 3-neck, round bottom, Pyrex flasks equipped with an overhead stirrer and addition funnel. Polyurea syntheses were conducted at room temperature using the two step prepolymer method in solution. In the first step, calculated amount of amine terminated oligomer solution was added dropwise onto the HMDI solution in the reactor, under strong agitation. After prepolymer was formed, stoichiometric amount of chain extender in IPA was added dropwise. The synthesis was followed by the disappearance of strong isocyanate peak at 2270 cm^{-1} in FTIR spectra. The films were then cast on Teflon molds, kept overnight in oven at 55°C and subsequently dried in vacuum oven prior to analysis.

The polyureas synthesized were of two different types according to their backbones. The polymers containing only Jeffamine ED2003 as the soft segment were synthesized in IPA. However, DMF was used in the synthesis of polymers where mixed Jeffamine ED2003 and PTMO-NH_2 soft segments were used. In the latter case, Jeffamine ED2003 was added prior to PTMO-NH_2.

2.2.3. Polyurethane synthesis

Polyurethane syntheses were conducted in 3-neck, round bottom, 250 mL Pyrex flasks equipped with an overhead stirrer and thermometer. Desired amounts of PTMO-2000 and diisocyanate (HMDI) were allowed to react for approximately 1.5 h at reflux in THF in the presence of 1 drop of T-12 catalyst solution (1% in toluene). After the preparation of the prepolymer, the system was cooled down to room temperature and diluted with IPA and THF. Stoichiometric amount of a chain extender in IPA was then added dropwise onto the prepolymer solution. The progress and completion of reactions were followed by the disappearance of isocyanate peak in FTIR spectra and formation of N-H and C=O peaks. The polymer solution was cast into Teflon molds, kept overnight in an air oven at 55°C and subsequently dried in vacuum oven.

2.2.4. Determination of the acid content of the acrylic copolymers

The amount of AA incorporated into the copolymer was determined by titrating the copolymer solution with methanolic 0.5 M NaOH solution, which was standardized against 0.1 M KHP (potassium hydrogen phthalate). Phenolphthalein was used as the indicator.

2.2.5. Neutralization of acrylic acid copolymers and preparation of ionomers

Ionomers were prepared through controlled neutralization of the copolymer solutions with standard methanolic sodium hydroxide. Neutralization was achieved by slow addition of the desired amount of methanolic NaOH solution into BA/AA copolymer solution in toluene/methanol solution under strong agitation. The ionomer solutions were then cast in Teflon molds, allowed to stay at room temperature overnight and then completely dried in an air oven at 50 ºC until constant weight.

2.2.6. Preparation of blends

Blends of polyacrylates with polyureas and polyurethanes were prepared in solution. Calculated amount of acrylic ionomer with desired chemical composition (ionomer content) was dissolved in IPA/toluene (1/1) mixture. Poly(ether urea) and poly(ether urethane)s were dissolved in IPA/THF (1/1) or IPA/DMF (5/1) mixture. Two solutions were thoroughly mixed by continuous stirring for 3 hours at room temperature. The film was cast on a Teflon mold and then placed in an air oven at 55°C overnight to remove the solvents.

2.3. Characterization Methods

2.3.1. Spectroscopic Analysis

FTIR analysis of solution cast films on KBr pellets were performed by using a Nicolet Impact 400 D spectrometer equipped with a DTGS-KBr detector. 20 scans were taken for each spectrum with a resolution of 2 cm^{-1}.

Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) measurements were performed under ambient conditions by using the same instrument. The spectrometer was equipped with a flat plate ZnSe crystal. The spectra of solvent cast films were collected at an angle of 45° and a resolution of 4 cm^{-1}. 64 scans were obtained for each spectrum.

2.3.2. Mechanical Tests

Stress-strain tests were carried out on an Instron Model 4411 Universal Tester, at room temperature with a cross-head speed of 25 mm/min. Dog-bone shaped specimens were prepared from polymer films according to ASTM D-1708 standard. For each polymer, at least three samples were tested and the values for Young's modulus, tensile strength and elongation at break were determined.

For self healing tests, dog-bone specimens were cut horizontally into half and the pieces were brought together without any delay. Tensile tests for these were also carried out under the same conditions after waiting for desired time intervals for healing.

Chapter 3

RESULTS AND DISCUSSION

The major goals of this study were (i) the synthesis, characterization and investigation of the self healing properties of novel acrylic and polyurea type thermoplastic elastomers and their blends and (ii) understanding the factors affecting the self healing behavior.

To achieve effective self healing, we mainly focused on two types of interactions, which were; (i) the hydrogen bonding and (ii) ionic interactions. For this purpose a series of acrylic copolymers, acrylic ionomers, segmented polyurethanes and polyureas were designed, synthesized, characterized and their self healing behaviors were investigated. Self healing behaviors of the blends of polyureas / polyurethanes and polyacrylates were also investigated.

3.1. Acrylic elastomers

Acrylic copolymers were all based on butyl acrylate (BA) and acrylic acid (AA) and covered a wide composition range. Copolymers obtained were neutralized to different extents and acrylic ionomers were obtained. The parameters that were investigated in self healing studies included:

i) Effect of annealing time at room temperature on the tensile properties of acrylic ionomers,
ii) Effect of neutralization ratio on mechanical properties and self healing behavior of acrylic ionomers,

iii) Effect of healing time on the recovery of mechanical strength,

iv) Effect of blend composition on the self healing behaviors of polyacrylate/polyurea and polyurethane blends

3.1.1. Preparation of acrylic copolymers and ionomers. Effect of chemical composition on T_g

It is well known that for self healing, (i) strong physical interaction between the polymer chains at the interface/interface and (ii) interpenetration of polymer chains through the newly formed interfaces are of great importance [51]. As long range molecular motions become effective only above T_g, the polymer to be synthesized should have a T_g preferably much lower than room temperature. However, at the same time the designed polymer must also have reasonable mechanical integrity and strength.

In this study, copolymers of butyl acrylate (BA) and acrylic acid (AA) with T_g values well below room temperature were prepared by free radical copolymerization, which is known to result in random copolymers. T_g of a random copolymer can be estimated by the Gordon Taylor equation given below.

$$1/T_g(\text{copolymer}) = w_A/T_g^A + w_B/T_g^B$$

Where w_A and w_B are the weight fractions of monomers A and B in the copolymer and T_g^A and T_g^B are the glass transition temperatures of homopolymers of A and B respectively. Figure 3.1 provides the change in the T_g values of poly(butyl acrylate-co-acrylic acid) random copolymers as a function of copolymer composition, calculated using Gordon-Taylor equation. In these calculations the T_g values of poly(butyl acrylate) and poly(acrylic acid) homopolymers were taken as -49 and 106 °C respectively.

