Effect of Soft Segment Structure and Molecular Weight on The Properties of Polyether Based Poly(urethaneurea)s

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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ABSTRACT

The effect of soft segment structure and molecular weight on the structure – property behavior of novel polyether based segmented poly(urethaneurea)s (PUUs) were investigated. Poly(propylene oxide) (PPO) or poly(ethylene oxide) (PEO) were used as soft segment, whereas the hard segment was composed of a cycloaliphatic diisocyanate (HMDI) and a low molecular weight diamine chain extender, 2-methyl-1,5-diaminopentane (MDAP). Copolymers were synthesized through the conventional two step "prepolymer" method. Many PUUs were designed with different soft segments, soft segment molecular weights and hard segment contents. The major goal of the study was to understand the effect of the soft segment entanglements on morphological, thermal and mechanical properties of PUUs. Hence, the range of the number average soft segment molecular weights $<M_n>$ selected was large enough ($<M_n>$ = 1000 g/mol – 12000 g/mol) and covered the soft segment critical entanglement molecular weight M_c for each soft segment utilized (M_c (PPO) = 7700 g/mol, M_c (PEO) = 4400 g/mol). Microphase behavior of the copolymers was indirectly studied by infrared spectroscopy (FTIR) by investigating the nature and extent of hydrogen bonding in these materials. Dynamic mechanical analysis (DMA) and atomic force microscopy (AFM) images of PPO based copolymers indicate better microphase separation for copolymers prepared by using higher molecular weight soft segments. Stress – strain behavior of PPO based PUUs with soft segments above M_c showed enhanced tensile properties compared to homologous copolymers with shorter soft segments. Copolymers with hard segment contents as low as 12 wt% displayed reasonably high tensile strength values. Constant initial stress creep experiments also revealed that PPO based PUUs exhibit higher creep resistance with increasing soft segment molecular weight. These results clearly demonstrated the effect of soft segment entanglements on polymer tensile properties. PEO based PUU series displayed superior tensile properties compared to PPO series. Increasing soft segment molecular weight increased tensile strength and modulus significantly. Also, at constant soft segment molecular weight, the modulus increased tremendously with decreasing hard segment content. The reason for these behaviors was attributed to the presence of PEO crystallites in the copolymers, which was confirmed through wide angle X-Ray diffraction (WAXD) measurements. However, a significant contribution of soft segment entanglements could not be concluded for PEO based PUUs.

ÖZET

Yeni bir bakış açısıyla, polieter bazlı çok kısımlı poli(üretanüre) kopolimerleri (PUU) sentezlendi. Yumuşak kısımların kimyasal yapıları ve molekül ağırlığının sentezlenen polimerlerin morfolojisi ve fiziksel ve mekanik özelliklerine etkisi incelendi. Yumuşak kısımlar için polipropilen oksit (PPO) veya polietilen oksit (PEO) kullanıldı. Sert kısımlar ise halkalı alifatik diizosiyanat (HMDI) ve düşük molekül ağırlıklı diamin zincir uzatıcı 2-metil-1,5-diaminopentan (MDAP) kullanılarak oluşturuldu. Kopolimerler iki aşamalı metot (prepolimer yöntemi) kullanılarak sentezlendi. Farklı yumuşak kısım yapısına, molekül ağırlığına ve sert kısım miktarına sahip birçok polimer sentezlendi. Bu çalışmanın öncelikli amacı yumuşak kısım dolanmalarının (entanglement) PUU'nun termal ve mekanik özelliklerine etkisini anlamaktır. Bu nedenle, yumuşak kısım sayı ortalama molekül ağırlıkları ($<M_n>$ = 1000 g/mol – 12000 g/mol) kullanılan yumuşak kısımların kritik dolanma molekül ağırlığını (M_c) kapsayacak geniş bir aralıkta seçildi (M_c (PPO) = 7700 g/mol, M_c (PEO) = 4400 g/mol). PPO bazlı PUU kopolimerlerine ait dinamik mekanik analiz (DMA) sonuçları ve atomik kuvvet mikroskopu (AFM) görüntülerinden, bu kopolimerlerin yumuşak kısım molekül ağırlığı artıkça daha iyi bir mikrofaz ayrımı gösterdikleri anlaşıldı. Yumuşak kısımları M_c'nin üzerinde kalan PPO bazlı PUU kopolimerler, daha kısa yumuşak kısımlı benzerlerine göre daha gelişmiş çekme – kopma özellikleri gösterdi. Bu kopolimerler, %12 gibi oldukça düşük bir sert kısım kompozisyonuna sahip oldukları durumlarda dahi kopma anında oldukça iyi mukavemet gösterdi. Sabit başlangıç kuvvetiyle uzama (creep) testlerinde, yumuşak kısım molekül ağırlığı arttıkça, PPO bazlı polimerlerin uzamaya karşı direncinde artış gözlendi. Bütün bu sonuçlar yumuşak kısım dolanmalarının polimerin çekme – kopma özellikleri üzerine olumlu etkisini açıkça göstermiştir. PEO bazlı PUU serisi PPO serisine nazaran üstün çekme – kopma özellikleri gösterdi. Artan yumuşak kısım molekül ağırlı ile beraber kopma sırasındaki mukavemet ve gerilme modülü belirgin bir şekilde arttı. Ayrıca, yumuşak kısım molekül ağırlığı sabitken, sert kısım miktarı azaldıkça gerilme modülü oldukça büyük bir artış gösterdi. Tüm bu özellikler kopolimerlerdeki PEO yapılarındaki kristallerinin varlığı ile açıklandı. Bu kristallerin varlığı X-ışını kırınımı ölçümleriyle kanıtlandı. Ancak, yumuşak kısım dolanmalarının PEO bazlı PUU üzerinde etkisi hakkında belirgin bir kanıya varılamadı.

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NOMENCLATURE

$<M_n>$	Number average molecular weight
AFM	Atomic force microscopy
ATR-FTIR	Attenuated Total Reflection Fourier Transform Infrared Spectroscopy
BD	1,4-butanediol
DBTDL	Dibutyltindilaurate
DMA	Dynamic mechanical analysis
DMAc	Dimetylacetamide
DMF	Dimethylformamide
MDAP	2-methyl-1,5-diaminopentane
EDA	Ethylenediamine
EG	Ethylene glycol
FTIR	Fourier Transform Infrared Spectroscopy
H	Hydrogen Atom
HDI	Hexamethylene diisocyanate
HMDA	1,6-hexamethylene diamine
HMDI	4,4'-dicyclohexylmethane diisocyanate
HS	Hard Segment
IPA	Isopropylalcohol
IPDI	Isophorone diisocyanate
M_c	Critical entanglement molecular weight
MDI	1,4-diphenylmethane diisocyanate
MPa	Megapascal
PCL	Polycaprolactone
PDMS	Polydimethylsiloxane

PEO	Poly(ethylene oxide)
*p*PDI	*para*-phenylene diisocyanate
PPO	Poly(propylene oxide)
PS	Polystyrene
PTMO	Poly(tetramethylene oxide)
PUU	Poly(urethaneurea)
SAXS	Small angle X – Ray scattering
rpm	Rounds per minute
SBS	Poly(styrene –*block*-butadiene – *block*-styrene)
SIS	Poly(styrene – *block*-isoprene – *block*-styrene)
TDI	Toluene diisocyanate
T_g	Glass transition temperature
THF	Tetrahydrofuran
T_m	Crystalline melting temperature
TPEs	Thermoplastic elastomers
TPUs	Thermoplastic polyurethane elastomers
WAXD	Wide angle X – Ray diffraction
WAXS	Wide angle X – Ray scattering
wt%	Weight percent
ν	Wavenumber

Chapter 1

INTRODUCTION

1.1 Thermoplastic Elastomers

The word *elastomer* is used to define materials which display rubber-like properties such as high reversible deformation upon stretching or compression [1]. This elastomeric behavior is a consequence of the molecular structure of elastomers, which is a network of flexible chains tied with crosslinks. These flexible chains exhibit weak intermolecular forces and are capable to reorient their conformation upon stretching. As the stress is removed the flexible chains retract their disordered conformation. The crosslinks present in the network system anchor the chains to the adjacent chains mostly through covalent bonds to prevent plastic flow during deformation [2, 3]. The crosslinks are obtained through a complex and irreversible process, called vulcanization, usually under high temperature conditions.

Thermoplastic elastomers (TPEs) have been developed in early 1960s as an alternative to crosslinked rubber. They exhibit many of the properties of covalently crosslinked elastomers or rubbers such as high tensile strength, flexibility and resilience without having a chemically cross-linked network.

TPEs exhibit elastomeric properties due to presence of physical crosslinks occurring as a result of physical phenomena such as, microphase separation, hydrogen bonding, ionic interactions or crystallization [3]. These features allow TPEs to be soluble in organic solvents and to be processable through thermal treatment. TPEs change their physical condition from a rubberlike solid to a viscous processable melt upon heating, which can be returned to its initial state by cooling. This fast transition gives the manufacturers the possibility to process TPEs with common techniques such as injection molding, extrusion, blow molding etc. Thus, TPEs combine the mechanical properties of conventional vulcanized rubbers with the manufacturing techniques of thermoplastics.

Generally, TPEs consist of two phases chemically bound to each other; a soft phase and a hard phase. The soft phase is a rubberlike fluid with low glass transition temperature (T_g) well below room temperature, whereas the hard phase has a T_g or a crystalline melting temperature (T_m) much higher than the ambient temperature [2]. TPEs exhibit the characteristic properties of each constituent phase, which are combined on a single

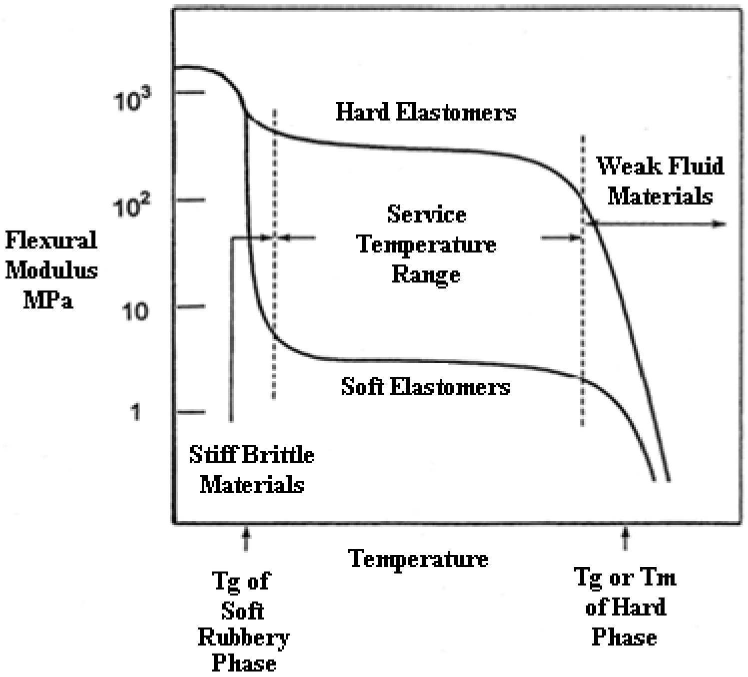


Figure 1.1. Mechanical properties of TPEs in varying temperatures [3]

macromolecule. TPEs are stiff and brittle at temperatures below T_g's of both phases. As temperature increases T_g of the soft phase will be exceeded, so that TPEs will exhibit elastomeric properties. As soon as T_g or T_m of the hard phase is reached, the hard phase will start to soften resulting in a weak material. Thus, TPEs usually have a fairly wide service temperature range, the limits of which are set by the T_g and T_m of the soft and hard phases (Figure 1.1). It is possible to design TPEs in a wide range of properties just by changing the relative ratio and average molecular weights of the constituent phases.

TPEs can be considered in two important groups according to their composition and molecular architecture [4]:

i. A-B-A type triblock copolymers

ii. $(A\text{-}B)_n$ type segmented or multiblock copolymers

1.1.1. A-B-A Type Triblock Copolymers

In this type of elastomers the end blocks (A Blocks) constitute a high T_g or T_m oligomer or polymer, such as polystyrene, poly(methyl methacrylate) or polydiphenylsiloxane [5]. B or the central block is the soft and rubbery phase, such as polyisoprene, polybutadiene or polydimethylsiloxane. Poly(styrene –*block*-butadiene – *block*-styrene) (SBS) and poly(styrene – *block*-isoprene – *block*-styrene) (SIS) triblock copolymers are the most widely studied copolymers of this kind.

The two blocks are usually thermodynamically incompatible. Thus, they aggregate to form domains of hard and soft segments. At room temperature the hard domains provide strength serving as physical crosslink sites, whereas the soft domains give the elastomer its flexibility and extensibility.

A schematic description of the microphase separated SBS triblock copolymer is provided in Figure 1.2. Polystyrene (PS) domains consist of PS end blocks connecting the rubbery polyisoprene chains. As a result a three dimensional network is formed.

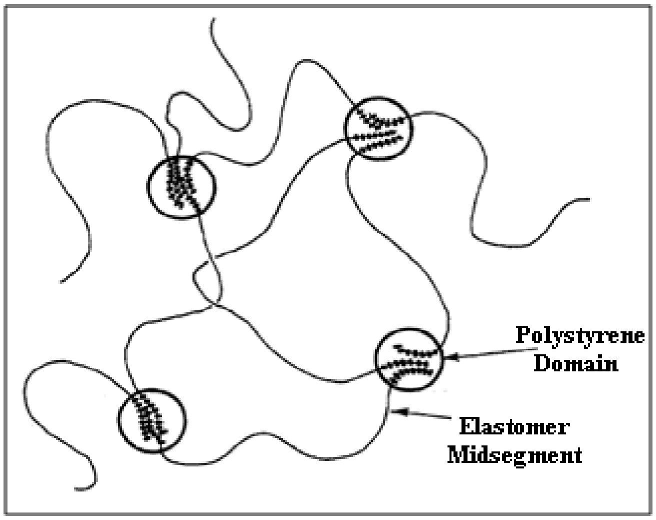


Figure 1.2. Microphase morphology of SBS triblock copolymer [3]

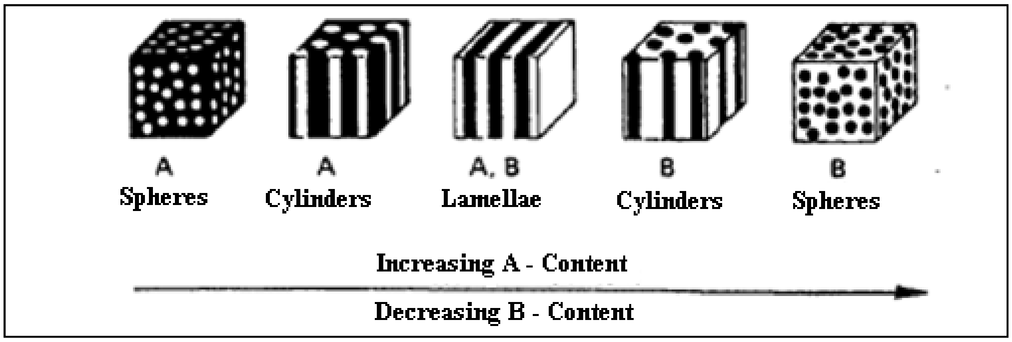


Figure 1.3. Change in morphology of A-B-A type block copolymers based on their block concentration [3]

It is well known that the mechanical properties of TPEs are strongly influenced by the nature and extent of microphase separation between hard and soft segments [4]. Domain morphology of triblock copolymers are mainly affected by the segment molecular weight and concentration of two phases relative to each other. The morphology of a particular domain will change from spherical to cylindrical and finally to lamellar, as its concentration increases from 20 to 50% by weight (Figure 1.3) [5].

ABA type triblock copolymers can be synthesized through many different polymerization techniques such as; living anionic polymerization, controlled free radical polymerization and ring opening polymerization [4]. These polymerization techniques provide good control over molecular weight distribution and enable the preparation of copolymers with precise block molecular weights. Segment lengths of triblock copolymers ranges between 10,000 to 100,000 g/mol and are always above the critical entanglement molecular weight of each segment.

1.1.2. $(A - B)_n$ Type Segmented or Multiblock Copolymers

Segmented copolymers are composed of alternating hard (A) and soft (B) segments along a linear backbone (Figure 1.4). Hard segments with high T_g or T_m provide physical crosslinks in a matrix of soft segment. The soft segments, on the other hand, have low T_g, thus they provide flexibility to the elastomer. Hence, these elastomers resemble triblock copolymers since they also contain hard and soft blocks; however they also have major differences, such as:

(i) Due to repeating $(A - B)_n$ structure of segmented TPEs, each polymer chain consists of multiple soft and hard segments. This results with larger number of hard segments taking part in physical crosslinks (Figure 1.5) [6, 7].

(ii) Segmented copolymers are conventionally synthesized through step-growth polymerization technique. Thus, the block molecular weight and the overall molecular weight of copolymer is more polydisperse than triblock copolymers.

