PREPARATION AND CHARACTERIZATION OF NOVEL

SILICONE-UREA COPOLYMERS AND COMPOSITES

by

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A Thesis Submitted to the

Graduate School of Engineering

in Partial Fulfillment of the Requirements for

the Degree of

Master of Science
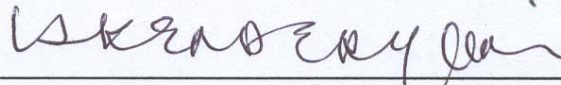
in

Materials Science and Engineering Program
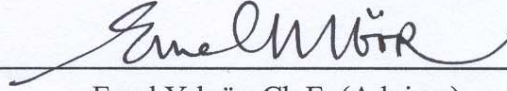
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October 2008

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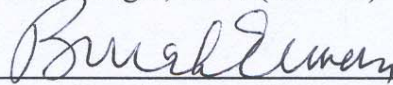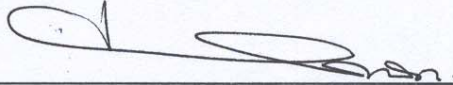examining committee have been made.

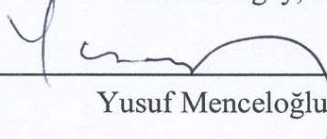Committee Members:

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ABSTRACT

Novel, segmented thermoplastic silicone-urea (TPSU) copolymers based on fairly high molecular weight aminopropyl terminated polydimethylsiloxane (PDMS) soft segments ($<M_n>$ 10,800 and 31,500 g/mole), a cycloaliphatic diisocyanate (HMDI) and various low molecular weight diamine chain extenders were prepared and characterized. One of our goals in this study was to understand the influence of PDMS soft segment length on the tensile properties and hysteresis behavior TPSU copolymers. Copolymers with very low urea hard segment contents of 1.24 to 5.14% by weight were prepared. Although the copolymers had fairly low hard segment contents, they all formed films, showed very good microphase separation and displayed reasonably good mechanical properties. When silicone urea copolymers with identical urea hard segment contents were compared, those based on PDMS-31,500 showed higher tensile strengths than those of PDMS-10,800. In addition, PDMS-31,500 based silicone-urea copolymers also displayed lower hysteresis values when compared with PDMS-10,800 based TPSU or even with chemically crosslinked silicone rubbers. Critical entanglement molecular weight (M_e) of PDMS is about 25,000 g/mol. We believe chain entanglement in PDMS-31,500 have a synergistic effect on the tensile properties and hysteresis behavior of the silicone-urea copolymers. Second goal of our research effort was to understand the effect of fumed silica fillers on the properties of silicone-urea copolymers. Hydrophobic silica filled silicone-urea copolymers, containing up to 37.5% by weight of silica were prepared for the first time. Incorporation of hydrophobic silica into silicone-urea copolymers based on PDMS-31,500 dramatically increased the modulus, tensile strength and elongation at break values of these copolymers. Silica incorporation had a slight negative effect on the hysteresis behavior. Presence of interaction between silica and the TPSU copolymers were also investigated by FTIR spectra.