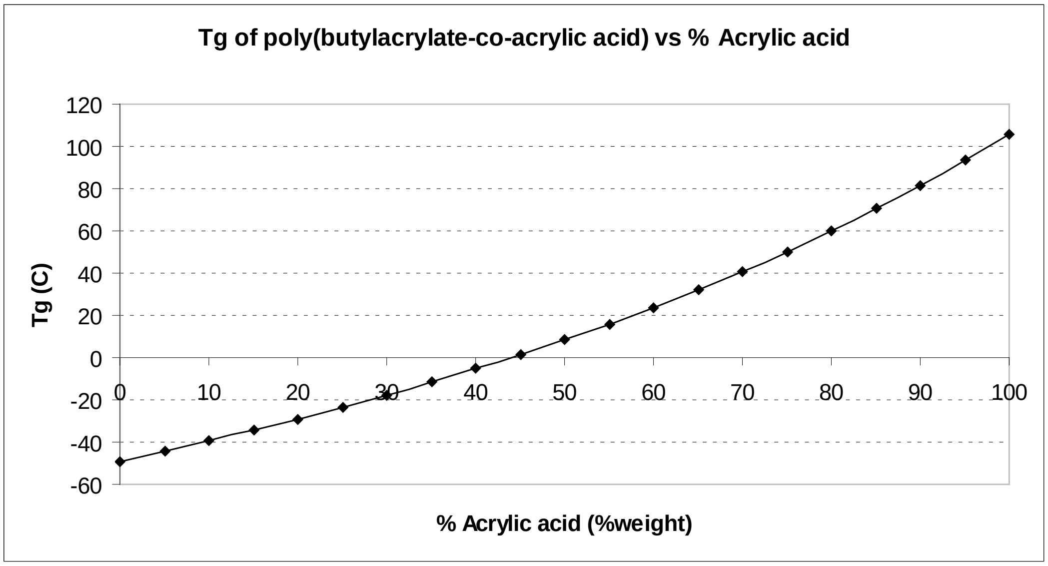


Figure 3.1. T_g as a function of AA content in BA-AA random copolymers calculated by Gordon-Taylor equation [52]

The feed compositions of random BA-AA copolymers prepared in this study are provided in Table 3.1. As can be seen from Table, the copolymerization reactions were performed in toluene solutions at solids contents in 50 to 63% by weight range, except one which was performed in bulk. Reactions were conducted for 24 hours at temperatures between 77 and 106 °C. Use of toluene as the reaction solvent helps to maintain reaction temperature below 110 °C and also reduces the viscosity of the final polymer solution, which is usually extremely high.

Yields obtained in the copolymerization reactions were determined for some reactions. The results are provided on Table 3.2. In general the yields are above 80% by weight which is fairly good for free radical polymerization reactions.

Table 3.1. Composition of the reaction mixtures for random AA-BA copolymers

Polymer Code	**Component**	**Solvent**	**Feed Ratio (wt/wt)**	**Feed Ratio (mol/mol)**	**Solid (%)**	**Reaction Temp (°C)**
SB-35	AA / BA	toluene	1/4	1.0 /2.25	50.5	106
SB-38	AA / BA	-	1/4	1.0 /2.25	Bulk	94
SB-39	AA / BA	toluene	1/4	1.0 /2.25	57.0	103
SB-41	AA / BA	toluene	1/4	1.0 /2.25	55.8	93
SB-42	AA / BA	toluene	1/4	1.0 /2.25	60.0	87
SB-43	AA / BA	toluene	1/9	1.0 /5.00	57.6	85
SB-50	AA / BA	toluene	1/19	1.0 /10.6	62.5	90
SB-53	AA / BA	toluene	1/9	1.0 /5.00	57.3	90
SB-54	AA / BA	toluene	1/9	1.0 /5.00	57.3	84
SB-59	AA / BA	toluene	1/4	1.0 /2.25	62.6	85
SB-60	AA / BA	toluene	1/4	1.0 /2.25	55.7	90
SB-67	AA / BA	toluene	1/4	1.0 /2.25	55.7	80
SB-68	AA / BA	toluene	1/4	1.0 /2.25	55.8	85
SB-78	AA / BA	toluene	1/1	1.75 /1.00	49.9	85
SB-81	AA / BA	toluene	3/2	2.7 /1.00	50.1	77
SB-172	AA / BA	toluene	1/4	1.0 /2.25	55.5	86

In addition to polymer yields, the level of acrylic acid incorporation into the copolymers was also determined through the titration of the carboxylic acid groups in polymers with standard sodium hydroxide solution in toluene/methanol solution. Since the reactivity ratios of monomers are generally different from each other in free radical copolymerization reactions, the monomer ratios in the feed and in the copolymer can be quite different from each other. The copolymer reactivity ratios, r_1 and r_2, for BA and AA monomers are reported to be 1.080 and 0.590, respectively [53]. Since r_1 is close to 1, there is no preference of BA to react either with AA or BA. On the contrary, AA, with much lower reactivity ratio has a tendency to react with BA rather than AA. The effect of reactivity ratios becomes more obvious especially when one type of monomer is in high concentration. For instance, the copolymers synthesized with a feed ratio of 90% BA and 10% AA resulted in much lower incorporation of AA into the backbone with respect to feed. Levels of AA incorporated into the copolymer backbone for some select AA/BA copolymers are provided on Table 3.2. As can be seen from this Table, almost the entire AA in the feed is incorporated into the copolymers for mixtures where the feed ratio is 1.0/2.25 (mol AA/mol BA). On the other hand for 1.0/5.0 blends the level of incorporation is around 60% of the feed.

Table 3.2. The yield and AA incorporation of the copolymers with respect to feed

Polymer Code	**Component**	**Feed Ratio (wt/wt)**	**Feed Ratio (mol/mol)**	**Time (hrs)**	**Yield (wt %)**	**AA reacted (%)**
SB-41	AA / BA	1/4	1.0 /2.25	24	87.2	98.6
SB-42	AA / BA	1/4	1.0 /2.25	24	66.3	-
SB-59	AA / BA	1/4	1.0 /2.25	22	-	99.0
SB-60	AA / BA	1/4	1.0 /2.25	24	87.6	-
SB-68	AA / BA	1/4	1.0 /2.25	24	-	99.5
SB-172	AA / BA	1/4	1.0 /2.25	24	90.6	96.5
SB-53	AA / BA	1/9	1.0 /5.00	24	83.7	60.3
SB-54	AA / BA	1/9	1.0 /5.00	24	83.1	60.3

After the determination of their carboxylic acid contents, some of the copolymers were neutralized by using standard sodium hydroxide solution to produce acrylic ionomers. The extent of neutralization was varied between 1 and 100% in terms of the mole percent COOH content of the copolymer. The list of ionomers prepared is provided on Table 3.3 together with their parent copolymers and neutralization percentages in terms of % mole of acid group neutralized.