(iii) Molecular weight of soft and hard blocks of segmented TPEs is relatively low. Soft segment molecular weights vary in the region of 1000 – 3000 g/mol [8].

(iv) Soft segments are chosen from α,ω-difunctionally terminated oligomers, which can either be amorphous or semi – crystalline.

(v) Hard blocks of segmented TPEs are usually low molecular weight species when compared with ABA triblock copolymers. Hard segments are generally urethane, urea, urethaneurea, ester and amide type linkages [4].

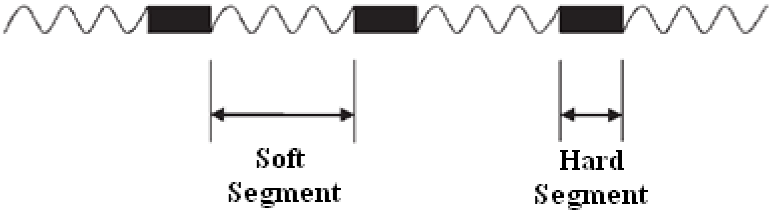


Figure 1.4. Schematic representation of segmented TPEs [4]

Many different segmented TPEs can be produced, since it is possible to select soft and hard segments from a wide range of materials [4, 6]. Soft segments of multiblock TPEs are usually hydroxyl terminated oligomeric aliphatic ethers, such as poly(ethylene oxide), poly(propylene oxide) and poly(tetramethylene oxide). Other possible soft segments available are aliphatic polyesters, such as poly(butylene adipate) and polycaprolactone, oligomeric alkylenes such as poly(ethylene/butylenes) and siloxane oligomers such as polydimethylsiloxane. It is also possible to find polyethers and siloxane oligomers with primary amine end-groups. Hard segments can be chosen from aliphatic or aromatic diisocyanates to synthesize polyurethanes or polyureas, as well as from diacids, diesters or acid anhydrides to form polyesters and polyamides.

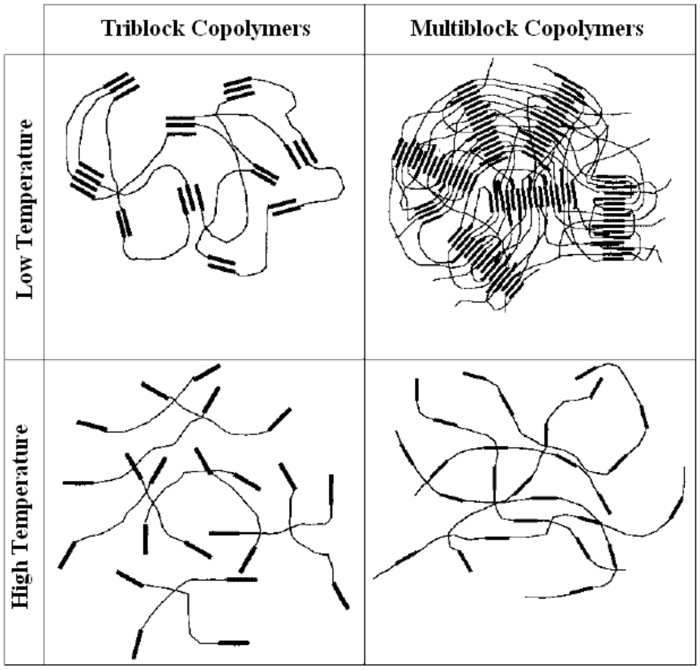


Figure 1.5. Microphase separation of triblock and multiblock copolymers [6]

Similar to triblock copolymers, mechanical properties of segmented TPEs are also strongly affected by the nature and extent of microphase separation between hard and soft domains [9]. The main driving force for this is the polarity differences of constituent soft and hard segments. However, there are many other factors affecting the microphase separation of segmented TPEs in addition to the difference in the polarities or solubility parameters of the segments. Factors affecting microphase separation and domain formation in segmented TPEs can be listed as:

(i) Miscibility of soft and hard segments
(ii) Molecular weight and molecular weight distribution of soft and hard segments
(iii) Chemical structure and crystallizability of soft and hard segment
(iv) Relative ratio of soft and hard segments in the copolymer
(v) Competitive electrostatic interactions between soft and hard segments
(vi) Polymerization method
(vii) Thermal history of the polymer

Thus, the morphologies of segmented TPEs are not as well-defined as triblock TPEs, since there are so many variables to consider.

1.2. Thermoplastic Polyurethane Elastomers

Thermoplastic polyurethane elastomers (TPUs) represent a subclass of segmented TPEs, which cover polyurethanes, polyureas and poly(urethaneurea)s. TPUs constitute one of the most important classes of segmented TPEs. They find applications in various areas such as; textile fibers, adhesives, coatings, membranes and biomaterials [8, 10, 11].

TPUs are synthesized by the step-growth polyaddition reactions, which was first suggested by Otto Bayer in 1937 [12]. Following this invention, first report on synthesis of segmented TPUs was submitted by Schollenberger in 1955 [13].

Isocyanates are highly reactive towards nucleophilic additions[14]. Thus, they can react with groups containing active hydrogen, such as alcohols, amines and carboxylic acids. Through the reaction of an isocyanate group with a hydroxyl group a urethane linkage forms without any byproduct. Urea groups are formed from the reaction of the isocyanate group with an amine group. These two basic reactions, which are shown in Figure 1.6., are widely used in the synthesis of polyurethane elastomers.

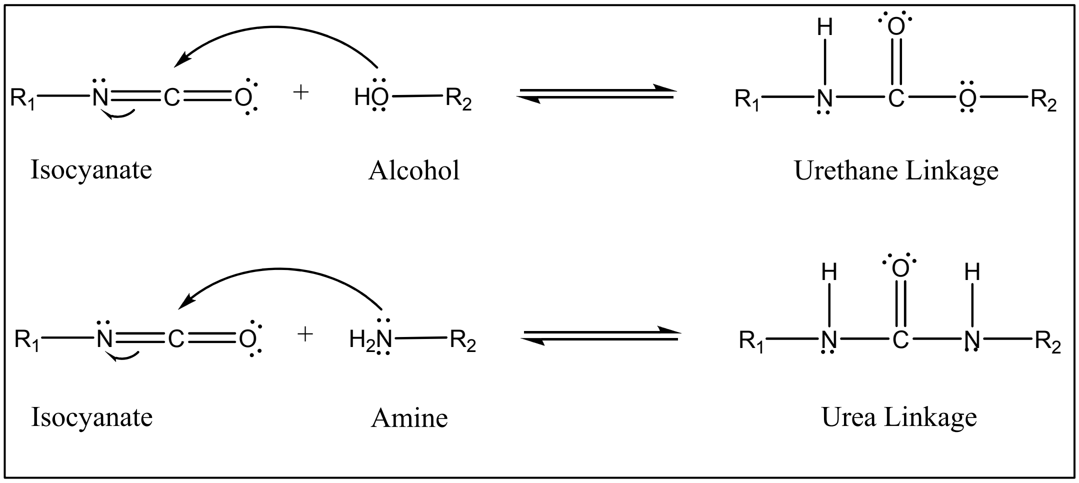


Figure 1.6. Reactions of isocyanate group to form urethane and urea linkages

Three basic materials are used for the synthesis of TPUs;

(i) Long chain diols; usually hydroxyl terminated oligomers of polyethers or polyesters
(ii) Aromatic or aliphatic diisocyanates
(iii)Low molecular weight diols, diamines and water as chain extenders.

Segmented TPUs are synthesized commonly through a two – step polymerization process, which is also called the "prepolymer" method [8]. In the first step excess amount of diisocyanate reacts with a long – chain diol and produce the diisocyanate terminated prepolymer. This prepolymer is further reacted with stoichiometric amount of a chain extender to obtain a high molecular weight elastomer. When the prepolymer is extended with a diol chain extender, the resulting elastomer is called a polyurethane, whereas in case of diamine chain extender it is called a poly(urethaneurea).

Conventionally used polyethers are poly(propylene oxide) (PPO) and poly(tetramethylene oxide) (PTMO). Polyesters of commercial interest are usually hydroxyl terminated polycaprolactone (PCL) and aliphatic polycarbonates. Diisocyanates of aromatic nature include 1,4-diphenylmethane diisocyanate (MDI), toluene diisocyanate (TDI) and *para*-phenylene diisocyanate (*p*PDI). Examples of aliphatic diisocyanates are isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HDI) and 4,4'-dicyclohexylmethane diisocyanate (HMDI) [3]. Most commonly used chain-extenders are ethylene glycol (EG), 1,4-butanediol (BD) and 1,6-hexanediol as low molecular weight diols and ethylenediamine (EDA) and 1,6-hexamethylene diamine (HMDA) as low molecular weight diamines [11]. Water can also be used as a chain extender to synthesize thermoplastic poly(urethaneurea)s [15-17].

1.3. Factors that affect TPU properties

Cooper and Tobolsky were the first ones who have suggested a microphase separated morphology for segmented TPUs in 1966 [18]. Now it is generally accepted that this morphology is responsible for the excellent mechanical properties of TPUs. The microphase separated hard segments act as physical cross-links and reinforcing fillers in a network of flexible chains. This phase separated morphology enhances the properties of elastomers and provides them desirable physical properties comparable with those of chemically cross-linked systems.

As mentioned before, there are many factors that influence microphase morphology of segmented TPEs. It is a very complex issue to design and control structure – morphology – property behavior of TPUs as well. Three of these factors will be discussed in the following sections.

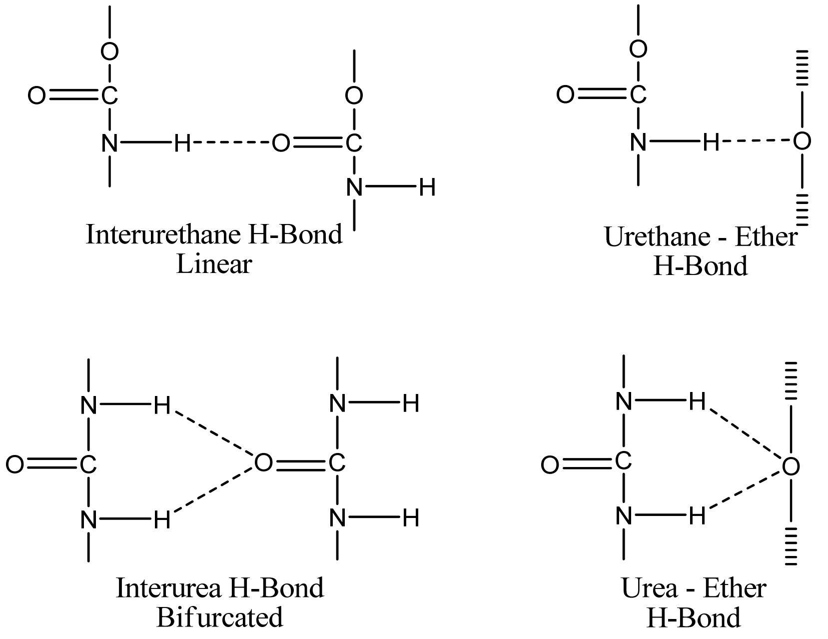
1.3.1. Effect of hydrogen bonding on TPU properties

One of the major driving forces for the microphase separation of segmented TPUs is strong intermolecular interactions between urethane and urea units. These units are highly polar and are capable of forming hydrogen bonds between their proton donating N – H and proton accepting C = O functional groups [19]. The type and the extent of intermolecular hydrogen bonds determine the extent of microphase separation, which in turn influence the mechanical properties of TPUs [20].

Sung et al. has proven that introducing urea groups to TPUs provide stronger hard domain interconnectivity and enhance mechanical properties due to improved microphase separation [21, 22]. On the other hand, presence of proton acceptor sites induces phase mixing, which makes it a complex issue to interpret the effect of hydrogen bonds on mechanical properties.

Hydrogen bonds between urea groups are stronger than those between urethane groups [19, 23-25]. The reason behind this fact can be explained as follows: Each urethane group consists of one proton donor and one acceptor group, which are capable of forming a monodentate hydrogen bond. On the other hand, a urea group carries two N – H functional groups. Both of them bind to the carbonyl oxygen of another urea unit forming bidentate hydrogen bonds.

Additional proton acceptor sites are introduced to a TPU, if the soft segment carries ether or ester linkages. This situation causes for a competition for hydrogen bonding between soft and hard segments [19, 25-27]. Quantum mechanical calculations have proven that the hydrogen bond interaction between urea and ether is very strong, even stronger than interurethane hydrogen bond [24, 28]. Systems studied on model urethane and urea compounds revealed that the hydrogen bond energy between urethane – urethane and urethane – ether are 46.5 and 23.6 kJ/mol, respectively, whereas for urea – urea and urea – ether systems these values are 58.5 and 29.4 kJ/mol, respectively. Intermolecular hydrogen bonds of urethane and urea groups discussed above are schematically represented in Figure 1.7.


Interurethane H-Bond
Linear

Urethane - Ether
H-Bond

Interurea H-Bond
Bifurcated

Urea - Ether
H-Bond

Figure 1.7. Intermolecular hydrogen bonds of urea and urethane linkages

1.3.2. Effect of soft segment crystallinity on TPU properties

Soft segment crystallinity and its effect on TPU properties have been investigated by various scientists. Martin et al. designed polyurethanes using novel polyether macrodiols as soft segment [29]. These macrodiols were in the form of $[(CH_2)_nO]$ with (n) being an even number in the range of 2 – 10. Increasing the number of methylene units caused an increase in the crystallinity of soft segments. Polyurethanes with increased stiffness and hardness have been observed as a result of increased crystallinity.

Based on the observations of Skarja and Woodhouse[30], one of the major factors contributing to enhanced mechanical properties is the soft segment crystallization. The authors worked on a series of biodegradable polyurethanes based on PCL and amorphous hard segments. Their observations revealed that increasing soft segment molecular weight increased segment crystallinity, phase separation and mechanical properties; such as tensile strength and tensile modulus.

Sonnenschein et al. have worked on polyurethanes with low hard segment contents having highly crystalline polyester diols as soft segments [31]. They have shown that semi-crystalline diols with lamellar crystal morphologies provide additional reinforcement to the polyurethane elastomer. The polymers exhibited increased toughness and modulus at sufficiently high crystal concentrations.

One of the most recent studies was published by Korley et al. [32]. Poly(ethylene oxide) (PEO) of different molecular weights have been used as crystallizable soft segments. Mechanical properties of high molecular weight polyurethanes were investigated by tuning soft and hard segment crystallinity. It is observed that introducing crystalline PEO units enhanced toughness and extensibility of polyurethanes compared to their amorphous analogs with equal amount of hard segment. It is suggested that PEO crystallites act as additional load bearing units, which are capable of absorbing strain energy. Following this work, Waletzko et al. have performed *in situ* deformation tests on the same set of polyurethanes[33]. Rearrangements of hard and soft domains during tensile stretch and their effect both on morphology and mechanical properties has been studied by performing small and wide angle X – Ray scattering (WAXS).

1.3.3. Effect of soft segment molecular weight on TPU properties

Soft segment molecular weight used for TPU synthesis usually varies between 1000 – 3000 g/mol. There are many valuable works in the literature on the possible effects of the change in soft segment molecular weight on polymer properties. As mentioned in the previous sections, it is important for TPUs to have microphase separated morphology to exhibit considerable mechanical properties. That is why many scientists have mainly focused on the effect of soft segment molecular weight on microphase separation.

Kinetics of microphase separation of PTMO based polyurethanes was studied by Chu et al. [34]. Soft segment molecular was varied from 1000 to 2000. Shorter relaxation times were observed with longer soft segments. This was explained with the increased soft segment mobility with increasing molecular weight, which results in a faster relaxation for these polyurethanes.

Cooper and Velankar have designed PCL based polyurethanes with varying soft segment molecular weight (830 – 3000 g/mol) to investigate rheological properties of polyurethane melts[35]. They have observed that increasing molecular weight affect both microphase separation and melt rheology of the polyurethanes designed.

Effect of soft segment molecular weight on PPO based poly(urethaneurea)s was investigated by O'Sickey et al. [36]. Soft segment molecular weight has been varied between 2000 – 8000 g /mol. It is observed that increasing soft segment molecular weight caused better microphase separation as evidenced by small angle X – Ray scattering (SAXS), atomic force microscopy (AFM) and thermomechanical analysis. A similar work on polyurethanes with PPO soft segments (1000 – 4000 g/mol) were conducted by Van der Schuur and Gaymans [37]. Except enhanced microphase separation, these polyurethane systems showed lower compression set values, as the soft segment molecular weight increased. The longer ether segments were able to endure a larger part of the strain, so that the hard segments are less deformed.

A comparative study conducted by Sheth et al., has focused attention to the importance of entanglements on polymer properties [38]. In their study PPO and PTMO based linear and branched copolymers were prepared. At constant hard segment content, soft segment molecular weight was increased systematically to values above critical entanglement molecular weight (M_c) of the soft segment. Dynamic mechanical analysis (DMA) showed that branched copolymers displayed a comparable rubbery plateau to their linear analogues, when the soft segment molecular weight was well above M_c. This behavior was explained with the possible contribution of soft segment entanglements to mechanical properties.