ÖZET

Termoplastik silikon-üre (TPSU) kopolimerleri, yeni bir bakış açısıyla, içerisinde yüksek molekül ağırlıklı ve amin sonlu PDMS oligomerleri, halkalı alifatik diizosiyant (HMDI) ve düşük molekül ağırlıklı diamin zincir uzatıcılar ile hazırlandı ve karakterize edildi. Bu çalışmadaki amaçlarımızdan biri, PDMS zincir uzunluğunun termoplastik silikon-üre (TPSU) kopolimerlerinin çekme-uzama ve yorulma özelliklerine olan etkisini anlamaktı. Kütlece üre sert kısım oranları %1,24 ile %5,14 arasında değişen kopolimerler hazırlandı. Bu kopolimerlerin, oldukça düşük sert kısım oranlarına rağmen oldukça kuvvetli film oluşturdukları ve mikro faz ayrımlı bir morfolojiye sahip oldukları gözlendi. Eşit üre miktarlarına sahip silikon-üre kopolimerleri karşılaştırıldığında, PDMS–31,500 ile hazırlanan kopolimerler, PDMS–10,800 ile hazırlananlara göre kopma anında daha yüksek kuvvet gösterdiler. Buna ek olarak, PDMS–31,500 içeren silikon-üre kopolimerlerinin, PDMS–10,800 içerenlere ve hatta kimyasal çapraz bağlı silikon kauçuklara göre daha düşük yorulma değerleri gösterdikleri gözlendi. PDMS zincirlerinin kendi kendilerine dolanmaya başladığı kritik molekül ağırlığı (M_e) 25,000 g/mol'dür. Elde ettiğimiz sonuçlar molekül ağırlığı M_e değerinin üzerinde olan PDMS oligomerlerinin silikon-üre kopolimerlerinin çekme-kopma ve yorulma davranışları üzerinde önemli bir sinerjik etkisi olduğunu göstermektedir. Bu çalışmadaki ikinci amacımız, şu ana kadar hiç çalışılmamış olan silika dolgu malzemelerinin silikon-üre kopolimerlerinin özellikleri üzerindeki etkisini incelemekti. Bu amaçla hidrofobik silika içeriği kütlece %37,5'e varan silikon-üre kopolimerleri ilk kez hazırlandı. PDMS- 31,500 bazlı silikon-üre kopolimerlerine silika dolgu malzemelerinin eklenmesi ile modül, çekme-kopma ve kopma anındaki uzama değerlerinde çok büyük artılar gözlendi. Silika ilavesini yorulma davranışlarında az da olsa olumsuz bir etkiye neden olduğu gözlendi. Silika ile termoplastik silikon-üre kopolimerleri arasındaki etkileşim FTIR spektroskopisi kullanılarak incelendi.

ACKNOWLEDGEMENTS

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NOMENCLATURE

AFM	Atomic Force Microscopy
DMA	Dynamic mechanical analysis
DMAC	Dimethylacetamide
DMF	Dimethylformamide
DYTEK A	2-Methyl-1,5-diaminopentane
E'	Storage modulus
ED	Ethylene diamine
FTIR	Foruier Transform Infrared Spectroscopy
GPC	Gel Permeation Chromatography
HMDI	Bis(4-isocyanatocyclohexyl)methane
HS	Hard segment
IPA	Isopropyl alcohol
M_n	Number average molecular weight
M_w	Weight average molecular weight
MWD	Molecular Weight Distribution
NBA	N-butylamine
NMP	N-methylpyrolidone
PDMS	Polydimethylsiloxane
PS	Polystyrene
SBS	Polystyrene-Polybutadiene-Polystyrene triblock copolymer
T	Temperature
Tan δ	Tangenet-delta (Storage modulus over loss modulus)
T_g	Glass Transition Temperature
THF	Tetrahydrofuran

TPE	Thermoplastic Elastomer
TPSU	Thermoplastic Silicone-Urea
TPU	Thermoplastic Polyurethanes
TPUU	Thermoplastic Poly(urethane urea)
TRIS	Tris(2-aminoethyl)amine