Table 3.3. Composition of ionomers produced by neutralization of AA/BA copolymers

Base Polymer	Polymer Code	Feed Ratio (AA/BA)	Acid % neutr by NaOH
SB35	SB-37a	1/4	25
	SB-37b	1/4	50
	SB-37c	1/4	100
SB39	SB-40a	1/4	5
	SB-40b	1/4	10
	SB-40c	1/4	15
SB43	SB-47a	1/9	100
	SB-47b	1/9	50
	SB-47c	1/9	35
SB50	SB-51	1/19	100
SB54	SB-57a	1/9	100
	SB-57b	1/9	75
SB59	SB-63a	1/4	100
	SB-63b	1/4	75
	SB-63c	1/4	50
	SB-64a	1/4	12.5
	SB-64b2	1/4	8.4
SB60	SB-65a	1/4	1
	SB-65b	1/4	3
	SB-66a	1/4	5
	SB-69	1/4	3
SB68	SB-128	1/4	100
	SB-72a	1/4	5
	SB-72b	1/4	3
SB78	SB-82	1/4	3
SB-172	SB-175	1/4	5
	SB-176a	1/4	8.5
	SB-178a	1/4	15

Ionomer films were prepared by solution casting into Teflon molds. The solvent was first evaporated in an air oven at 50 ºC, followed by drying in a vacuum oven at 50 ºC until constant weight. Films were kept in sealed polyethylene bags until further testing.

FTIR spectroscopy is used to qualitatively follow the neutralization reactions and observe the formation of the ionomers by monitoring the changes in the carbonyl peaks in 1800 – 1500 cm^{-1} region. Infrared spectroscopy (IR) is a relatively simple technique, which is widely used for the investigation of the nature of the hydrogen bonding or electrostatic interactions. The basic principle that makes IR useful is its sensitivity to peak shifts as a result of the extent of interaction (e. g. hydrogen bonding) between carbonyl groups. In fact, Pimentel and Sederholm [54] have proposed a direct relationship between the hydrogen bond length (R) and frequency shift ($\Delta\nu$) in hydrogen bonded H·····O=C absorption bands, which was given as follows:

$$\Delta\nu = 0.548\text{x}10^{3}\,(3.21 - R)$$

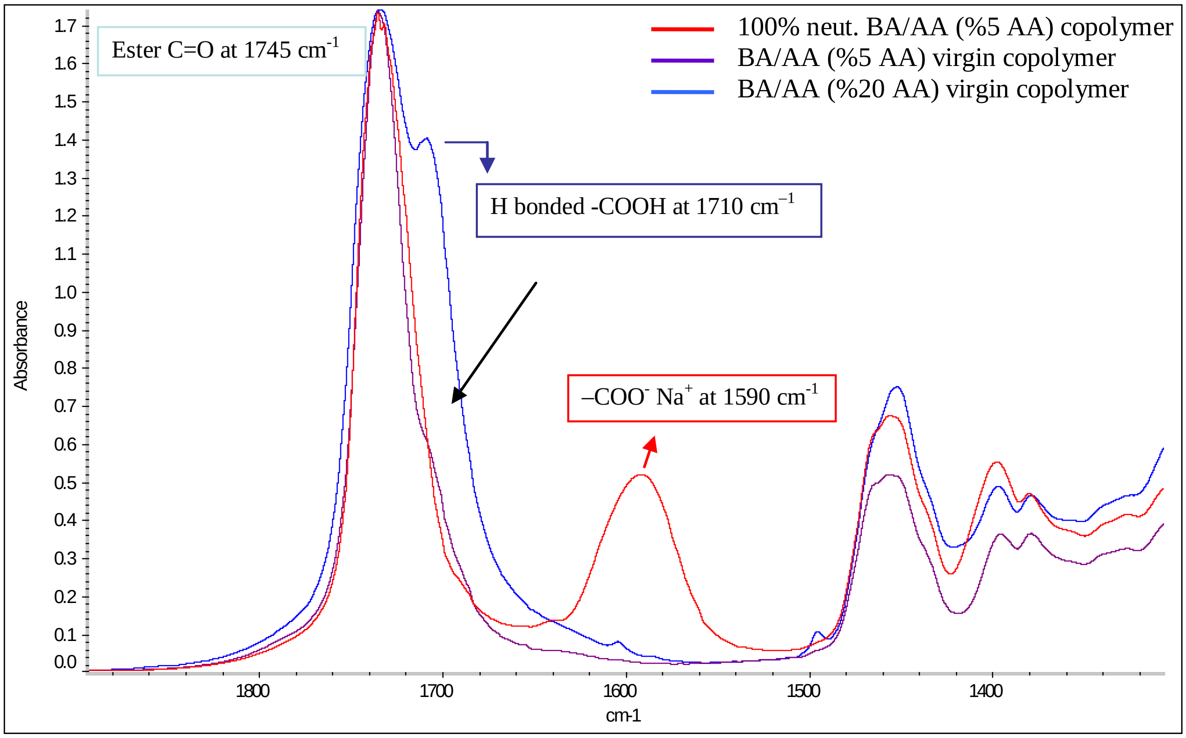


Figure 3.2. FTIR absorbance spectra of virgin copolymers with different compositions and 100% neutralized copolymer

Figure 3.2 gives the absorbance spectra of two virgin BA/AA copolymers with AA contents of 5 and 20 mole percent and a completely neutralized copolymer containing 5% AA. Virgin copolymer with 5% AA (purple spectrum) shows a very strong and symmetrical carbonyl (ester) absorption peak centered at 1745 cm^{-1}. When carefully examined a small shoulder at 1710 cm^{-1}, due to hydrogen bonded carbonyl group (carboxylic acid) is also visible. This shoulder is clearly visible as a strong peak in the copolymer containing 20% acrylic acid (blue spectrum). It is important to note that when copolymer containing 5% AA is neutralized with NaOH (red spectrum) the shoulder at 1710 cm^{-1} disappears completely and a new fairly strong carbonyl peak centered at 1590 cm^{-1}, due to the formation of sodium carboxylate is formed. Due to very strong ionic interaction between sodium carboxylate groups, the carbonyl peak shifts dramatically (120 cm^{-1}) to lower wavenumbers.

The effect of neutralization can also be observed in the hydroxyl (O–H) absorption band of the carboxylic acid groups in the FTIR spectra. Figure 3.3 gives the ATR FTIR transmission spectra of various copolymers before and after neutralization. The broad and strong OH peak of carboxylic acid extending from 2500 to 3300 cm^{-1}, which also overlaps with C-H peaks, diminishes with neutralization percentage and disappears completely for 100% neutralized sample.

When the fingerprint region (1900-1100 cm^{-1}) of the ATR FTIR absorbance spectra of virgin and neutralized copolymers is investigated, it is clearly seen that $COO^{-}Na^{+}$ peak at 1590 cm^{-1} becomes intense with neutralization (Figure 3.4). Also C=O vibration of carboxylic acid groups, which is observed as a shoulder at 1710 cm^{-1} in virgin copolymer disappears completely in fully neutralized copolymer.