A new aspect on effect of soft segment molecular weight on mechanical properties of TPUs is provided by the recent works of Yılgör et al. [39, 40]. Novel segmented thermoplastic polyureas based on PDMS soft segments have been designed. The uniqueness of these polymers was based on their very high soft segment molecular weights (10800 and 31500 g/mol). The aim of their study was to investigate the effect of the critical entanglement molecular weight of the soft segments on mechanical properties, which is known to be an important parameter influencing many polymer properties. They have revealed that there is a considerable contribution of soft segment entanglements on mechanical properties of these particular polymers. It is found that polyureas with soft segments above critical entanglement molecular weights exhibit high elongation at break and tensile strength. In addition to that, extremely low hysteresis and instantaneous set values have been observed.

1.4. Objectives of this study

There are many factors affecting the properties of TPUs. There has been numerous valuable works to understand the effect of each factor onto polymer properties. Recently, with the novel approach of Yılgör et al., it has been suggested that soft segment entanglements may have a considerable effect on mechanical properties of TPUs. In order to expand our knowledge on this issue we have designed novel segmented poly(urethaneurea)s (PUUs) based on polyether soft segments. For this purpose, we have used PPO and PEO soft segments with a wide range of molecular weights. Thermal and mechanical properties and morphological behaviors of these PUUs with soft segment molecular weights below and above critical entanglement molecular weights were investigated. Effect of soft segment type and molecular weight on polymer properties was discussed.

Chapter 2

EXPERIMENTAL

2.1 Materials

Bis(4-isocyanatocyclohexyl)methane (HMDI) was kindly provided by Bayer AG, Germany and was used as received. The purity of HMDI was better than 99.5 % as determined by dibutylamine back titration. Poly(ethylene oxide) (PEO) with $<M_n>$ = 1000 g/mol (Merck), $<M_n>$ = 2000 g/mol (Merck). $<M_n>$ = 4600 g/mol (Aldrich), $<M_n>$ = 8500 g/mol (Aldrich) and $<M_n>$ = 11500 g/mol (Aldrich) were used as received. Poly(propylene oxide) (PPO) with $<M_n>$ values 1000, 2030, 4040, 7960 and 11810 g/mol were calculated from the OH (hydroxyl) number provided by Bayer MaterialsScience and were used as received. 2-Methyl-1,5-diaminopentane (MDAP) was provided by DuPont and used as chain extender. The catalyst dibutlyltin dilaurate (DBTDL) was obtained from Air Products. Reagent grade tetrahydrofuran (THF), dimethylformamide (DMF) and isopropanol (IPA) were purchased from Merck and were used without further purification. Chemical structures of reactants used during synthesis are provided in Table 2.1.

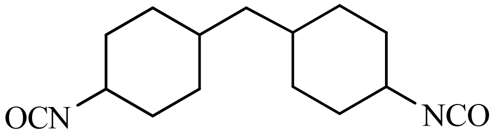
2.2. Synthesis of Polyether based Poly(urethaneurea)s

All reactions were conducted in 250 mL 3-neck, round bottom, Pyrex flasks equipped with an overhead stirrer and a thermometer. All poly(urethaneurea) (PUU) polymers were synthesized by “prepolymer” method in two steps. In the first step, isocyanate end capped prepolymers were synthesized by the reaction of either PEO or PPO with excess amount diisocyanate (HMDI). In the second step, PUUs were obtained from the reaction of the prepolymer with the chain extender (MDAP).

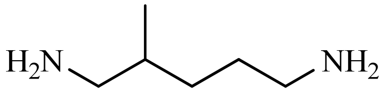
Prepolymer reactions were conducted at elevated temperatures either in presence of a solvent or in bulk. Chain extension step was conducted at room temperature. Chain extender was dissolved in an appropriate solvent and added dropwise through an addition funnel onto the prepolymer solution under continuous stirring. The progress of the prepolymer reactions was followed by FTIR spectroscopy by monitoring the disappearance of hydroxyl (O-H) peak around 3500 cm^{-1} and formation of amine (N-H) and carboxyl (C=O) peaks around 3300 cm^{-1} and 1700 cm^{-1} respectively. Completion of the chain extension reaction was followed by the disappearance of strong isocyanate (N=C=O) peak at 2270 cm^{-1}.

To produce films for characterization experiments, the polymer solutions were poured into Teflon molds, kept overnight to allow the solvent to evaporate slowly at room temperature, and subsequently dried in oven at 60^{o}C until constant weight.

Table 2.1. Chemical structures of the reactants used



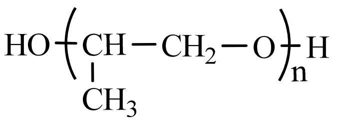
Bis(4-isocyanatohexyl)methane (HMDI)



2-Methyl-1,5-diaminopentane (MDAP)

$HO\left(CH_2-CH_2-O\right)_n H$

Poly(ethylene oxide) (PEO)



$HO\left(\underset{CH_3}{\underset{|}{CH}}-CH_2-O\right)_n H$

Poly(propylene oxide) (PPO)

2.2.1. Synthesis of PEO based Poly(urethaneurea)s

Detailed procedure followed during the synthesis of PEO-4K based PUU (Figure 2.1.) is provided as an example. All other reactions were also performed the same way.

3.50 g (0.76 mmol) PEO-4K and excess amount of HMDI (1.10 g, 4.19 mmol) were introduced into the reaction flask. 3.20 g (~60 wt%) THF was added. The mixture was heated and stirred for about 20 minutes, until a homogeneous mixture was obtained. When the mixture reached 60°C, 2 drops of 1 wt% DBTDL in THF (30 ppm) was added as catalyst. Reactants were allowed to reflux for about 2 hours with continuous stirring (~85 rpm). Prepolymer formation was monitored by FTIR spectroscopy as mentioned in 2.2. The prepolymer solution was further diluted with THF upon increase of viscosity in the reaction flask. At the end of the prepolymer reaction, the concentration of the reaction mixture was approximately 45 wt% solids. After the prepolymer was obtained, the system was further diluted with DMF to increase the polarity of solvent before chain extension. The prepolymer solution was then cooled down to room temperature. For chain extension, stoichiometric amount of MDAP (0.40 g, 3.43 mmol) was dissolved in 28.0 g DMF (~1.5 wt%). The diamine mixture was added dropwise onto the prepolymer solution over 1.5 h under continuous stirring (125 rpm). Viscosity increased with addition of chain extender. Polymer solution was diluted with DMF. The final concentration of the polymer solution was approximately 10% by weight. The completion of the reaction was again monitored by FTIR spectroscopy. At the end of the reaction, amount of diamine added was determined. Usually 80-85% of the theoretical amount of the chain extender was utilized. This is expected, since during prepolymer formation in the presence of DBTDL catalyst inevitable side reactions take place consuming extra isocyanate [41].

Also, a set of PEO based PUUs were synthesized, in which the chain extender was dissolved in IPA. Chain extender concentration was approximately 5% by weight. During chain extension insoluble particles have formed which caused slight haziness. As the copolymer became viscous, further dilution was conducted by addition of IPA. Final concentration of the polymer solution was about 10% by mass.

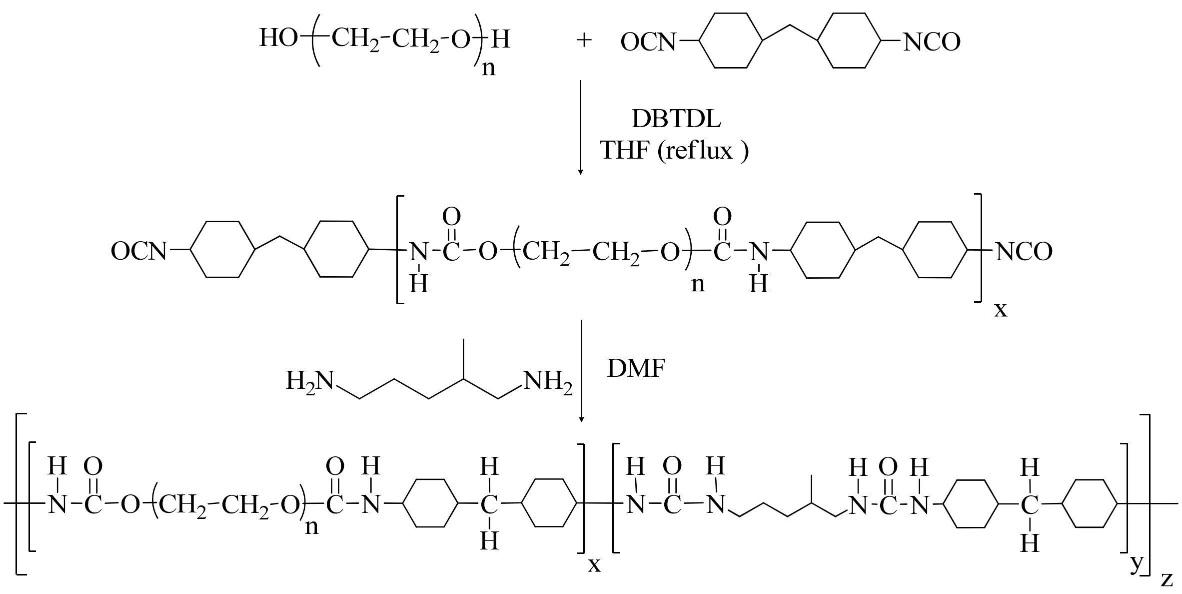


Figure 2.1 Reaction scheme for the synthesis of PEO based poly(urethaneurea)s

2.2.2. Synthesis of PPO based Poly(urethaneurea)s

Synthetic procedure for the preparation of PPO-4K based PUU with 30 wt% hard segment is presented as an example.

3.47g (0.86 mmol) PPO-4K and excess amount of HMDI (1.13g, 4.30 mmol) were weighed into the reaction flask. Reactants were heated and stirred (~70 rpm) for about

15 min. until the mixture reached 60°C. 2 drops of 1wt% DBTDL in THF (50 ppm) was added to the system as catalyst. Prepolymer formation was completed in about 45 minutes. The progress of the reaction was monitored by FTIR spectroscopy. Upon completion of the prepolymer reaction, the mixture was cooled down to room temperature. Stoichiometric amount of MDAP (0.40 g, 3.44 mmol) was dissolved in IPA, so that the chain extender concentration is about 5 % by mass. Before chain extension reaction, IPA was also added onto the cooled prepolymer mixture, in order to increase the polarity of the solvent system. The prepolymer concentration before chain extension was approximately 55% by weight. The chain extender solution was added dropwise onto the prepolymer solution over a time period of 1 hour and with continuous stirring (120 rpm). As more diamine solution was added, viscosity of the polymer solution increased. IPA was used for further dilution. At the end of the reaction, the final concentration of the polymer solution was about 17 % solids by weight. The completion of the reaction was monitored by FTIR spectroscopy following the disappearance of isocyanate peak around 2270 cm^{-1}. Amount of diamine added was about 80% of the theoretical amount. Again, this was a result of side reactions encountered during polyurethane reactions.

All polymers of PPO based PUUs were synthesized in a similar manner. As one exception, during synthesis of PPO-2K based PUUs with 30 wt% hard segment, the prepolymer was diluted with THF before chain extension, so that the prepolymer concentration was about 37 wt%. No further dilution was needed until the end of prepolymer reaction.

Different than the other copolymers, the prepolymer of PPO-12K based PUU with 30% hard segment was synthesized in THF reflux. The prepolymer concentration was kept around 60 wt%. During chain extension both THF and IPA was used for dilution with a relative amount of 1:2.

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. 32 scans were taken for each spectrum with a resolution of 4 cm^{-1}.

Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) measurements were performed under ambient conditions by using a Nicolet iS10 spectrometer. The spectrometer was equipped with a flat diamond plate. The spectra of solvent cast films were collected at an angle of 42º and a resolution of 4 cm^{-1}. 16 scans were obtained for each spectrum.

2.3.2. Mechanical Tests

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

Dynamic mechanical analysis (DMA) were performed on a TA Model Q800 instrument. The test specimens (approximately 9 x 5 x 0.5 mm) were cut from solution cast films. Measurements were performed in tensile mode between –100 and +250 °C. The frequency was 1 Hz and the heating rate was 3 °C/min. Tests were conducted under dry nitrogen atmosphere.

Constant initial stress creep behavior of PPO based PUUs were tested at room temperature. A home-built setup was used as illustrated in Figure 2.2. A dog-bone shaped specimen (ASTM D-1708) was clamped on a sample holder which was attached to a metal frame. A constant weight was loaded on the free end of the specimen through a metal grip. The amount of weight applied was determined depending on the thickness of the specimen. A ruler was attached to measure the extension of the specimen. Each specimen was left hung for up to 10 days (240 hours). The collected data is plotted on a time versus strain graph.

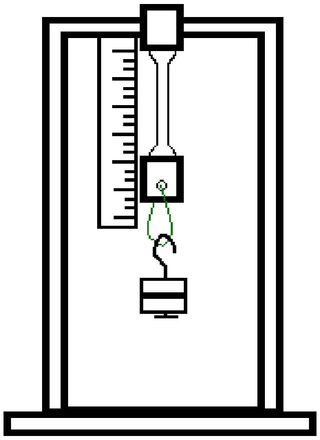


Figure 2.2. Schematic description of the set-up used in creep experiments

2.3.3. Wide Angle X-Ray Diffraction

Wide angle X-ray diffraction (WAXD) was performed using a Bruker D2 Phaser difractometer. CuKα radiation was generated at 30kV and 10 mA. Nickel filter was used to observe a wavelength of 0.154 nm. Specimens were cut from solvent cast films and from uniaxially stretched samples. Scans were taken with a step width of 0.02^o in 3700 steps. Total counting time per step was kept 0.25 seconds. The specimen was scanned in a region of $2\theta = 5^o – 50^o$. Intensities of WAXD reflections were plotted against 2θ values.

2.3.4. Atomic Force Microscopy

Atomic Force Microscopy (AFM) images were taken by using Nanomagnetics Instruments Multimode Atomic Force Microscope. Images of free surfaces of solvent cast films were captured in magnifications 5x5 μm^2 and 1x1 μm^2. AFM images were taken in dynamic mode by using Tap300 aluminum coated tip with a force constant of 40 N/m and resonance frequency of 300 kHz. Engagement set points between 0.4 and 0.6 of the free amplitude oscillations were used.

Chapter 3

RESULTS AND DISCUSSION

3.1. Designing Polyether Based Poly(urethaneurea)s

Synthesis, characterization and structure-property behavior of polyether based segmented polyurethanes have been extensively studied over the past 50 years. In most of these studies the number average molecular weight of the polyether oligomers was in 1000 – 3000 g/mol range. In this study we used polyether oligomers with a wide range of molecular weights from 1000 to 12500 g/mol.

The major goals of this study were to understand the effect of:

(i) soft segment structure (PPO versus PEO),
(ii) soft segment molecular weight (oligomer molecular weights below and above critical entanglement molecular weight) and
(iii) hard segment content,

on the structure–morphology–property behavior of polyether based poly(urethaneurea)s (PUUs). For this purpose two different soft segments PPO (amorphous) and PEO (semi-crystalline) were used. Moreover, PUUs were synthesized by using soft segments with a wide range of molecular weights, including values below and above critical entanglement molecular weight. Hard segment contents were also varied between 10-47% by weight.

Hydroxyl terminated poly(propylene oxide) (PPO) and poly(ethylene oxide) (PEO) were used as soft segments. PPO has a glass transition temperature (T_g) around – 83°C, which may vary slightly with varying molecular weight [42]. PPO oligomers with molecular weights higher than 700 g/mol are hydrophobic. Due to its atactic stereochemistry PPO oligomers are unable to crystallize. PEO, on the other hand, is a water soluble semi-crystalline polyether [43]. Both glass transition and crystal melting temperature (T_m) vary with varying molecular weight. Nevertheless, the highest T_g obtained lies still well below room temperature, whereas T_m varies between 30 – 60 ^oC. It is reported that PEO homopolymers with $<M_n>$ = 6000 g/mol exhibit the highest percentage of crystallinity. Above this value crystallinity is reduced due to incorporation of chain entanglements.

Previous studies in our laboratories on polydimethylsiloxane (PDMS) based polyureas with very high soft segment molecular weights have suggested that soft segment entanglements may have an effect on mechanical properties of resultant polymers [39, 40]. Also comparison of PPO based hyperbranched copolymers with different soft segment molecular weights revealed that chain entanglements are decisive for many mechanical properties of copolymers [38]. It is reported that critical entanglement molecular weights (M_c) of PPO and PEO are around 7700 g/mol and 4400 g/mol, respectively [42]. Soft segment oligomers with molecular weights below and above M_c were used in this study.

3.1.1. Preparation of Polyether Based Poly(urethaneurea)s

A large number of PUUs were prepared. A complete list of the polymers synthesized and their compositions are provided in Table 3.1 and Table 3.2.