Chapter 1

A SURVEY OF SEGMENTED THERMOPLASTIC ELASTOMERS AND SILICONE-UREA COPOLYMERS

1.1 Thermoplastic Elastomers

Segmented or multiblock thermoplastic elastomers (TPE) constitute one of the most important classes of polymeric materials. Segmented thermoplastic elastomers mainly include thermoplastic polyurethanes and polyureas, polyesters and polyamides. Segmented TPEs are obtained by step-growth polymerization through the chemical combination of soft segment oligomers (T_g values well below room temperature), usually with $<M_n>$ values of 1000-3000 g/mol and short urethane, urea ester or amide hard segments along a macromolecular backbone, as schematically shown in Figure 1.1.
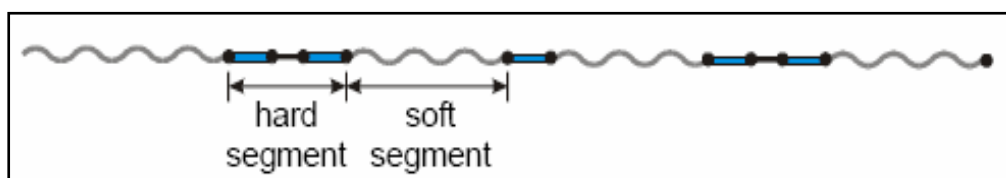
Figure 1.1: Schematic representation of a segmented copolymer [1].

Especially after the Second World War, there have been major developments in the science and technology of TPEs both in industrial and academic research laboratories. Some segmented TPEs that have been commercially available since 1950s include thermoplastic polyurethanes by Goodrich, Mobay and Upjohn under the trade names

Estane[®], Texin[®], and Pellethane[®], respectively [2]; in 1965 first segmented polyester based TPE Hytrel was commercialized by DuPont. Following the successful applications and growing use of these early products, extensive research was devoted to their further development and commercialization in 1960s and 1970s. The decade of the 1980s witnessed the growth of TPEs to maturity. TPEs combine the advantages of thermoplastics and crosslinked elastomers [1]. TPEs not only display processability at elevated temperature like thermoplastics, but also they exhibit physical properties of crosslinked rubbers such as flexibility, and elasticity [1-3].

TPEs can be divided into several groups based on their chemical structures, compositions and architectures. The largest group of TPEs consists of the ABA triblock copolymers. The second group includes segmented or multiblock copolymers. Third group of thermoplastic elastomers are based on graft copolymers, ionomers, star block copolymers and polymer blends, especially polyolefins [4].

A very common thermoplastic triblock copolymer is styrene-butadiene-styrene (SBS) copolymer, which is made of low to medium molecular weight ($<M_n>$ 30,000 to 50,000 g/mol) polystyrene (PS) end-blocks, chemically linked to a long chain of butadiene (PBd) middle block ($<M_n>$ 50,000 to 100,000 g/mol). Due to their reasonably different polarities or solubility parameters, PS and PBd are incompatible with each other. This results in microphase separation of PBd and PS, which is strongly dependent on the block lengths of each segment and percent composition. In triblock TPE elastomers polybutadiene generally forms a continuous matrix, in which polystyrene end groups act as multi-junction points (or physical crosslinks) for polybutadienes to form three-dimensional elastomeric network [5]. The microphase arrangement of SBS copolymer is schematically shown in Figure 1.2. [6]. Triblock copolymers, such as SBS, which are prepared by anionic polymerization, have

fairly narrow molecular weight distributions (MWD). Commercially important SBS and hydrogenated SBS type triblock copolymers include those marketed under Kraton®, Monprene®, and Dynaflex® trade names by various companies [4, 7].
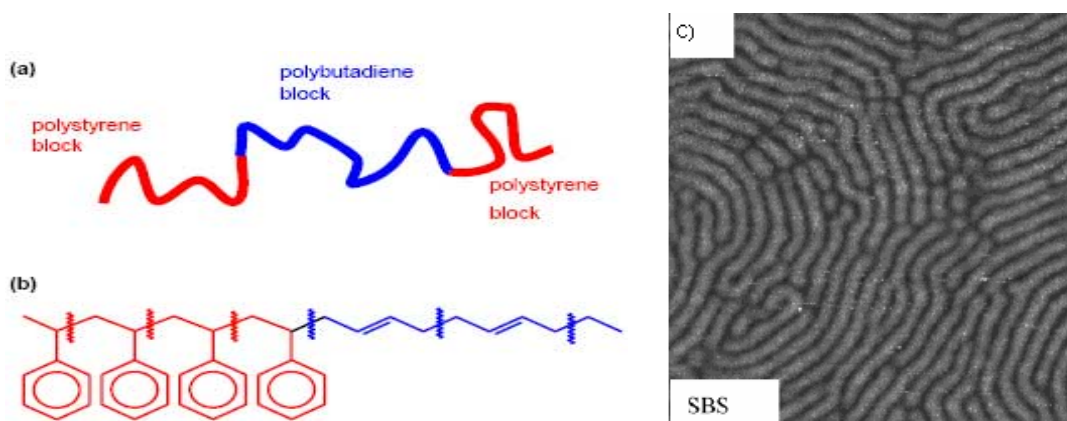
Figure 1.2. (a) A simple schematic view of the SBS block copolymer. (b) Chemical structures of the polystyrene and 1,4-polybutadiene sections. (c) AFM phase image of an SBS triblock copolymer. Dark areas correspond to polybutadiene, bright areas to polystyrene [6]. The molecular weight of the sample used here was 140,000 g/mol. PS content was percent (Image size 1 μm x 1 μm)