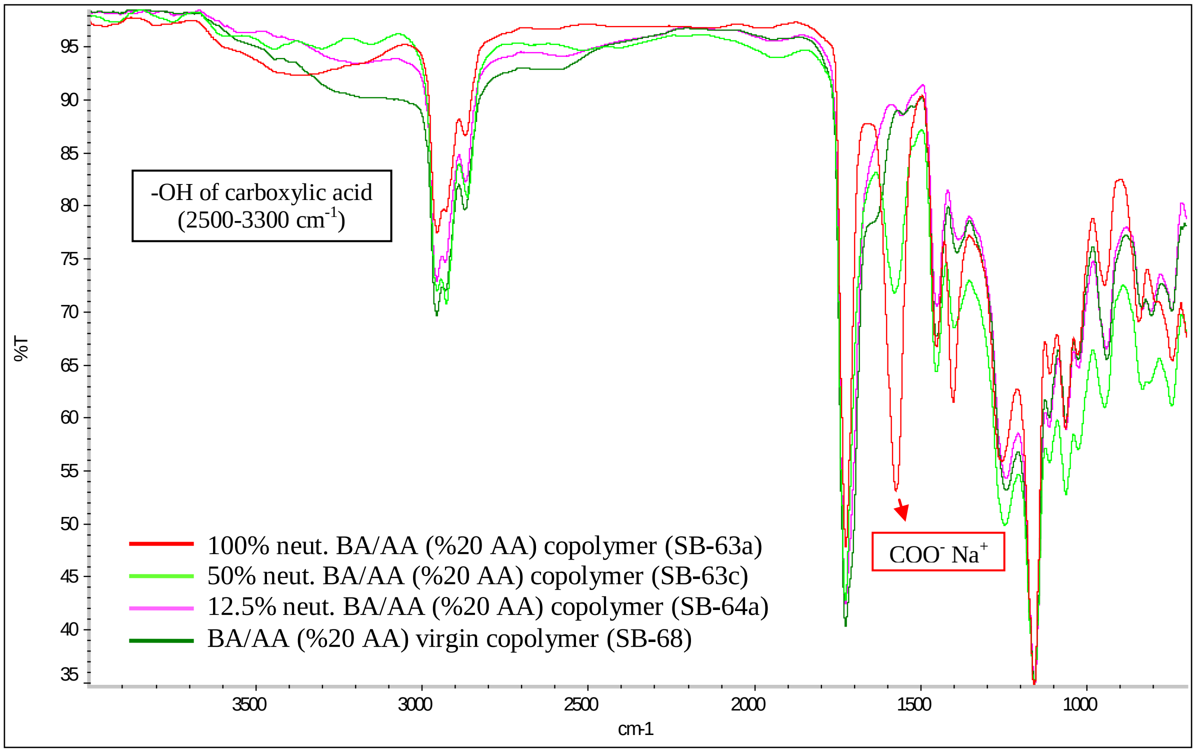


Figure 3.3. ATR FTIR transmission spectra of virgin and neutralized copolymers

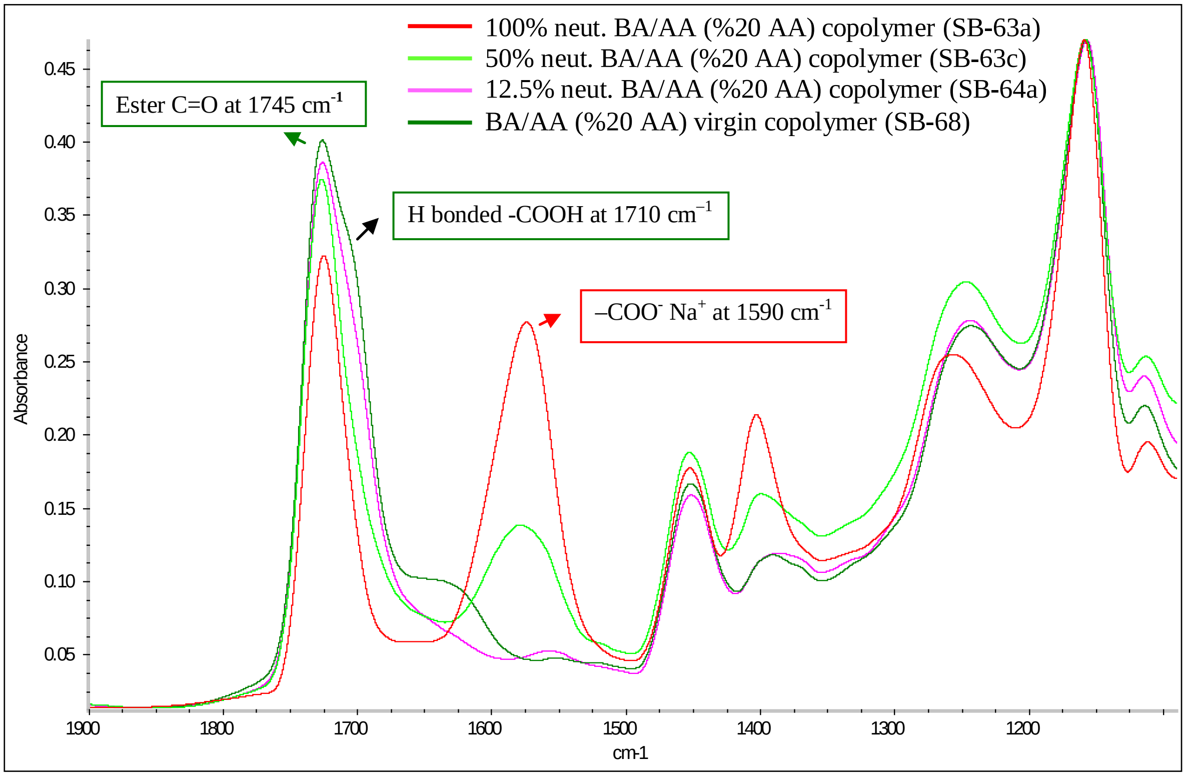


Figure 3.4. Comparative ATR FTIR absorbance spectra at 1900 - 1100 cm^{-1} of virgin and neutralized copolymers

3.1.2. Effect of the Extent of Neutralization and Annealing Time on Tensile Properties

It is well known that as the percentage of neutralization in soft and rubbery BA/AA random copolymers increase, the T_g of the copolymer also increases. In addition, due to strong electrostatic interactions in the ionomers formed, tensile and mechanical properties also display major improvements. To investigate the effect of neutralization on tensile properties, stress-strain tests were performed. In order to achieve complete equilibrium in the microphase morphologies formed, all ionomer samples were annealed under ambient conditions before testing. The results are given in Table 3.4.

Table 3.4. Tensile properties of BA/AA ionomers as a function of degree of neutralization and annealing times at RT

Polymer Code	**Components**	**Neutralized AA (%)**	**Modulus (MPa)**	**Tensile Str. (MPa)**	**Elong. (%)**	**RT annealing (months)**
SB63 c	AA/BA (1/4)	50	7.4	1.7	540	6
SB64 a	AA/BA (1/4)	12.5	1.4	0.6	610	6
SB64 b2	AA/BA (1/4)	8.4	0.8	0.1	540	6
SB 66 a	AA/BA (1/4)	5	0.4	0.1	125	5
SB63 a	AA/BA (1/4)	100	-	10.4	150	9
SB63 c	AA/BA (1/4)	50	-	13.7	230	9
SB 72 a	AA/BA (1/4)	5	0.8	1.6	1050	8

As can be seen from the results provided on Table 3.4 there is an increasing trend in the modulus values and the tensile strengths of ionomers with increasing degree of neutralization and annealing time, which are expected. While the tensile strengths go up with annealing time, a dramatic reduction in the elongation at break values is also observed. 50% neutralized copolymer displays slightly higher tensile strength and modulus values when compared with 100% neutralized copolymer. This may indicate that neutralization may be beneficial up to a certain value. As the ion content increases, ionic interactions dominate, clusters begin to overlap and the polymer starts becoming more rigid. In order to achieve the desired mechanical properties and effective self healing, an optimization should be made for ionic interactions.