As mentioned in Chapter 2, all polymers were synthesized through conventional two step “prepolymer” method. During chain extension highly polar urea groups are introduced into the copolymer, through the use of diamine chain extenders. Strong hydrogen bonding capability of these urea groups may cause physical gelation during polymerization reaction. To prevent this phenomenon highly polar solvents are used: usually, dimethylformamide

(DMF) or dimethylacetamide (DMAc). As proposed by Yılgör et al., isopropyl alcohol (IPA) is an excellent solvent with high polarity and can be used during chain extension of polyether based PUUs with cycloaliphatic diisocyanates [44]. That is why, PPO based copolymers were synthesized by using IPA as the solvent during chain extension step.

Two sets of PEO based PUUs were synthesized. Different chain extender solvents were used for each set: one set was prepared by using IPA and the other DMF. Copolymers prepared in presence of IPA displayed weak mechanical properties compared to copolymers prepared with DMF as chain extender solvent. This is due to the slight coagulation of the copolymer formed during chain extension reaction, which is known to limit the overall polymer molecular weight. On the other hand when DMF was used as the solvent during chain extension a homogeneous solution was observed throughout the reactions. Hence, for PEO based PUUs, data collected from copolymers prepared in THF/DMF solvent system will be taken into account for further discussions. For comparison, mechanical properties of PEO based PUUs synthesized in presence of IPA were provided Table 3.5.

Table 3.1. Number average molecular weight of soft segments, molar ratio and hard segment content of PPO based PUUs

Polymer Code	PPO $<M_n>$ (g/mol)	Molar Ratio (PPO/HMDI/MDAP)	Hard Segment (wt%)
PPO-1K-30	1006	2.2/3.2/1	29.4
PPO-2K-30	2033	1/2.6/1.6	29.2
PPO-2K-45	2033	1/5/4	45.3
PPO-4K-20	4036	1/3.3/2.3	20.9
PPO-4K-30	4036	1/5/4	29.3
PPO-8K-18	7957	1/5/4	17.5
PPO-8K-30	7957	1/9.3/8.3	28.8
PPO-12K-12	11810	1/5/4	12.4
PPO-12K-30	11810	1/13.7/12.7	29.9

Table 3.2. Number average molecular weight of soft segments, molar ratio and hard segment content of PEO based PUUs

Polymer Code	PEO $<M_n>$ (g/mol)	Molar Ratio (PEO/HMDI/MDAP)	Hard Segment (wt%)
PEO-1K-30	1000	2.3/3.3/1	30.5
PEO-1K-40	1000	1/2.1/1.1	38.0
PEO-2K-20	2000	1/1.6/0.6	19.1
PEO-2K-30	2000	1/2.6/1.6	28.5
PEO-2K-40	2000	1/3.8/2.8	39.1
PEO-2K-50	2000	1/5.5/4.5	47.4
PEO-4K-20	4600	1/3.3/2.3	19.3
PEO-4K-30	4600	1/5.5/4.5	28.0
PEO-8K-10	8484	1/2.8/1.8	9.8
PEO-8K-20	8484	1/5.5/4.5	18.4
PEO-8K-30	8484	1/10/9	28.3
PEO-12K-20	12500	1/7.9/6.9	18.6

The coding system used to identify the copolymers is as follows: First three letters are abbreviations for the type of oligomer used. The following number represents the $<M_n>$ value of the oligomer. The final numbers indicate the hard segment content of the copolymer in weight percent. Thus, a copolymer composed of PPO with $<M_n>$ = 4000 g/mol and with a hard segment content of 30% by weight will be coded as: PPO-4K-30.

Progress of the polymerization reactions were followed by using FTIR spectroscopy. Figure 3.1 represents various steps of synthesis of a polyether based PUU (PEO-2K-30). The red curve was taken after complete mixing of PEO-2K and HMDI in the reaction flask. Hence it represents the initial prepolymer mixture where strong hydroxyl (OH) and isocyanate (NCO) absorption peaks around 3500 cm^{-1} and 2270 cm^{-1} are observed respectively. The OH peak disappears gradually as hydroxyl groups are consumed by NCO groups during prepolymer formation. The completion of the prepolymer reaction is understood by complete disappearance of OH peak, reduced intensity of NCO peak and formation of strong amine (N-H) and urethane carbonyl (C=O) peaks around 3300 cm^{-1} and 1700 cm^{-1}, respectively (Green curve). Towards the end of the chain extension reaction, excess NCO groups will be consumed by addition of the diamine chain extender, which results in formation of urea linkages along with its corresponding peak around 1630cm^{-1}. The blue curve indicates the end of the chain extension or the polymerization reaction with the absence of the strong NCO peak around 2270 cm^{-1} and formation of urea carbonyl peak.

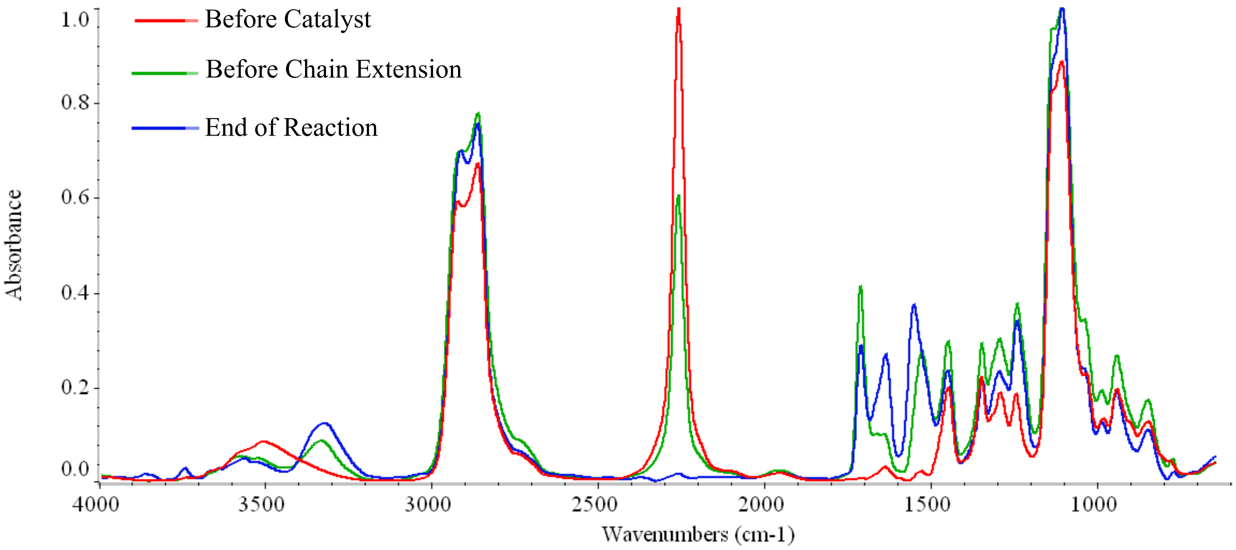


Figure 3.1. FTIR spectra of PEO-2K-30 taken at various stages of the synthesis.

3.1.2. Studies on the determination of the extent of phase separation

As already mentioned before, one of the major factors influencing microphase separation is hydrogen bonding. Hydrogen bonding may form between N-H and C=O groups of hard segments, as well as between N-H group and ether oxygen in case of polyether based polyurethanes. Infrared spectroscopy is a useful technique to investigate the interactions of these groups and to predict the extent of microphase separation.

Presence of hydrogen bonding disturbs the vibrational motion of the groups involved, which results in a shift of peak position to lower frequencies. According to Coleman et al. N-H stretching region does not give reliable results for quantitative analysis [45]. As mentioned, N-H groups may be involved in hydrogen bonding both with hard segment carbonyls and with soft segment ether oxygen of polyethers. Moreover, non-hydrogen bonded and hydrogen bonded N-H groups give peaks in close regions, which makes it difficult to distinguish between them.

On the other hand, analysis of carbonyl peak positions gives valuable information about hydrogen bonding character (nature and extent) of urethane and urea groups. Hydrogen bonded and non-hydrogen bonded carbonyl peaks can be observed at distinct positions. Moreover, these groups are sensitive to order. IR absorption frequencies of urethane and urea groups are schematically represented in Figure 3.2.

In this discussion, ATR-FTIR spectra of PPO and PEO based PUUs of similar hard segment content will be provided. This technique is chosen to monitor the absorption spectra of copolymers at their equilibrium morphologies. In order to interpret the extent of microphase separation, carbonyl regions will be focused and discussed in detail.

Carbonyl region of FTIR spectra for PPO based PUUs with 30% HS content are represented in Figure 3.3. Peak observed at 1716 cm^{-1} corresponds to non-hydrogen bonded urethane carbonyls. Its distinct shoulder around 1695 cm^{-1} indicates presence of hydrogen bonded urethane carbonyl groups in the copolymer. It is believed that the microphase separation is disturbed by contribution of soft segment ether oxygen to hydrogen bond structure. Whenever an amine hydrogen is bonded to an ether oxygen, a carbonyl group will be liberated, which will be observed at higher frequencies [25, 26]. Interestingly, if compared with Figure 3.2, free urethane carbonyls still appear at lower frequencies than expected. It is proposed by Coleman et al. that the urethane groups in a copolymer are not truly isolated, since they are always subjected to an intermolecular attraction [26]. This is a reasonable explanation for the observed urethane peaks at lower wavenumbers.

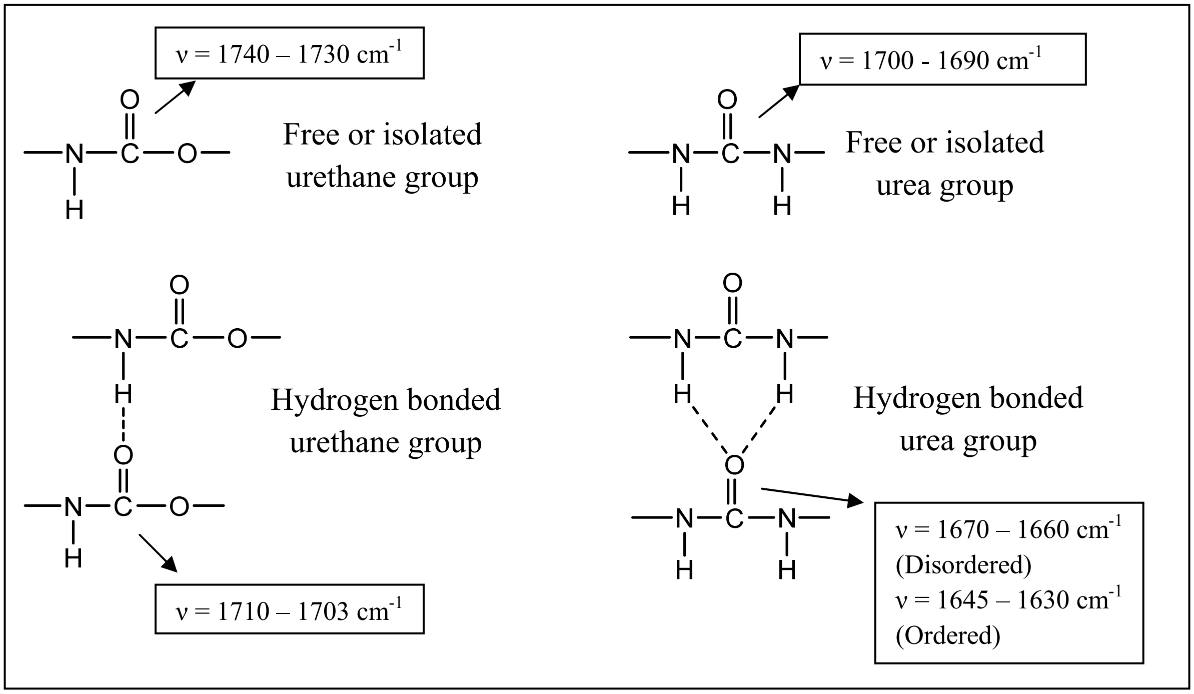


Figure 3.2. Characteristic IR peak regions for urethane and urea carbonyls [19, 23, 46].

Urea carbonyls give a peak around 1630 cm^{-1}. The skewed shape of the peak towards higher frequencies indicates that there are hidden less intense peaks at higher wavenumbers. These are believed to be urea peaks, which are weakly hydrogen bonded. The reason for these hidden peaks may be again the contribution of ether oxygen to hydrogen bonds, which liberate free urea groups. Another explanation can be the disordered hard segment domains due asymmetry of HMDI and MDAP. This may disturb the ordered hydrogen bonded structure resulting in disordered, weakly bonded urea peaks.

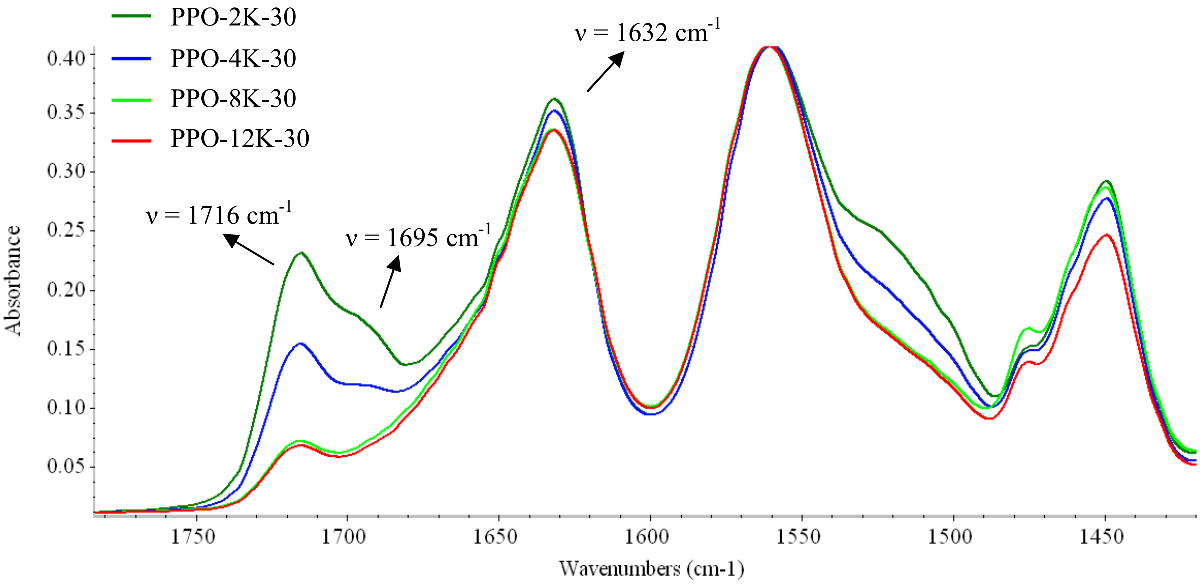


Figure 3.3. Carbonyl region of the ATR - FTIR spectra of PPO based PUUs with 30% hard segment content

It is also remarkable that the peak intensity of urethane carbonyl decreases with increasing soft segment molecular weight. This is an expected observation. At constant hard segment content, hard segment length increases with increasing soft segment molecular weight (Table 3.1). Thus, the relative ratio of urethane groups with respect to urea groups decrease. As a result, the intensity of urethane peaks observed in FTIR spectra decrease with increasing soft segment molecular weight.

Similar observations can be made for PEO based PUUs with constant hard segment content (Figure 3.4). Free and hydrogen bonded urethane carbonyls are distinguishable as a peak and as its shoulder at lower frequencies, 1714 and 1698 cm^{-1} respectively. Likewise, urea peak exhibits similar skewed character as PPO based PUUs, indicating presence of weakly hydrogen bonded urea groups. Moreover, urethane peak intensity decreases with increasing soft segment molecular weight, hence, hard segment length.