3.1.3. Effect of Healing Time on Tensile Properties

One of the major aims of this study was to investigate the self healing behavior of acrylic elastomers and ionomers. We were especially interested in developing a relationship between the self healing behavior and (i) copolymer composition (BA/AA ratio), (ii) ionic content of the copolymer (percent neutralization), and (iii) healing time. For self healing tests, a dog-bone specimen was cut in half by a scissor and then freshly cut surfaces were connected firmly without any delay. After a predetermined time of contact, stress-strain test was performed and recovery of the tensile properties was determined by comparing the results with the tensile properties of control sample. Table 3.5 gives the mechanical properties of the control copolymer and samples self healed for various time periods for (SB 72 a) 5% neutralized ionomer.

Table 3.5. Tensile properties of 5% neutralized sample for different healing times

Polymer Code	**Components**	**Neut. AA (%)**	**Mod. (MPa)**	**Tensile Str. (MPa)**	**Elong. (%)**	**Healing time**	**HE (%)**
SB 72 a	AA/BA (1/4)	5.0	2.2	1.4	1240	0	-
			0.9	0.2	1380	30 min	14
			1.5	0.4	400	1 h	29
			1.0	0.6	800	4 h	43
			1.0	0.6	900	24 h	43

As can be seen from the results provided on the Table 3.5, control copolymer is moderately strong and has a modulus of 2.2 MPa and a tensile strength of 1.4 MPa. It shows 1240% elongation at break. Self healing behavior of this copolymer was studied from 30 minute to 24 hours of healing times. The copolymer shows self healing and the extent of healing is strongly dependent on the contact time of the cut surfaces as indicated by the tensile properties. The healing efficiencies (HE) of the polymers were calculated in terms of the recovery of mechanical strength by the formula: HE= [TS (healed) / TS (initial)]x100. It is interesting to note that after about 4 hours the extent of healing does not improve and stays around 45% HE. The effect of time on the healing efficiency up to 4 hours is shown in Figure 3.5.

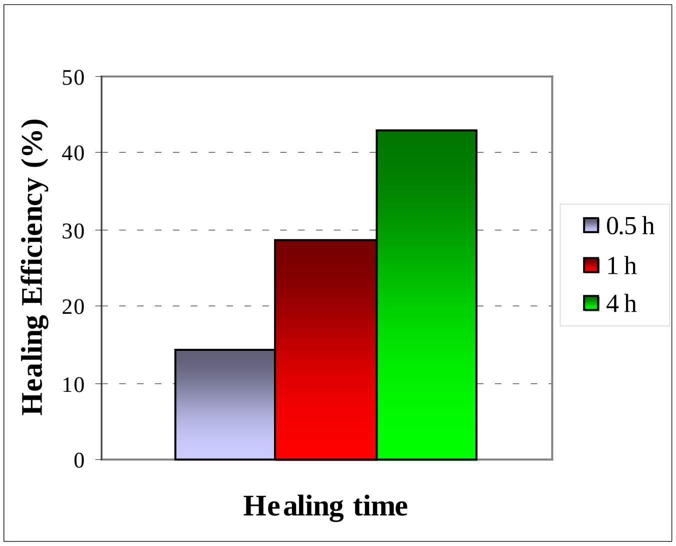


Figure 3.5. Healing efficiency for 0.5, 1 and 4 hour samples

3.1.4. Effect of Neutralization on Self Healing

The self healing ability of ionomers was demonstrated by the recovery of tensile strength. Table 3.6 gives the mechanical properties of various cut and uncut ionomers. It is clearly observed that for ionomers with low neutralization percentages, the recovery is almost 100%. The drawback of low neutralization percentage is that the material does not exhibit enhanced mechanical properties. The inferior properties of the ionomers with low neutralizated acid content were compensated by blending with appropriate polymers. This will be discussed in part 3.2.

Table 3.6. Mechanical properties of cut and uncut samples for ionomers

Polymer Code	AA/BA mol ratio	Neutralization (% AA)	Modulus (MPa)	Tensile Str. (MPa)	Healing time
SB64 a	1.00/2.25	12.5	1.40	0.56	-
			1.43	0.55	8 h
SB64 b2	1.00/2.25	8.4	0.76	0.14	-
			0.45	0.13	30 h
SB 66 a	1.00/2.25	5	0.40	0.08	-
			2.03	0.08	30 h

3.2. Blends of Polyacrylates with segmented polyurea, polyurethane and poly(urethane urea)s

In addition to polyacrylates and acrylic ionomers, we also investigated the self-healing behaviors of novel polyacrylate or acrylic ionomer/segmented polyether-urea and polyether-urethane blends. Strong hydrogen bonding capabilities of urea and urethane groups are well documented. In this study our aim was to combine the superior tensile strengths of segmented polyureas and polyurethanes, which display very strong hydrogen bonding and ionic interactions present in acrylic ionomers to create a hybrid polymer system that could efficiently self heal and also display improved tensile properties. In order to have effective interaction between urea or urethane hard segments and the ionic groups in acrylic ionomers we planned to prepare segmented copolymers which do not display very good microphase separation. For this purpose we chose poly(ethylene oxide) as one of the soft segments in these copolymers. This is because of relatively strong interaction between urea or urethane and ether groups, usually leading to an incomplete microphase separation.

3.2.1. Synthesis of segmented poly(ether urea)s and poly(ether urethane urea)s

To understand the influence of the backbone composition of the polyureas and poly(urethane urea)s on the healing behavior of the blends, as shown on Table 3.7, several different poly(ethylene oxide) (PEO) and poly(tetramethylene oxide) based polyureas were prepared. As can be seen from this Table, copolymers with different soft segments and with hard segment contents in 24-30 % range were prepared. All copolymers formed nice films.

Table 3.7. Compositions of polyureas and poly(urethane urea)s used in blend preparation

Polymer Code	Soft Segment (SS)	MW of SS	Chain Extender	Weight Ratio (HMDI/SS/Chain Ext)	HS (%)
SB-73	$PEO-NH_2$/ $PTMO-NH_2$	2000/ 1100	Dytek	5.7/2.0/1.0/2.7	26
SB167	$PEO-NH_2$/ $PTMO-NH_2$	2000/ 1100	Dytek	5.7/2.0/1.0/2.7	24
PEU 3	$PEO-NH_2$	2000	HMDA	2.6/1.0/1.6	30
MI-14	$PEO-NH_2$	2000	HMDA	2.5/1.0/1.5	30
MI-28	$PEO-NH_2$	2000	HMDA	2.5/1.0/1.5	30
MI-29	$PEO-NH_2$	2000	HMDA	2.5/1.0/1.5	30
SB-168	$PEO-NH_2$	2000	Dytek	2.5/1.0/1.5	30
SB-122	PTMO	2000	Dytek	2.6/1.0/1.6	24
SB-139	PTMO	2000	Dytek	2.6/1.0/1.6	20

Polyurea and poly(urethane urea) formation reactions were followed by taking FTIR spectra at various stages of the synthesis. Figure 3.6 provides the representative transmission IR spectra at various stages of a polyurea (SB73) based on HMDI, amine-terminated PEO-2000, amine terminated PTMO-1100 and Dytek as the chain extender. The violet spectrum was taken after the complete addition of PEO-2000 onto HMDI in the reactor, which indicated the formation of the PEO-prepolymer. The strong N-H absorption peak at 3370 cm^{-1} (N─H) and C=O absorption peaks at 1700 cm^{-1} (weakly H-bonded C=O) and 1630 cm^{-1} (strongly H-bonded C=O) indicated the formation of the urea linkages. The red spectrum was taken after all PTMO-NH_2 was added onto the PEO-prepolymer. The carbonyl peak of urea linkage intensified and the isocyanate peak at 2270 cm^{-1} diminished. The reaction completion was confirmed by the disappearance of -NCO peak depicted by the blue spectrum taken after chain extension.

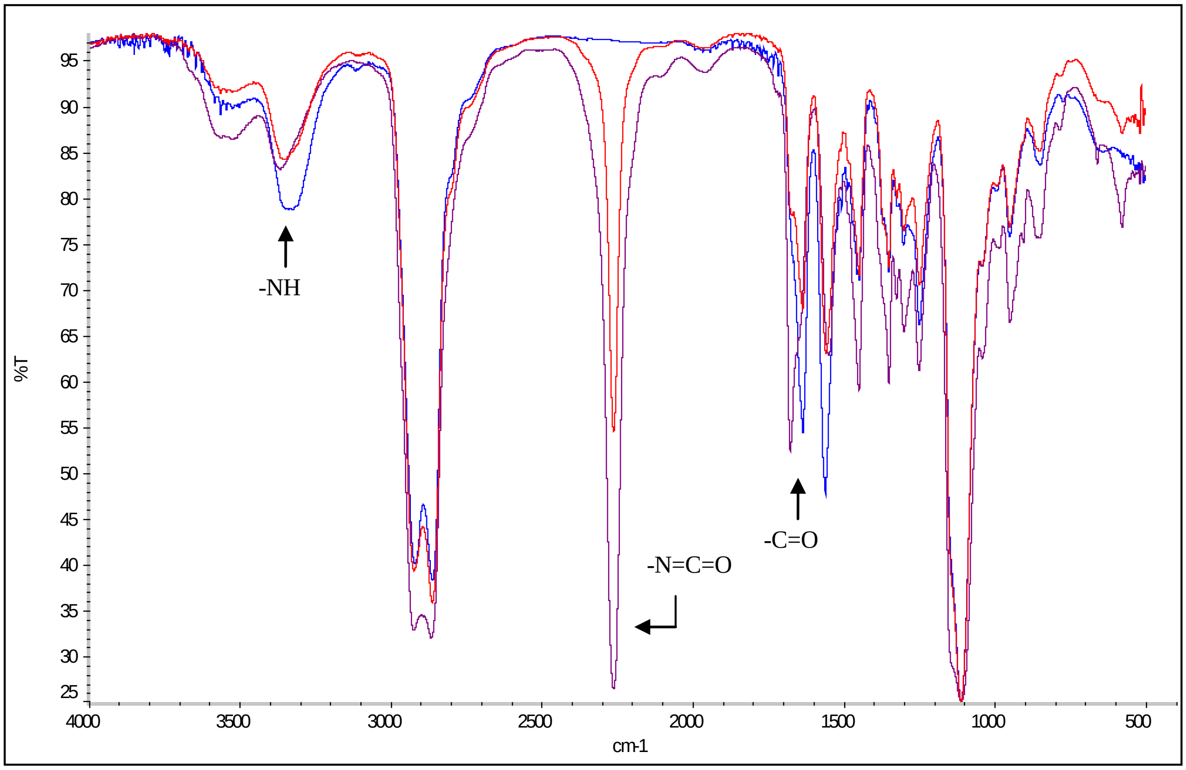


Figure 3.6. FTIR spectra of the polyurea (SB73) taken at various stages of the synthesis. Note that the isocyanate peak (2270 cm^{-1}) disappears at reaction completion.

3.2.2. Preparation of Blends

Blends of acrylic ionomers with segmented polyureas/polyurethanes were prepared at different compositions. Compatible blends were obtained as a result of favorable interactions between urea/urethane hard segments and ether soft segments with carboxyl and hydroxyl groups of acrylate chains, respectively. Chemical compositions and various characteristics of the blends are provided on Table 3.8 where PAc, PU and PUU refer to polyacrylate, polyurea and poly(urethaneurea) respectively.

Table 3.8. Chemical compositions of the blends

Blend Code	**PAc**		**PU or PUU Code**	**PAc/ PU or PUU Weight Ratio**	**Solvent**
	Mole Ratio (AA/BA)	Neutr. (%)			
SB-83b	1.0 /2.25	-	PEU3	1:1	IPA/tol/DMF
SB-85a	1.0 /2.25	-	PEU3	1:3	IPA/THF/DMF
SB-85b	1.0 /2.25	-	PEU3	1:9	IPA/THF/DMF
SB-90a	1.0 /2.25	-	MI 14	6:4	IPA/THF/DMF
SB-90b	1.0 /2.25	-	MI 14	4:6	IPA/THF/DMF
SB-93	1.0 /2.25	-	MI 14	3:7	IPA/THF
SB-173b	1.0 /2.25	-	MI 28	1:3	IPA/THF
SB-173a	1.0 /2.25	-	MI 28	1:1.85	IPA/THF
SB-170a	1.0 /2.25	-	MI 28	1:1.85	IPA/THF
SB-170b	1.0 /2.25	8.4	MI 28	1:1	IPA/THF
SB-176b	1.0 /2.25	8.5	MI 29	1:1.85	IPA/THF
SB-126a	1.0 /2.25	-	SB 122	1:1	THF/IPA/tol/meth
SB-123	1.0 /2.25	12.5	SB 122	1:1	THF/IPA/tol/meth
SB-177	1.0 /2.25	-	SB 139	1:1.85	IPA/THF
SB-80a	1.75 /1.00	-	SB 73	1:1	IPA/tol/THF
SB-80b	1.75 /1.00	-	SB 73	3:1	IPA/tol/THF
SB-80c	1.75 /1.00	-	SB 73	9:1	IPA/tol/THF

The type and extent of interaction in blends was investigated by using ATR FTIR spectra. Figure 3.7 provides comparative transmission spectra of a polyurethane (SB122), an ionomer (SB64a) and their blend. The polyurethane (red spectrum) exhibits a fairly strong N-H stretching peak centered at 3370 cm^{-1}. In blend (black spectrum) this peak becomes extremely broad because of H-bonding with acrylate groups. The intensity of C-H peak at 2780 cm^{-1} decreases since the stretching motion is hindered as a result of the interaction of oxygen in the polyether backbone with other chains. A similar explanation can also be made for the reduction in the H-bonded C=O peak of the urea groups at 1630 cm^{-1}. Since the spectrum was obtained using solid polymer film samples, the constraint effect of H bonding on molecular motions is more evident.