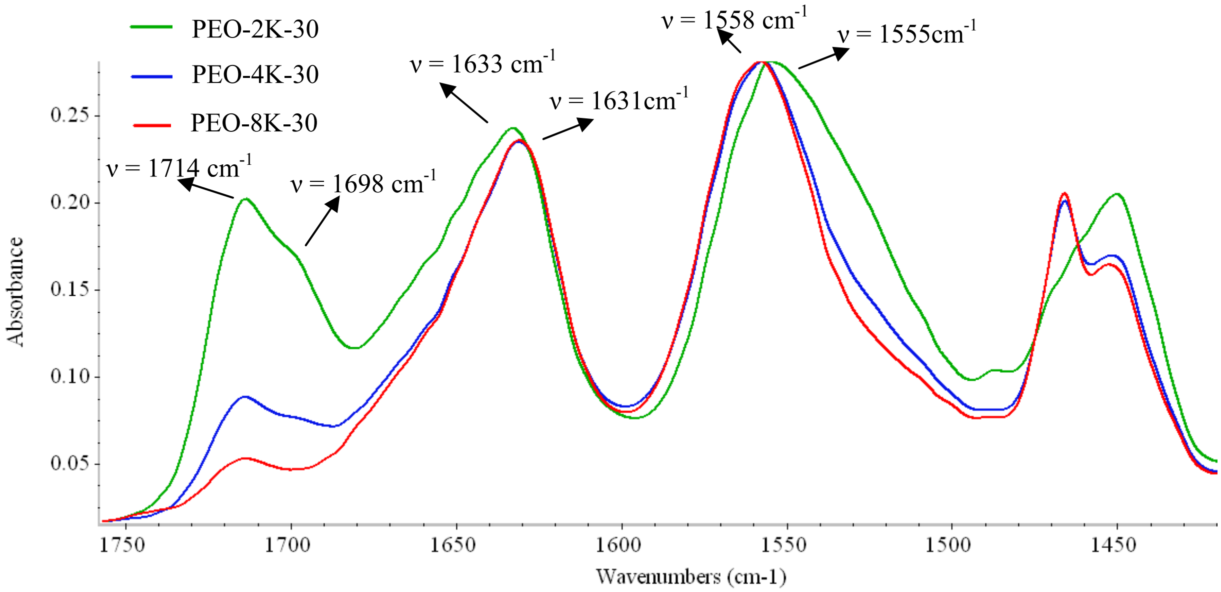


Figure 3.4. Carbonyl region of the ATR - FTIR spectra of PEO based PUUs with 30% hard segment content

Different than PPO based PUUs, in semi-crystalline PEO based PUUs, urea carbonyl peak shifts to slightly lower frequencies with increasing soft segment molecular weight. Probably, increasing hard segment length changes and strengthens the hydrogen bonding character by introducing more urea groups to the copolymer. It can be suggested that the microphase separation increases with increasing soft segment molecular weight.

Similar behavior is observed for the peak around 1550 cm^{-1}, which is also called amide II peak. With increasing soft segment molecular weight peak at 1555 cm^{-1} shifts to slightly higher frequencies (1558 cm^{-1}). Amide II peak has a complex structure mainly affected by N – H bending and C – N stretching vibration modes. There were a few systematic studies to understand the behavior of this peak in polyurethanes and polyureas [47, 48]. These studies were conducted on urethane and urea model compounds and revealed that amide II peak shifts to lower frequencies with incorporation of stronger hydrogen bonds. However, Coleman et al. observed just the opposite [45]. Increasing temperature resulted in a decrease of amide II peak to lower frequencies. Hence, the amide II region is very complex and can give ambiguous information. However, the shift in peak position is still indicative for a change in vibrational motions. Thus, it is believed that there may be weakly phase separated morphology for PEO-2K-30 copolymers, meaning that hard segments may be partially distributed in the soft segment matrix. The extent of phase separation increases with increasing soft segment molecular weight and hard segment length.

Another interesting change occurs for the peak around 1450cm^{-1}. It is known that the region between 1480 – 1450 cm^{-1} correspond to bending motions of CH_2 groups in the polyether backbone [49]. It is believed that this change is caused by the change of crystallinity with increasing PEO molecular weight, which will be discussed more in detail in the following sections.

3.2. Polymer Characterization

3.2.1. Dynamic Mechanical Analysis

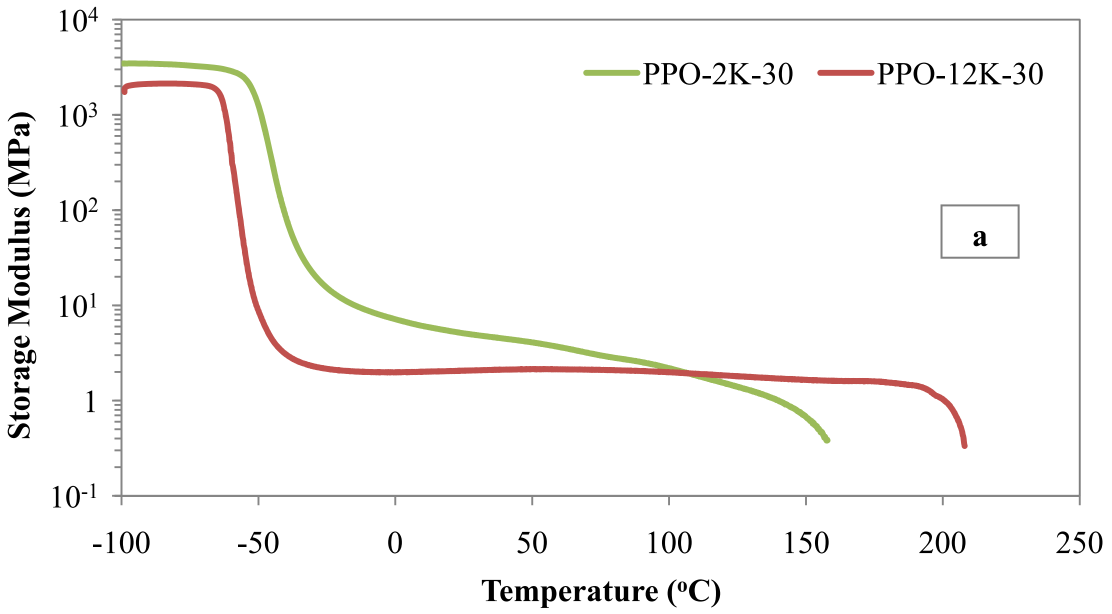
The molecular weight between entanglements (M_e) is inversely proportional to the modulus in the plateau region and can be calculated through stress relaxation experiments. The relationship between these values is expressed as:

$$G' \cong \frac{\rho RT}{M_e}$$

In this expression; (G’) is the storage modulus measured during stress relaxation experiments, (ρ) is the polymer density under test conditions, (R) is the gas constant and (T) is the temperature. Thus, the breadth of the rubbery plateau is affected by the extent of entanglements. As the number of entanglements in a polymer increases, the rubbery plateau will become wider. Although M_e is normally calculated from stress relaxation experiments, value of the storage modulus and the temperature range of the rubbery plateau obtained by dynamic mechanical analysis (DMA) also provides reliable results [50].

Storage modulus-temperature and tan δ-temperature curves for PPO-2K-30 and PPO-12K-30 PUUs are reproduced in Figure. 3.5.(a). and 3.5.(b). As can clearly be seen from Figure 3.5.(a)., PPO-2K-30 and PPO-12K-30 display remarkably different behaviors. PPO-2K-30 behaves as a rigid solid up to approximately –50°C, followed by a sharp soft segment (PPO-2K) glass transition which is at –42 °C, as obtained from the maxima of tan δ peak. The subsequent rubbery region seems to be temperature sensitive, since the modulus decreases gradually with increasing temperature. Finally, the polymer starts to flow around 150 °C. The sensitivity of the plateau region of PPO-2K-30 is an expected result, since PPO-2K soft segment has an M_n value well below the M_c of PPO, which is 7700 g/mol [42].

On the other hand, as expected PPO-12K-30 shows a slightly lower glassy modulus and exhibits a T_g at –55 °C. Extremely long wide rubbery plateau, which extends from –40 to almost +200 °C is relatively temperature insensitive. The breadth of this region is indicative for the presence of a pseudo-network formation, thus entanglements. In addition to that, relatively low T_g of the copolymer indicates that this sample possesses a much better microphase separated morphology. Moreover, the breadth of the tan δ peak also decreases with increasing soft segment molecular weight. The reason behind this is that the soft segments are subjected to fewer restrictions as their molecular weight increases. Thermoplastic polymer starts to flow above 200 °C, typical for such polyurethaneureas [3].



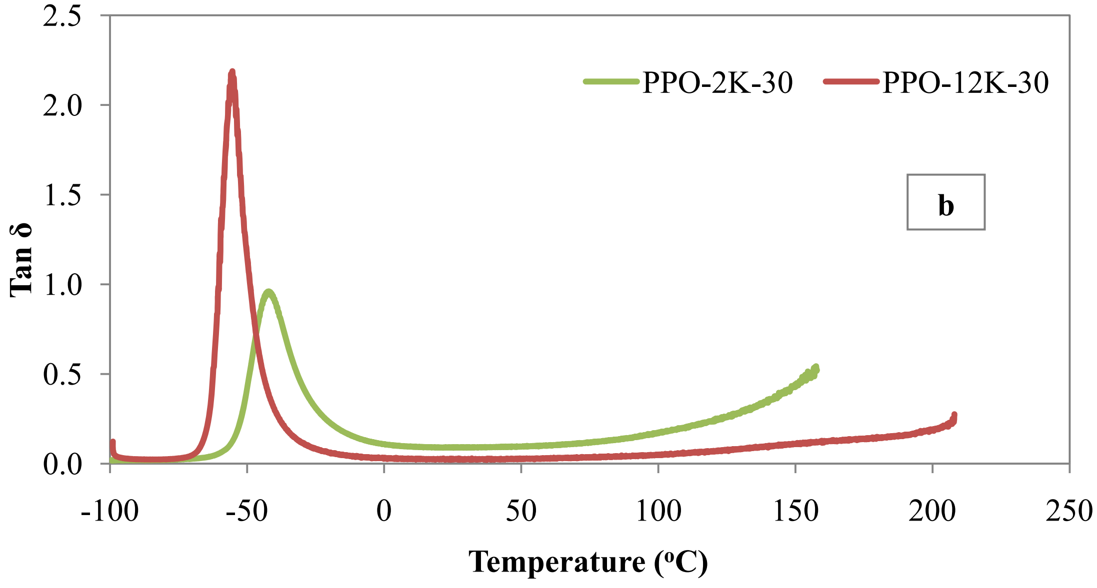


Figure 3.5. Comparative storage modulus–temperature and tan δ–temperature curves for PPO-2K-30 and PPO-12K-30

Comparative DMA curves for PPO-2K-30 and PPO-4K-30 are reproduced on Figure 3.6.(a) and 3.6.(b). PPO-4K-30 exhibits a lower storage modulus in the glassy state compared to PPO-2K-30. This is followed by a glass transition region with a T_g of –49 °C obtained from tan δ curve provided in Figure 3.6.(b). This T_g value is in between to those of PPO-2K and PPO-12K, which is expected. The rubbery plateau extends from -36 to about +180 °C is much wider than that of PPO-2K-30 copolymer as can be seen in Figure 3.6.(a). It is also fairly temperature insensitive similar to PPO-12K-30. The extended rubbery plateau again indicates good microphase separation in the system. Sheth et al. observed similar behavior in PPO based PUUs [38]. They have also mentioned that the overall molecular weight of the copolymer can be a reason for the extended rubbery plateau. Thus, combining the results of creep measurements (which will be discussed in Section 3.2.3.) and the DMA measurements, we may explain the unexpectedly good creep resistance of PPO-4K-30, which seems to be due to better microphase separation than that of PPO-2K-30 and stronger hydrogen bonding between longer urea hard segments (Table 3.6.).

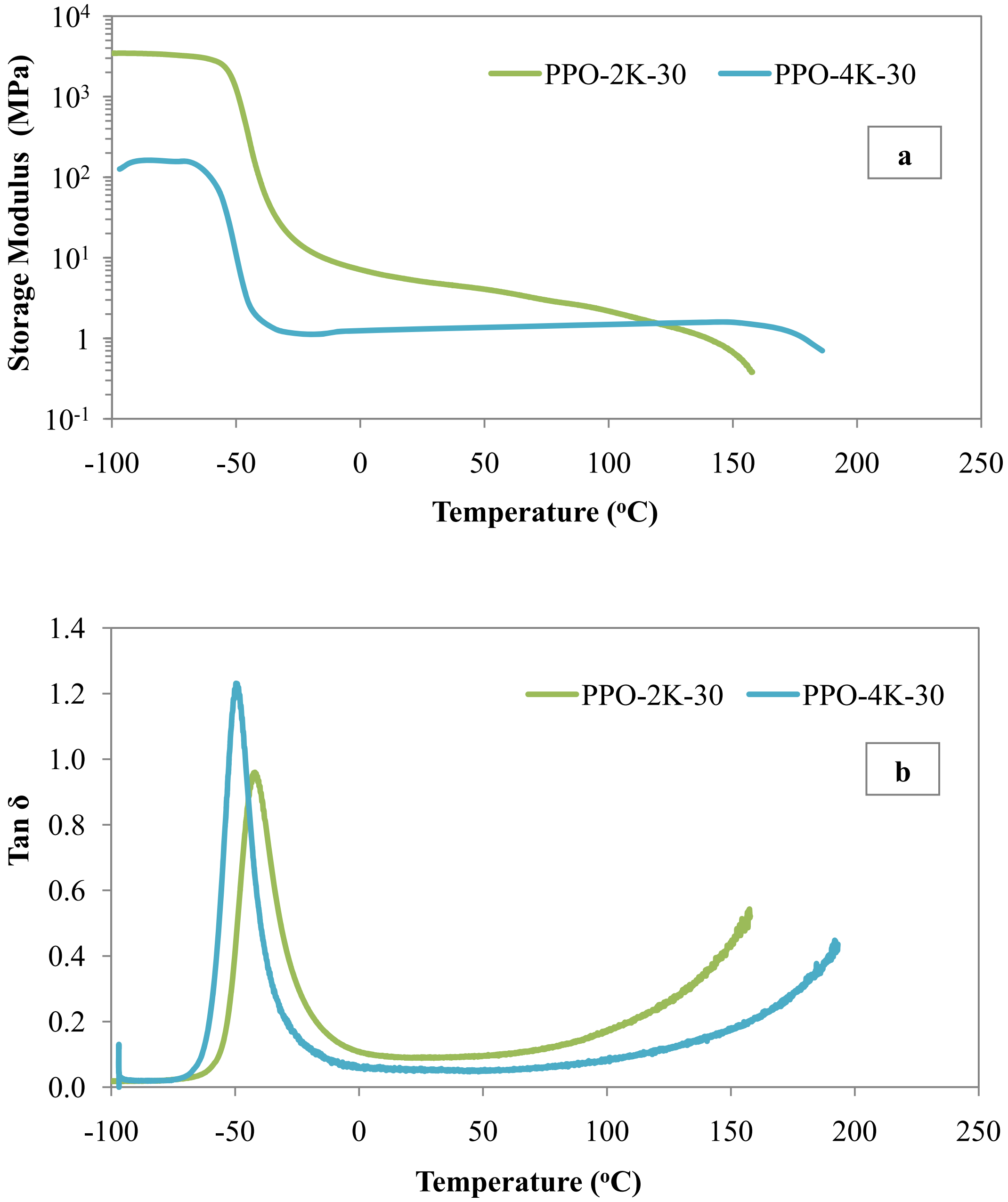


Figure 3.6. Comparative storage modulus–temperature and tan δ–temperature curves for PPO-2K-30 and PPO-4K-30

3.2.2. Tensile Measurements

In order to understand the synergistic effect of soft segment entanglements and hard segment content on mechanical properties of polyether based segmented PUUs, stress–strain tests were performed.

Complete list of stress–strain data obtained for PPO and PEO based poly(urethaneurea)s are tabulated in Table 3.3 and Table 3.4, respectively. Copolymers with the codes PPO-1K-30, PEO-1K-30 and PEO-2K-20 formed tacky and soft films at room temperature, therefore we were unable to perform stress–strain tests on these samples. Also PEO-12K-20 exhibited very brittle behavior and could not be tested. The synthesis of this copolymer was repeated several times under different conditions. However, a very rigid film was obtained at all times. This is most probably due to very high crystallinity of PEO-12K matrix in the copolymer leading to the formation of very rigid films. That is why, no data is provided for this copolymer.

As mentioned before, PEO based PUUs prepared in presence of IPA as chain extender solvent displayed weaker mechanical properties. For comparison, stress – strain data of this series are provided on Table 3.5. PEO-1K-40-IPA and PEO-2K-30-IPA resulted in very weak polymers, so that their tensile data could not be collected. For all of the copolymers synthesized white particles were formed during the chain extension step. O'Sickey et al. have reported similar observations [36]. An inhomogeneous polymer solution was obtained during chain extension. This was explained as a result of formation of insoluble urea blocks due to rapid reaction of diisocyanates with diamines. In this study, the reason for formation of the precipitates is believed to be in a similar manner. IPA seems to be either a poor solvent to dissolve the long urea segments formed or acts as a coagulant for the polymer formed. As a result, the mechanical properties of the final product are affected in a negative way.

Table 3.3. Tensile properties of PPO based PUUs with different soft segment molecular weights and hard segment contents.

Polymer Code	Molar Ratio (PPO/HMDI/MDAP)	Modulus (MPa)	Tensile Strength (MPa)	Elong. (%)
PPO-1K-30	2.2/3.2/1	-	-	-
PPO-2K-30	1/2.6/1.6	6.0	17.8	1010
PPO-2K-45	1/5/4	69.8	26.7	480
PPO-4K-20	1/3.3/2.3	2.1	4.5	530
PPO-4K-30	1/5/4	3.1	17.4	990
PPO-8K-18	1/5/4	1.2	8.4	1550
PPO-8K-30	1/9.3/8.3	4.5	17.0	980
PPO-12K-12	1/5/4	0.8	4.6	1470
PPO-12K-30	1/13.7/12.7	4.1	20.9	990

Table 3.4. Tensile properties of PEO based PUUs with different soft segment molecular weights and hard segment contents.

Polymer Code	Molar Ratio (PEO/HMDI/MDAP)	Modulus (MPa)	Tensile Strength (MPa)	Elong. (%)
PEO-1K-30	2.3/3.3/1	-	-	-
PEO-1K-40	1/2.1/1.1	3.1	13.2	1060
PEO-2K-20	1/1.6/0.6	-	-	-
PEO-2K-30	1/2.6/1.6	8.3	38.5	1020
PEO-2K-40	1/3.8/2.8	16.0	39.8	670
PEO-2K-50	1/5.5/4.5	54.8	43.6	590
PEO-4K-20	1/3.3/2.3	240	37.9	830
PEO-4K-30	1/5.5/4.5	270	35.4	670
PEO-8K-10	1/2.8/1.8	490	17.9	14
PEO-8K-20	1/5.5/4.5	300	35.7	790
PEO-8K-30	1/10/9	400	46.6	740
PEO-12K-20	1/7.9/6.9	-	-	-

Table 3.5. Tensile properties of PEO based PUUs prepared with IPA as chain extender solvent

Polymer Code	Molar Ratio (PEO/HMDI/MDAP)	Modulus (MPa)	Tensile Strength (MPa)	Elong. (%)
PEO-1K-40-IPA	1/2.1/1.1	-	-	-
PEO-2K-30-IPA	1/2.6/1.6	-	-	-
PEO-2K-50-IPA	1/5.5/4.5	44.3	30.8	590
PEO-4K-30-IPA	1/5.5/4.5	90	16.1	560
PEO-8K-20-IPA	1/5.5/4.5	410	16.4	200
PEO-8K-30-IPA	1/10/9	810	26.9	162

To investigate the effect of soft segment entanglements, tensile properties of PUUs with identical soft / hard segment ratios are compared. Stress-strain plots of PPO based PUUs with 30 wt% hard segment is represented in Figure 3.7. It is observed that area under the curve increases with increasing soft segment molecular weight. Tensile strength of the copolymers decreases slightly with increasing soft segment molecular weight. However, PPO-12K-30, which has a soft segment with $<M_n>$ well above M_c, exhibit highest tensile strength compared to the other copolymers. It can be suggested that this enhancement could be a result of contribution of soft segment entanglements.

All of PEO based PUUs exhibit strain–induced crystallization during deformation, due to semi-crystalline nature of PEO as shown in Figure 3.8. As the soft segment molecular weight increases, necking is observed during deformation with a distinct yield point in stress–strain curves. These copolymers display remarkably high tensile strength and modulus compared to PPO based PUUs, which is believed to be due to incorporation of soft segment crystallites. Moreover, modulus increases with increasing soft segment molecular weight. As already mentioned, no stess–strain data could be collected for PEO-12K-20, since the films of the copolymer was very brittle. This is a good indication for increasing soft segment crystallinity with increasing soft segment molecular weight.

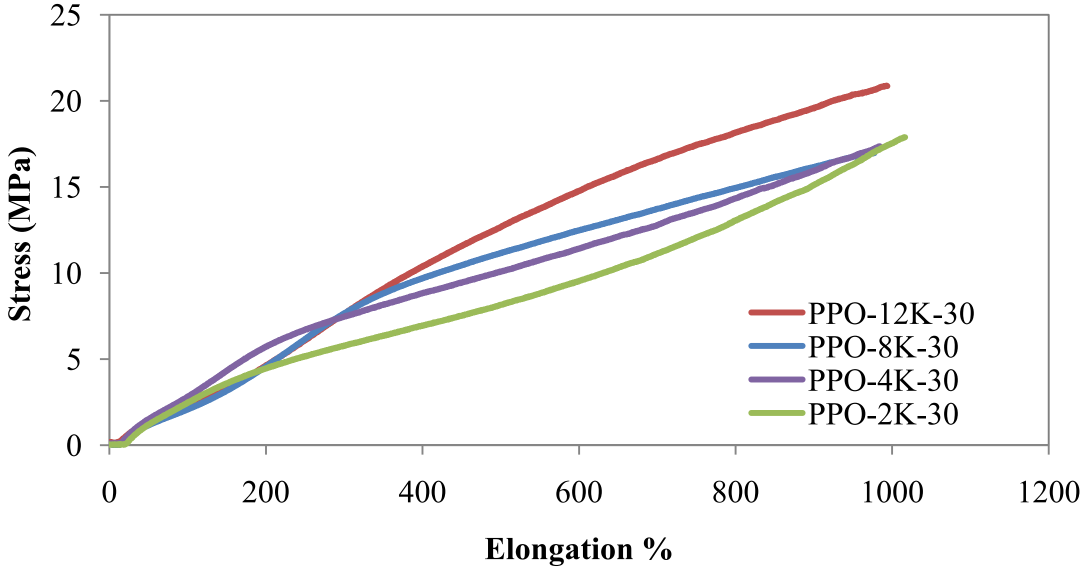


Figure 3.7. Stress – strain curves of PEO based PUUs with 30 wt% hard segment

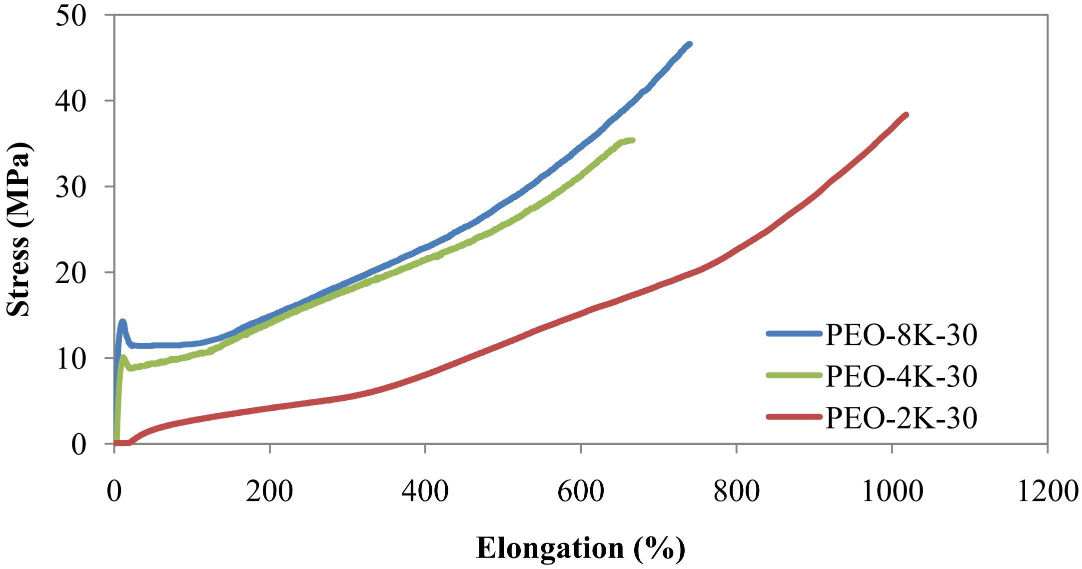


Figure 3.8. Stress – strain curves of PEO based PUUs with 30 wt% hard segment

PEO-8K-30, copolymer with a soft segment $\langle M_n \rangle$ well above M_c, which is reported to be 4400 g/mol exhibits the highest value for tensile strength and modulus. It is also known that homopolymers of PEO above 6000 g/mol have reduced crystallinity due to incorporation of chain entanglements [43]. Also, Sheth et al. recognized that M_c may be affected by copolymerization [38]. Hence, it is not clear at this point, whether soft segment entanglements or soft segment crystallites contribute to the enhancement in the tensile properties.

As mentioned before, at constant hard segment content, hard segment length increases with increasing soft segment molecular weight (Table 3.6). In order to understand the effect of hard segment length on polymer properties, PUUs of constant soft segment molecular weight with different hard segment contents were compared.

Table 3.6. Average hard segment molecular weight in PPO based PUUs, (n) is the average $(HMDI\text{-}MDAP)_n$ repeat unit in urea hard segments calculated from reaction stoichiometry

Polymer Code	HS (wt%)	Molar Ratio (PPO/HMDI/MDAP)	HS Repeat Unit (n)	HS $\langle M_n \rangle$ (g/mol)
PPO-2K-30	29.2	1/2.6/1.6	1.6	868
PPO-4K-30	29.3	1/5/4	4	1777
PPO-8K-30	28.8	1/9.3/8.3	8.3	3404
PPO-12K-30	29.9	1/13.7/12.7	12.7	5070
PPO-2K-45	45.3	1/5/4	4	1777
PPO-2K-20	20.0	1/1.7/0.7	0.7	527
PPO-12K-12	12.4	1/5/4	4	1777
PPO-12K-20	20.0	1/8.1/7.1	7.1	2950

Tensile strengths of homologous series of PPO-2K and PPO-12K based copolymers are plotted against their hard segment contents. Corresponding plots are represented in Figure 3.9. Data of PPO-2K-20 and PPO-12K-20 were gathered from copolymers previously synthesized in our laboratory by using the same polymerization procedure.

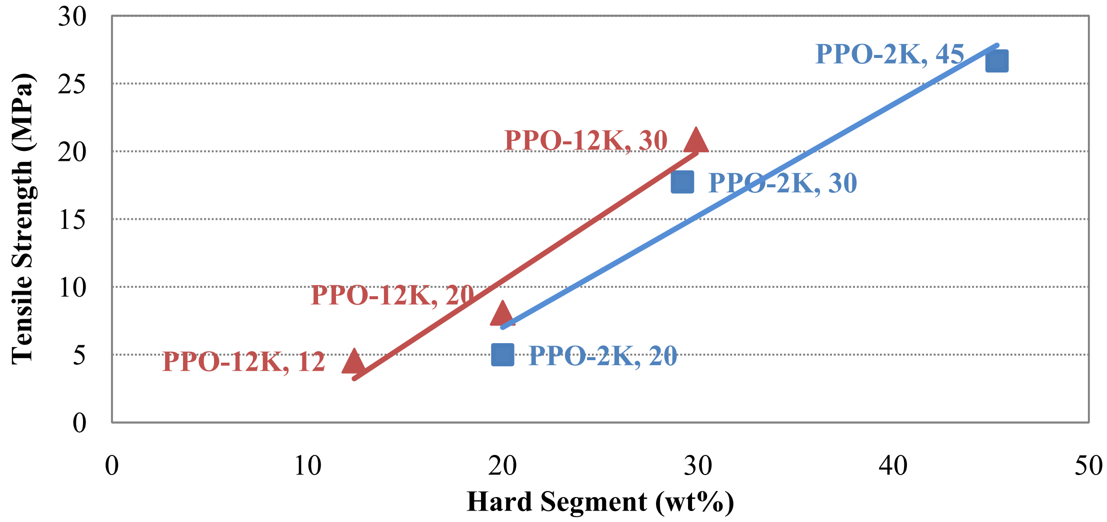


Figure 3.9. Effect of PPO molecular weight and hard segment content on tensile strength of PUUs

As can clearly be seen in Figure 3.9., tensile strength of copolymers increases linearly with increasing hard segment content. It is remarkable to note that copolymers based on PPO-12K always display higher tensile strength values when compared to its analogous series with similar soft/hard segment ratios. Even at lowest hard segment concentration, copolymers based on PPO-12K exhibit higher tensile strengths when compared with PPO-2K based systems as shown on Figure 3.9. These observations can be accepted as a good indication of the synergistic influence of soft segment entanglements on tensile properties.

Table 3.7. Average hard segment molecular weight in PEO based PUUs, (n) is the average $(HMDI\text{-}MDAP)_n$ repeat unit in urea hard segments calculated from reaction stoichiometry

Polymer Code	HS (wt%)	Molar Ratio (PPO/HMDI/MDAP)	HS Repeat Unit (n)	HS $<M_n>$ (g/mol)
PEO-2K-30	28.5	1/2.6/1.6	1.6	868
PEO-4K-30	28.0	1/5.5/4.5	4.5	1966
PEO-8K-30	28.3	1/10/9	9	3669
PEO-2K-40	39.1	1/3.8/2.8	2.8	1322
PEO-2K-50	47.4	1/5.5/4.5	4.5	1966
PEO-8K-10	9.8	1/2.8/1.8	1.8	944
PEO-8K-20	18.4	1/5.5/4.5	4.5	1966

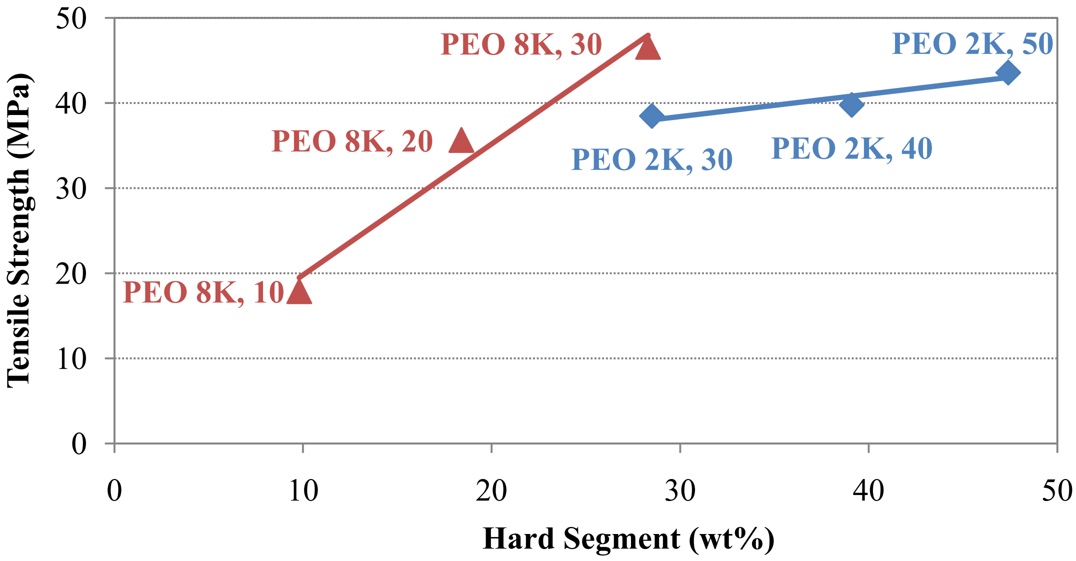


Figure 3.10. Effect of PEO molecular weight and hard segment content on tensile strength of PUUs

Similarly, when PEO based copolymers, PEO-2K and PEO-8K series, were compared (Table 3.7, Figure 3.10.). It is observed that tensile properties of PEO-2K based copolymers do not show a significant increase with increasing hard segment length. This may be due to low crystallinity or due to possible phase mixed morphology that was suggested during ATR-FTIR discussions. For PPO-8K based copolymers tensile strength seems to be more dependent on hard segment length. However, it is believed that incorporation of soft segment crystallites contribute to this large increase. This is strongly supported by the tremendously high modulus of PEO-8K based copolymers. PPO-8K-10 displays very high tensile strength and modulus even with very low hard segment content. Moreover, the extensibility of the copolymer is extremely low compared to the other PEO-8K based copolymers. This strongly suggests that crystalline nature of soft segment block prevents successful extensibility. High brittleness of PEO-12K-20 also supports the statement above. Thus, no conclusions can be drawn for the effect of soft segment entanglements.

3.2.3. Constant Initial Stress Creep Measurements

Creep is defined as the time dependent change in dimensions of polymers upon application of an instant constant stress [51]. Creep behavior of polymers reveals important information about their applicability for tasks which require dimensional stability.

It is known that the creep behavior of polymers depends on many factors such as; magnitude of initial stress applied, loading time, temperature, chemical structure of the polymer, topology and morphology. At sufficiently high initial stress or long loading time the polymer may extend until it ruptures. Creep resistance of a polymer decreases with increasing temperature. Also, polymers with high crosslink density display low creep. Hence, it is expected that creep behavior of copolymers to give information about the presence of soft segment entanglements.