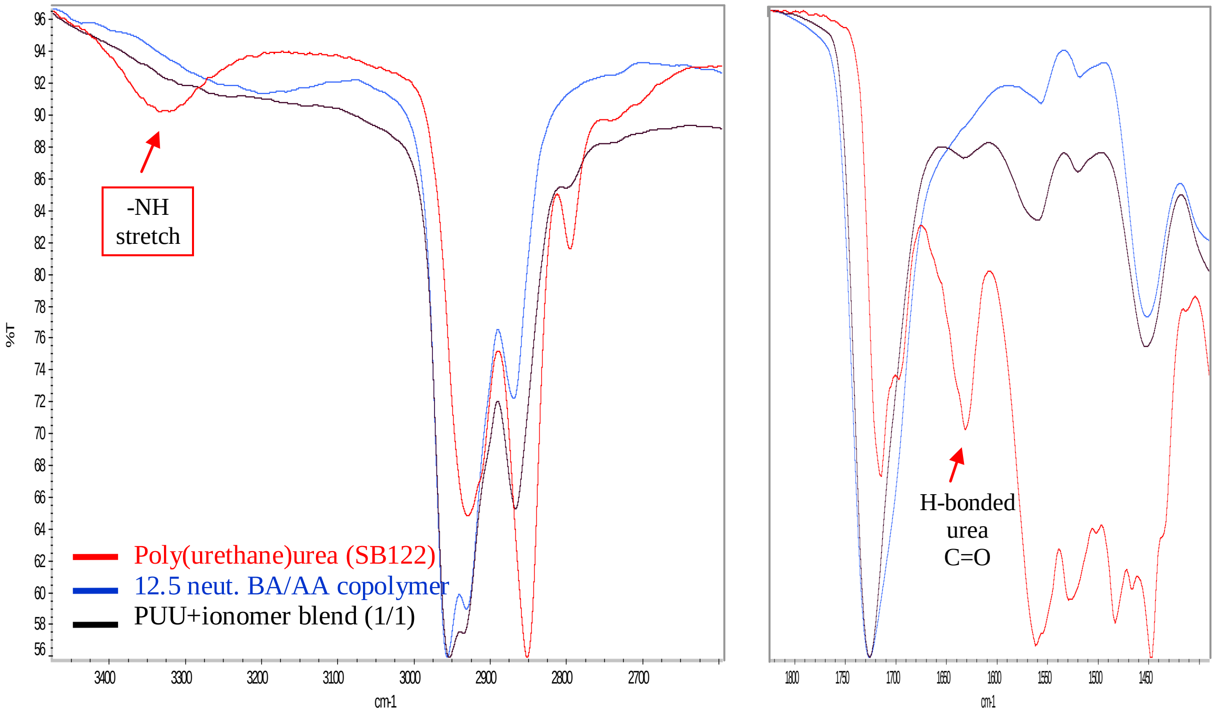


Figure 3.7. Comparative ATR FTIR spectra of virgin polyurethane (red spectrum), ionomer (blue spectrum) and their blend (black spectrum)

3.2.3. Mechanical Tests of Blends

Since the aim was to obtain both good mechanical properties and self healing, stress-strain tests of the blends were performed prior to healing tests. Although the poly(urethaneurea)s having only PTMO as the soft segment resulted in high ultimate tensile strength, their blends with polyacrylates displayed weak mechanical properties. The same pattern was observed for the polyurea/ionomer blends, which contain PEO-NH$_2$ in their backbones but here the decrease is not as sharp as the previous case. Polyureas with mixed soft segment compositions did not display sufficiently high mechanical strength so their blends were also weak. The trials which resulted in blends with relatively low tensile strength were provided in Table 3.9.

Table 3.9. Mechanical properties of the blends with different PAc and ionomer compositions

Code	**PAc content**		**PU/PUU Code**	**PAc/ Ionomer content (wt %)**	**Mod (MPa)**	**TS (MPa)**	**Elong. (%)**
	Mole Ratio (AA/BA)	Neutr. (%)					
SB-139	-	-	-	0	3.0	25.2	1050
SB-177	1.0 /2.25	0	SB-139	35	1.1	0.4	>1000
MI 28	-	-	-	0	4.0	5.8	930
SB-170b	1.0 /2.25	8.4	MI 28	50	0.7	1.0	1100
SB 73	-	-	-	0	2.0	1.4	>800
SB80a	1.0 /2.25	0	SB 73	50	1.0	0.7	1400

The blends with better mechanical properties were obtained by using only PEO-NH$_2$ containing polyureas at low polyacrylate contents as given in Table 3.10.

Table 3.10. Mechanical properties of the blends with different PAc compositions*****

Blend Code	**PAc (AA/BA mol ratio)**	**PU code**	**PAc/ PU weight ratio**	**Mod. (MPa)**	**Tensile Str. (MPa)**	**Elong. (%)**	**PAc content (wt %)**
PEU3	-	-	-	3.5	7.5	940	0
SB-85b	1.0 /2.25	PEU3	1/9	1.1	8.5	1300	10
SB-85a	1.0 /2.25	PEU3	1/3	1.5	6.6	1400	25
SB-83b	1.0 /2.25	PEU3	1/1	0.7	0.6	1350	50

*The results are averages of minimum two samples

Since PEU3 has 30% hard segment, it displays high modulus and tensile strength values. The synergistic effect of H bonding was obvious in blends with 10% PAc content, at which highest tensile strength was obtained. However, as the percentage of polyacrylate in the blends increases, tensile strength decreases. The drop is very sharp especially for 50 % PAc composition as depicted in Figure 3.8.