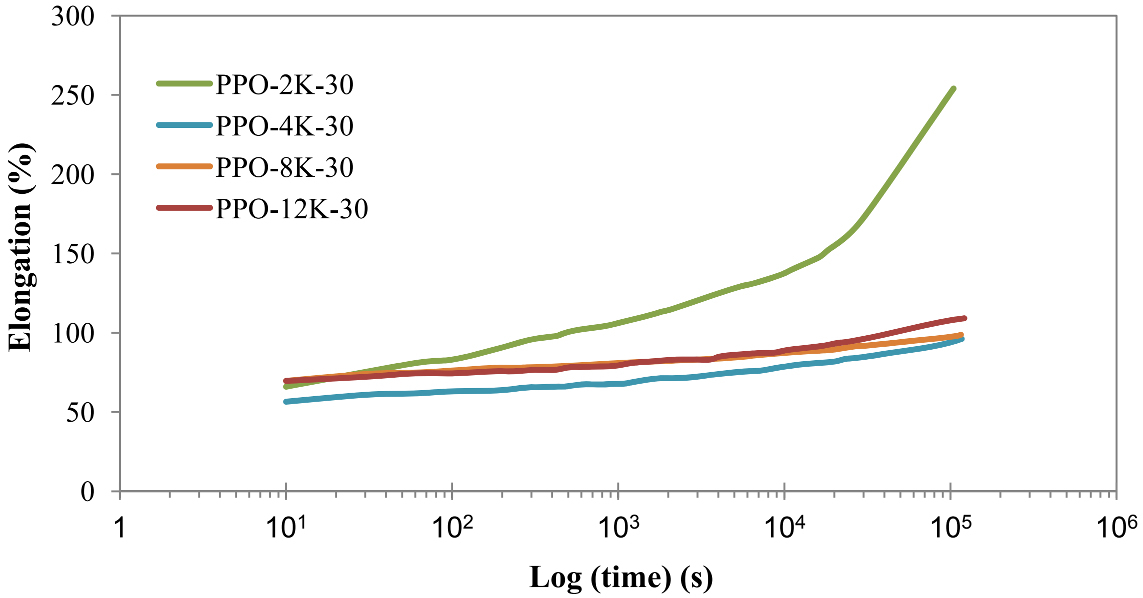


Figure 3.11. Constant initial stress behavior of PPO based copolymers with 30 wt% hard segment content

Time dependent deformation curves of PPO based copolymers with 30 wt% hard segment are represented in Figure 3.11. PEO based PUUs were not subjected to constant stress due to their capability to yield at low strains.

All copolymers were subjected to constant initial stress around 1.5 MPa. Their time dependent deformation was observed at room temperature conditions for about 10 days. As clearly seen in Figure 3.11, PPO-2K based PUU exhibits the lowest creep resistance. As the soft segment molecular weight increases, creep resistance also increases. Interestingly, PPO-4K-30 also displays high creep resistance, even though its soft segment is below M_c. The reason of this behavior is unknown at this point. One reason can be the change of M_c value after copolymerization as suggested by Sheth et al. [38]. Also the wide plateau modulus of PPO-4K-30 from DMA results suggests that the increased microphase separation may be a reason for this enhanced creep resistance. PPO-8K-30 and PPO-12K-30 exhibit high creep resistance, as expected.

As indicated before, the crosslink density of a material affects its response on creep deformation. As the hard segment length increases, the relative amount of hydrogen bonding sites also increases. Thus, it is an expected observation if the copolymers display increased creep resistance with an increasing hard segment length. This trend can be followed if PPO-2K-30 and PPO-2K-45 are compared. It was observed that PPO-2K-30 was relatively low creep resistant (Figure 3.11). As clearly seen in Figure 3.12, PPO-2K-45, which has a higher hard segment content, deforms much less than PPO-2K-30. PPO-2K-30 shows almost 70% initial elongation, which continues up to 600% within 10 days. On the other hand, PPO-2K-45 displays very low initial deformation (10%) and it does not elongate significantly even after 10 days.

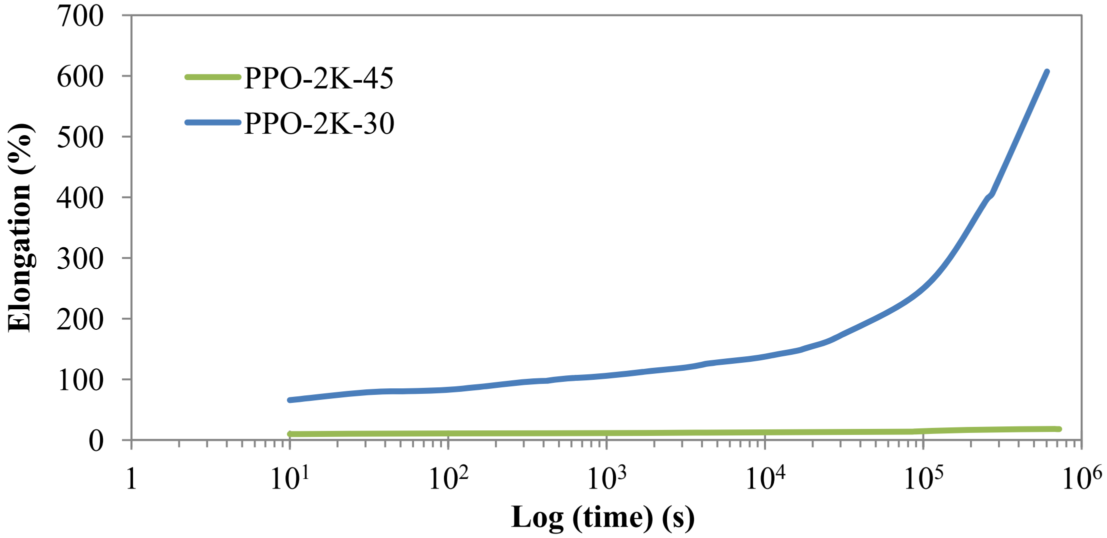


Figure 3.12. Comparison of creep behavior of PPO-2K-30 and PPO-2K-45

In order to understand the effect of possible soft segment entanglements, creep behaviors of PPO based copolymers with different soft segment M_n were compared, by keeping their hard segment length constant. Figure 3.13 represents time dependent deformation curves of copolymers with constant molar ratios and hard segment lengths (1/5/4 for PPO/HMDI/MDAP, HS $<M_n>$ = 1777 g/mol).

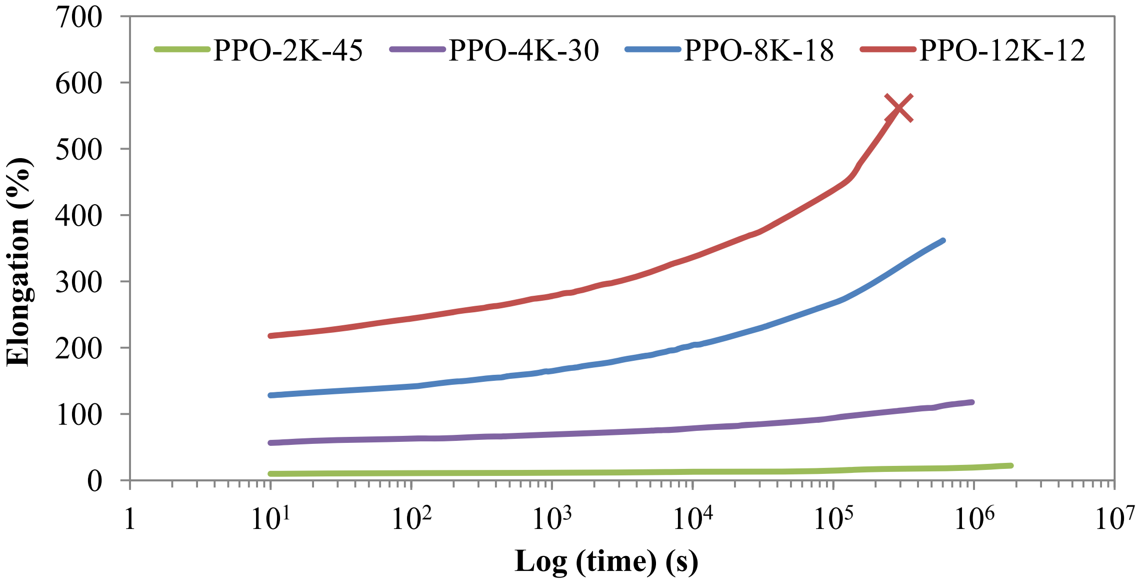


Figure 3.13. Constant initial stress behavior of PPO based copolymers with constant hard segment length

It is important to emphasize that when the hard segment length is kept constant, the hard segment content of the copolymer decrease with increasing soft segment molecular weight. As a result, with increasing soft segment molecular weight a decreasing trend of creep resistance is observed (Figure 3.13). The initial elongation of the copolymers also increases. PPO-12K-12 displays the lowest creep resistance. It is an expected result, since it has the lowest hard segment content among the compared samples. However, it endures the constant stress for about three days, until the copolymer ruptures.

PPO-12K-12 elongates initially approximately to 200% of its initial length. This value is almost three times larger compared to initial elongation of PPO-2K-30 (70% initial elongation). Before fracture, PPO-12K-12 reaches almost to 560% elongation. PPO-2K-30, on the other hand, reaches to 400% of its initial length in three days. Thus, although PPO-2K-30 has a higher hard segment content, PPO-12K-12 resists relatively more to creep. This can be understood from its relatively low rate of elongation compared to PPO-2K-30. Creep curves of PPO-2K-30 and PPO-12K-12 are represented in Figure 3.14.

All of the observations discussed above strongly support the possible effect of soft segment entanglements on mechanical properties of PPO based copolymers.

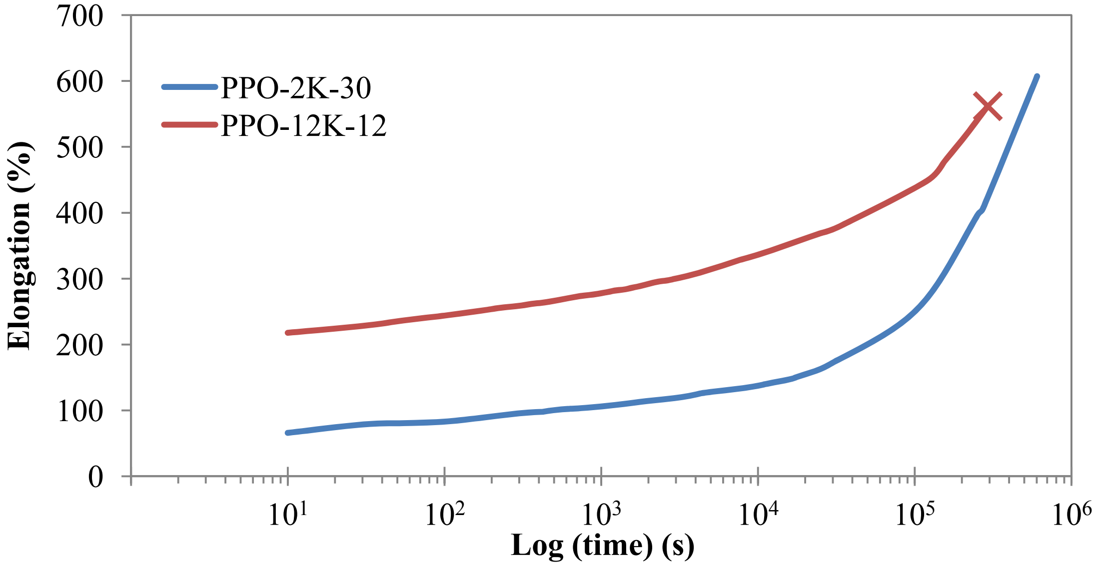


Figure 3.14. Comparison of creep behavior of PPO-2K-30 and PPO-12K-12

3.3. Qualitative Studies on Polymer Morphology

3.3.1. Wide Angle X-ray Diffraction

As it was discussed in previous sections, PEO based PUUs show remarkably different tensile properties when compared to PPO based PUUs. Stress – strain curves displayed strain induced crystallization. Also necking was observed with increasing soft segment molecular weight. ATR-FTIR spectra presented a different hydrogen bonding character for PEO-2K-30 compared to the other PEO based copolymers with similar soft/hard segment ratio. All of these behaviors of PEO based PUUs were attributed to the semi-crystalline nature of the soft segment. To further elucidate the morphological character of these copolymers wide angle X-ray diffraction (WAXD) patterns were collected.

WAXD patterns for PEO homopolymers are presented in Figure 3.15. Four peak maxima are observed from PEO-2K WAXD pattern at $2\theta = 13.9, 19.3, 23.5$ and $27.6°$. As molecular weight of the oligomer increases, peaks at $2\theta = 13.9^o$ and 27.6^o are suppressed. Peaks around $2\theta = 19.3^o$ and 23.5^o are dominant for all PEO oligomers, which correspond to a d–spacing of 0.463 nm and 0.380 nm, respectively. WAXD peak at 0.463 nm is attributed to (120) plane, whereas peak at 0.380 can be assigned to seven different planes [52].

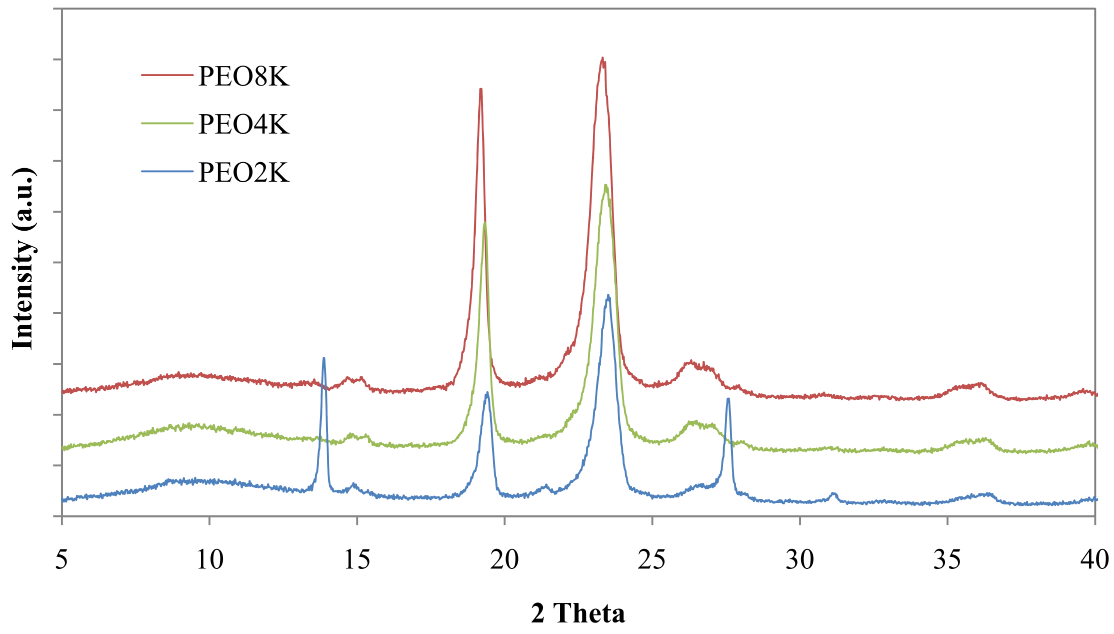


Figure 3.15. WAXD patterns for PEO homopolymers

Figure 3.16 represents WAXD patterns for PEO based PUUs with constant hard segment content of 30% by weight. For PEO-2K-30, negligibly small peaks are observed for 2θ around 19^o and 23^o. Compared to the homologous copolymers with higher soft segment molecular weight, PEO-2K-30 can be considered as amorphous. This correlates well with ATR-FTIR interpretations as discussed in section 3.1.2. Poorly phase separated PEO-2K-30 possibly contains hard segments dispersed/mixed in the soft segment matrix, which prevent mobility. PEO soft segments cannot fold successfully to form crystallites, which result in a relatively soft PEO based copolymer.

Peaks caused by soft segment crystallization become more apparent and more intense as the soft segment molecular weight in the PUU increases. Peak maxima in PUUs correlate well with the peak positions of PEO-4K and PEO-8K homopolymers. This can be attributed to increased crystallinity and increased modulus of copolymers with increasing soft segment molecular weight. However, extent of crystallinity cannot be discussed in detail without quantitative data.

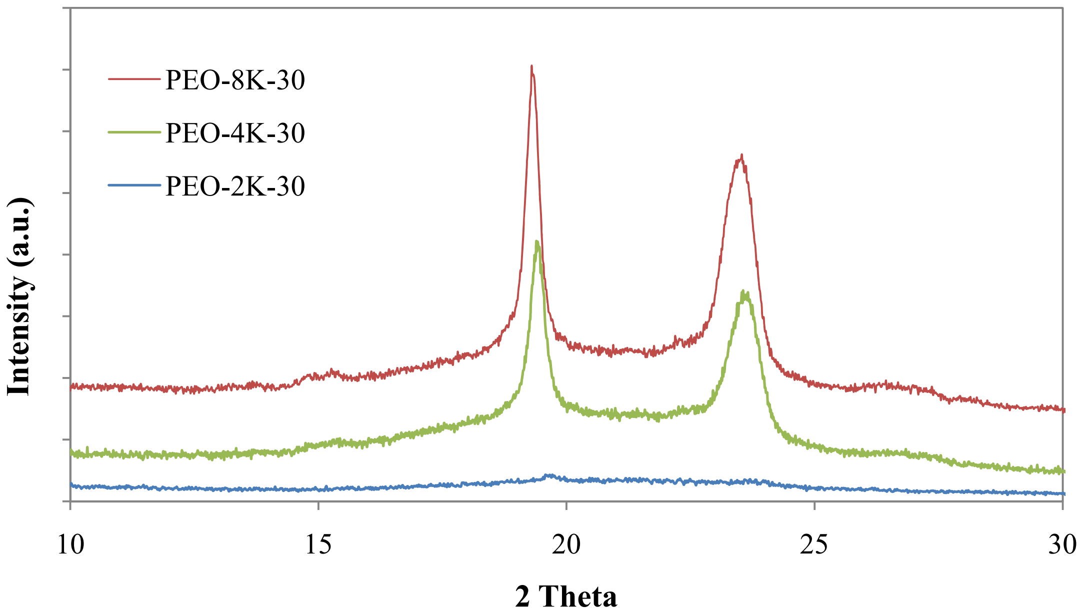


Figure 3.16. WAXD patterns for PEO based PUUs with 30 wt% hard segment

As it was determined form stress–strain curves, copolymers with soft segment $<M_n>$ higher than 2000 g/mol shows necking during stretching. It is known that crystallites within the necking region deform and reorient themselves in the stretch direction. This behavior can clearly be observed via WAXD measurement. Figure 3.17 shows WAXD patterns of PEO based PUUs before and after tensile stretching.

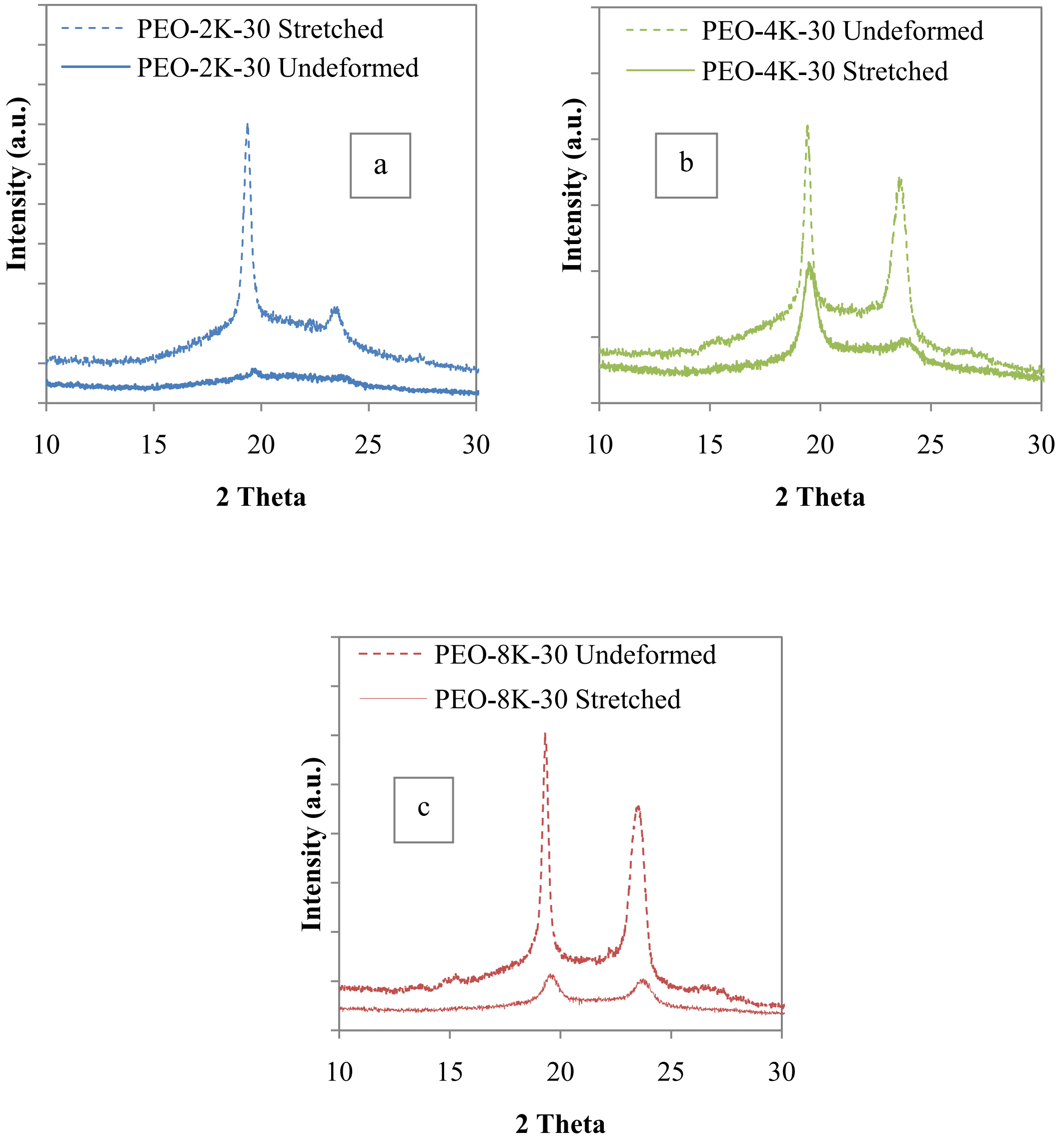


Figure 3.17. WAXD patterns for PEO based PUUs with 30 wt% hard segment before and after tensile stretching (a) PEO-2K-30 (b) PEO-4K-30 (c) PEO-8K-30

For PEO-2K-30 the formation of stress induced crystallites are clearly observed. The peak observed around d = 0.463 nm is apparently more intense, indicating that crystallites orient themselves on one plane during stretching. Reorganization in the PEO soft segment crystallinity is also observed in PEO-4K-30 and PEO-8K-30 copolymers. Interestingly, quite different than PEO-2K-30, intensity of diffraction peaks decrease significantly after stretching for PEO-4K-30 and PEO-8K-30 copolymers. Moreover, peaks become broadened. It is known that the broadening of diffraction peaks are caused by the change of the crystal size and the extent of broadening is inversely proportional to crystal size [53]. Thus, these observations indicate that the soft segment crystallites are disturbed and reformed during stretching, which correlates well with the expectations during neck formation.

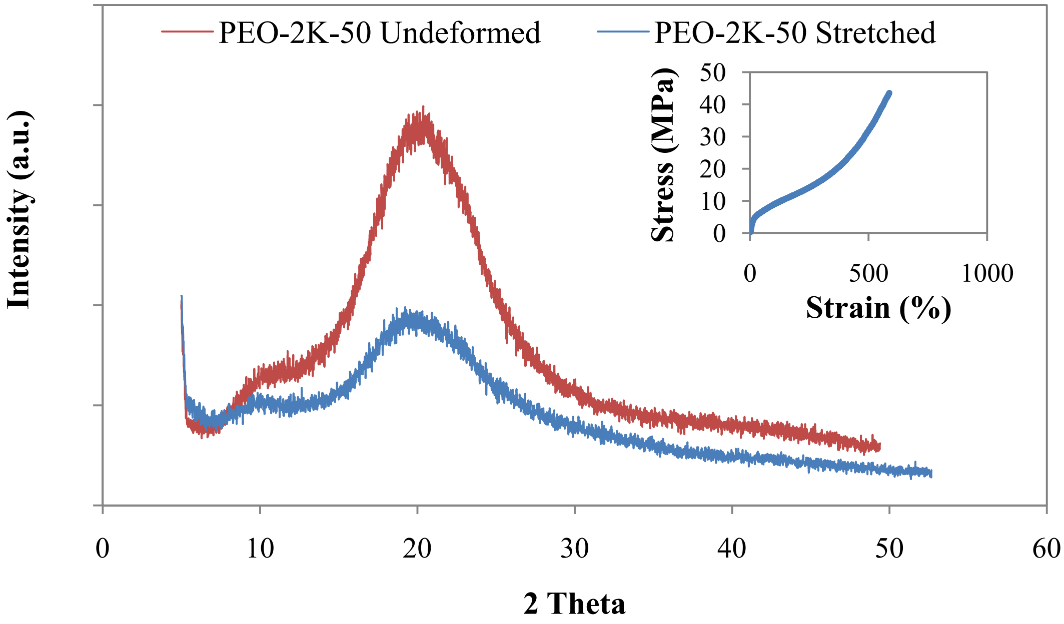


Figure 3.18. WAXD pattern for PEO-2K-50 before and after tensile stretching

It was also mentioned that tensile strength of PEO-2K based copolymers did not show significant increase with increasing hard segment length. WAXD patterns for PEO-2K-50 before and after stretching are provided in Figure 3.18. For both situations the WAXD pattern displayed a broad amorphous halo. This copolymer is composed of almost 50 wt% hard segment. Hence, soft segment crystallinity will likely be suppressed through incorporation of or upon mixing with hard segment units. It is also believed that PEO-2K copolymers are more phase mixed than their homologous copolymers with higher soft segment molecular weight. Also, stress–strain curve of PEO–2K–50 (inset of Figure 3.15.) does not exhibit any yield point, which clearly demonstrates that the hard segments are not percolated through the hard segment matrix. Thus, increasing hard segment content does not increase the strength of the copolymer significantly.

3.3.2. Atomic Force Microscopy

Atomic Force Microscopy (AFM) is a useful technique to characterize the surface morphology of materials. Tapping mode phase images of PPO-2K-30 and PPO-12K-30 are represented in Figure 3.19. In those images, hard segments appear as light colored regions, whereas soft segments are darker. Figure 3.19.a and 3.19.c display surface morphology of those copolymers in a scale of 5x5 μm^2. If compared, PPO-2K-30 displays less phase contrast than PPO-12K-30 (Figure 3.19.a and 3.19.b). The possible explanation for this observation is as follows: PPO-2K-30 possesses shorter hard segments compared to PPO-12K-30 (Table 3.6). As the hard segment length is increased, more hydrogen bonding sites are introduced to the copolymer. Thus, hard segments tend to form microdomains and phase separate. As observed from DMA measurements, PPO-12K-30 is suggested to have enhanced microphase separated morphology compared to PPO-2K-30. This suggestion is verified through the AFM images, where the light hard segment domains are more apparent.

If the scanning area is decreased to 1x1 μm^2, hard segment domains of PPO-2K-30 become more visible. The largest domains are in the size of 50 nm (Figure 3.19.c). There is still not much phase contrast, which suggests that the phase separation is not well enough. The microphase separated morphology is more apparent for PPO-12K-30 (Figure 3.19.d). As the soft segment molecular weight increases, the hard segment length increases. Hence, as stated above hard segment domains become larger. As seen in Figure 3.19.d, the domain sizes of PPO-12K-30 range from a few tens to thousands of nanometers. The largest domain visible on the image is on the order of approximately 120 nm. Furthermore, the distance between the hard domains is also increased with increasing soft segment molecular weight. This can be understood from increased contrast between soft and hard segments. Thus, the enhanced microphase separation is confirmed.

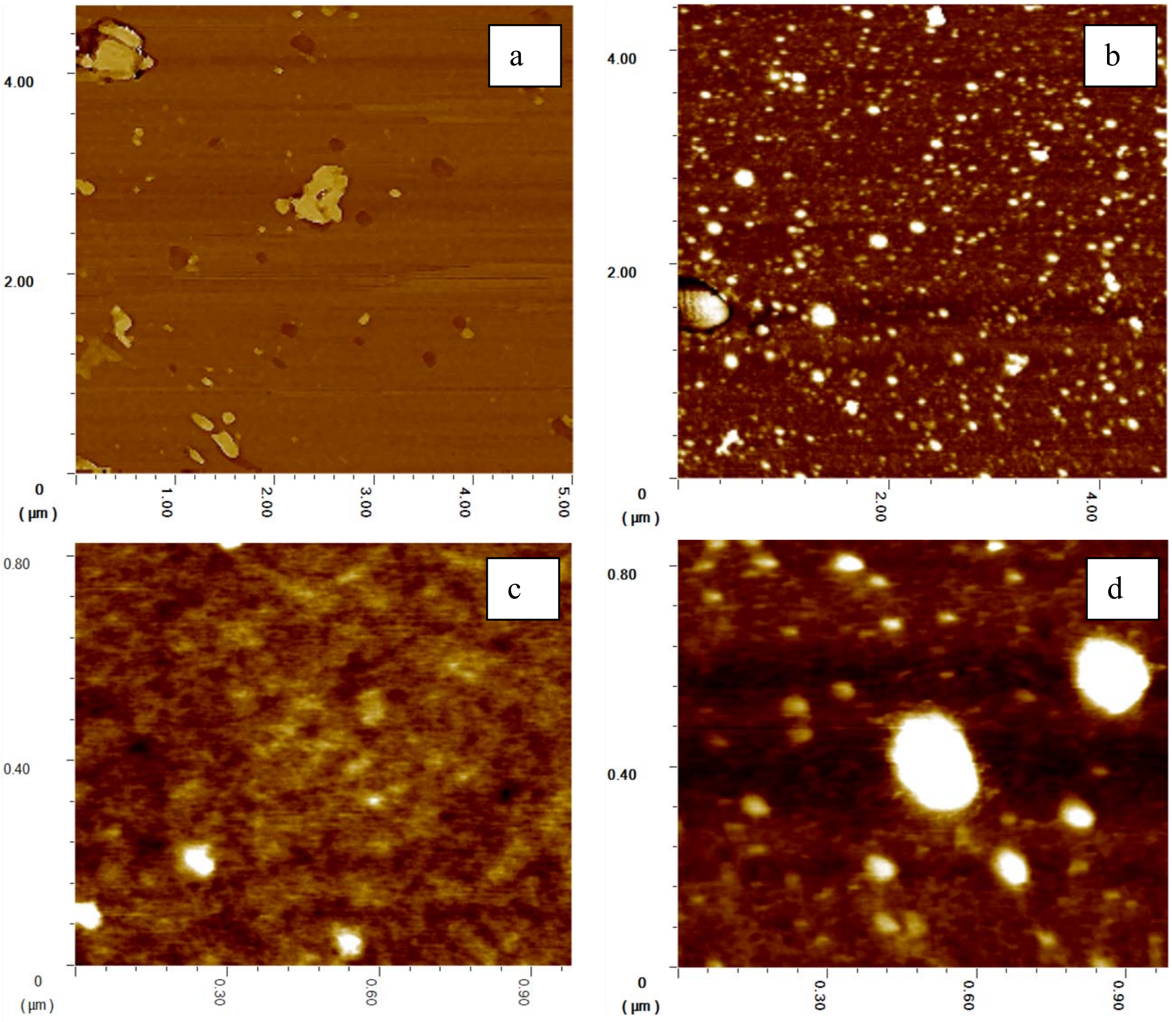


Figure 3.19. Tapping mode AFM phase images of PPO-2K-30 (a) 5x5 µm^2 (c) 1x1 µm^2 and PPO-12K-30 (b) 5x5 µm^2 (d) 1x1 µm^2

Chapter 4

Conclusions

Series of PPO and PEO based segmented poly(urethaneurea)s with different soft segment molecular weights and soft / hard segment ratios were successfully synthesized and characterized. Effect of soft segment structure, soft segment molecular weight and hard segment length on phase behavior and tensile properties was investigated. Main focus of the study was to understand the effect of soft segment entanglements on morphology and tensile properties of polyether based copolymers.

FTIR spectra revealed that both series has a phase mixed morphology due to the interaction between urea/urethane groups in the hard segments and ether oxygen present on the soft segment backbone. PPO based PUUs of homologous series did not show any significant difference in peak positions. Expectedly, urethane peak intensity decreased with increasing soft segment length. Similar behavior was observed for PEO based PUUs. Different than PPO based PUUs, amide peak positions changed slightly with increasing soft segment molecular weight, indicating for a change of hydrogen bonding character, thus morphology, of copolymer.

Modulus-temperature curves displayed interesting results regarding the microphase morphology of the PPO based copolymers, clearly indicating better microphase separation for copolymers prepared by using higher molecular weight soft segments. Microphase separated morphology of copolymers with higher molecular weight soft segments were also confirmed by AFM images. Also, as the PPO soft segment length increased, rubbery plateau of the copolymer got longer and more temperature insensitive, which may indicate the contribution of soft segment entanglement.

Tensile strength of PPO based PUUs increased linearly with increasing hard segment content, as expected. However, copolymers with similar hard segment contents displayed higher tensile strength, if their soft segment molecular weight was above M_c. Such copolymers also exhibited comparably high tensile strength even with very low hard segment contents, which can be interpreted as a good indication of contribution of soft segment entanglements. Constant stress creep measurements strengthened this idea, since copolymers exhibited increased creep resistance with increasing soft segment molecular weight.

Due to semi-crystalline nature of PEO, copolymers of this type of soft segment displayed strain – induced crystallization during deformation. It is observed that crystallinity of soft segment increased with increasing molecular weight, as it could be understood form very high modulus and tensile strengths of these copolymers compared to their PPO based homologues. Tensile strength of PEO-2K series did not show a significant dependence on hard segment content, which may be caused by lack of crystallinity or by possibly phase mixed morphology. This behavior was confirmed via WAXD measurements. Copolymers with PEO-8K displayed higher tensile strengths and more dependency on hard segment content. However, it is believed that the high tensile strength is mainly caused by the presence of soft segment crystallites, which also may prevent successful entanglements and extensibilities. Hence, effect of soft segment entanglements on PEO based PUUs could not be understood clearly. These results observed on PEO based PUUs suggest that crystallizability of the higher molecular weight soft segment strongly contributes to microphase separation and improved mechanical properties.

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