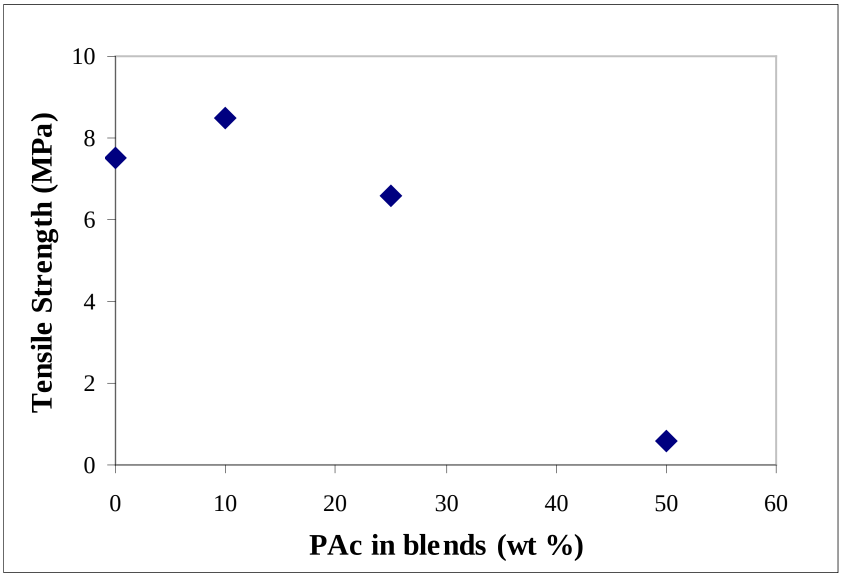


Figure 3.8. The change in tensile strength of the blends with respect to PAc content

3.2.4. Self Healing Tests of Blends

The healing tests were focused on polyurea / polyacrylate blends. There is an improvement in self healing ability of the samples with an increase in PAc component as shown in Table 3.10. The healing efficiency of SB90b is found to be 50% in terms of tensile strength whereas that of SB93 is 33% after 16 hours of contact.

Table 3.10. Self healing behavior of blends with different PAc content after 16 hours of contact

Code	PAc (AA/BA mol ratio)	PU code	PAc Content (wt %)	Mod. (MPa)	TS (MPa)	Elong. (%)	Healing time (hour)
MI-14	-	-	0	2.6	2.9	520	-
SB-93	1.0 /2.25	MI 14	30	0.7	1.2	530	-
				0.6	0.4	115	16
SB-90b	1.0 /2.25	MI 14	40	0.5	0.8	550	-
				0.5	0.4	180	16
SB-83b	1.0 /2.25	MI 14	50	0.7	0.6	1350	-
				0.6	0.5	600	16

* The results are averages of minimum two samples

Another set of blends were prepared and their properties are provided in Table 3.11. The blend containing 25% PAc recovered only about 40% of its original tensile strength upon healing for 1.5 hours. It did not show any improvement upon further waiting. The results indicate that the non-associated groups at the cut surfaces interact upon contact but come to equilibrium after a certain point.

The blend with 35% PAc content displayed higher efficiency whereas the tensile values were relatively low. The same conclusion was made in terms of the healing efficiency staying constant after 1 hour of contact.

3.3. Self Healing Tests of Polyureas

Self healing tests were also performed on some of the virgin polyureas. The mechanical properties of cut and uncut samples of SB-73 which is based on HMDI, PEO-NH_2 and PTMO-NH_2 and has a hard segment content of 26.3 % are given on Table 3.12. It is interesting that even at fairly short times of contact, healing efficiency was quite high. Nevertheless, the improvement in healing efficiency after 1 hour of contact was not as significant as expected. For instance, as shown on Table 3.12, there is almost no difference between the mechanical properties of 1 hour healed sample and that of 2670 minutes healed sample. Therefore, we can conclude that healing occurs up to a certain value for this type of polyureas.

Table 3.11. Self healing tests of blends with different healing times

Code	PAc (AA/BA mol ratio)	PU code	PAc Content (wt %)	Mod. (MPa)	Tensile Str. (MPa)	Elong. (%)	Healing time (hour)
MI-28	-	-	0	4.0	5.8	930	-
SB-173b	1.0 /2.25	MI 28	25	1.6	2.4	850	-
				1.3	0.9	140	1.5
				1.3	0.8	120	8
				1.7	0.9	140	18
SB-170a	1.0 /2.25	MI 28	35	0.9	2.1	780	-
				0.9	0.7	150	1
				0.8	0.6	130	3

Table 3.12. Self healing tests of polyurea for different healing times

Code	Components	Composition	HS (%)	Mod. (MPa)	Tensile Str. (MPa)	Elong. (%)	Healing time (min)
SB73	HMDI/ PEO-NH_2/ PTMO-NH_2/ DYTEK A	5.7/2/ 1/2.7	26.3	2.0	1.4	>800	-
				2.3	0.5	50	30
				2.0	0.7	115	60
				1.9	0.6	75	90

				2.0	0.7	90	120
				1.7	0.6	70	180
				2.1	0.7	90	2670

The mechanical tests indicated that as the HS content of polyureas increase, as expected a dramatic improvement is observed in the tensile strength of the material. As shown in Table 3.13, although SB99 and PEU4 have same components, tensile strength of the former is higher much than that of latter because of high urea hard segment content.

Self healing tests for SB99 (31% HS) and PEU4 (23% HS) indicates that the healing ability decreases with the hard segment content. The cut surfaces of the polymers were healed for approximately 2 days. It was observed that the one with higher HS ratio showed 21% healing whereas the other one had 70%. This may be explained the fact that as content of the urea groups increase, the density of tightly H-bonded chains increases; which in turn, may prevent interdiffusion of the chains at the cut surface.

Table 3.13. Mechanical properties of cut and uncut samples having same components with different compositions

Code	**Composition**	**Mol Ratio**	**HS (%)**	**Mod. (MPa)**	**Tensile Str. (MPa)**	**Elong. (%)**	**Healing time (min)**
PEU-4	HMDI/ PEO-NH$_2$/ HMDA	2/1/1	23	1.3	1.0	1480	-
				1.7	0.6	220	30
				1.6	0.6	290	60
				1.3	0.7	320	150
				1.3	0.4	780	2880
SB-99		2.6/1/1.6	31.3	2.5	3.8	760	-
SB-109				4.3	0.8	260	2700

The samples listed on Table 3.13 also showed a constant value of healing efficiency after a short time of contact. No significant differences were observed between the samples healed for 30 minutes or 2 days, which indicate the non associated groups seeking for partners at the cut surfaces combine but reach to equilibrium after a certain point.

The results may also indicate a competition between microphase separation due to hydrogen bonding in the hard segments of the copolymer within the cut surfaces versus self healing or cross-interaction between the groups at the two interfaces.

Chapter 4

CONCLUSIONS

A series of acrylic copolymers, acrylic ionomers, segmented polyurethanes and polyureas were successfully synthesized and characterized. The self healing behaviors of acrylic ionomers, polyureas and blends of acrylic copolymers with polyurethanes / polyureas were investigated at room temperature by monitoring the recovery of the tensile strength against time.

Acrylic ionomers with ultimate tensile strength values around or below 1 MPa displayed autonomic and complete self healing at room temperature. The healing efficiency generally increased with the contact time of the cut pieces, as expected. The modulus values and the tensile strengths of ionomers increased with increasing degree of neutralization and annealing time.

The blend constituents and composition had a dramatic effect on the mechanical properties and the healing ability. The blends of polyacrylates with PEO based polyureas showed higher tensile strength than acrylic copolymers and their ionomers. The healing efficiency was very high shortly after the initial time of contact but stayed constant after reaching a certain value. The results indicate that two competing mechanisms seem to exist during the healing process: the interaction of non-associated groups of the two cut pieces at the interface and the H-bonding interactions within the cut pieces leading to microphase separation and limiting the extent of healing.

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