As shown in Figure 1.1., segmented TPEs consist of alternating flexible soft and rigid hard segments which are linked chemically together on a linear polymer backbone. The specific properties of TPEs are mainly determined by their microphase morphologies or nanostructures. At ambient temperature elastomeric or rubber-like properties is provided by the amorphous rubbery matrix which is physically crosslinked by the hard segments through hydrogen bonding and or crystallization. These physical crosslinks are reversible and are broken at higher temperatures, so the materials can easily be reprocessed. The physical crosslinks in the thermoplastic elastomers can be provided through hydrogen

bonding, microphase separation, crystallization, reversible chemical bonding, or metal complexation [8, 9, 10].

A schematic representation of the microphase separated morphology of a segmented copolymer is shown in Figure 1.3, as proposed by Cella [11].
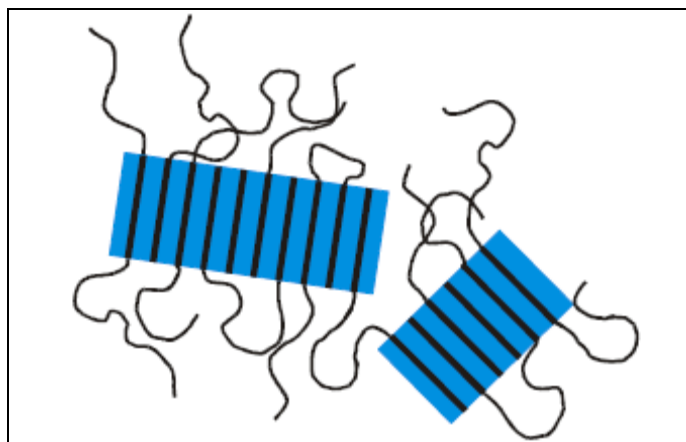
Figure 1.3. Schematic representation of the microphase morphology of a segmented block copolymer: (━) represents hard block and (~~~) represents soft block [11].

The soft segments have fairly low glass transition temperatures (T_g), usually below -50 °C, and form the flexible rubbery matrix. Hard segment domains are formed through hydrogen bonding and/or crystallization and have fairly high T_g and/or T_m values (usually between 100 and 250 °C). Hard segments provide the thermal and mechanical stability of the material, since they act as physical crosslinks. Above the glass transition temperature or melting point of the hard segment, viscous polymer is obtained, so the polymer can be

easily processed. Since the hard segments also behave like reinforcing fillers, increasing the hard segment content leads to the formation of a stiffer material.

Polymer composition, chemical structures, average molecular weights of the hard and soft segments and the hard/soft segment ratio determine the properties of thermoplastic elastomers. Segmented thermoplastic copolymers offer a much wider choice of materials and properties compared to triblock TPEs. As a result segmented copolymers find a much wider range of applications than triblock copolymers [4]. While urethane, urea, urethaneurea, amide and ester groups could be the hard segments, the soft blocks usually consist of aliphatic polyethers, aliphatic polyesters, or siloxane oligomers in segmented copolymers.

1.1.1   Segmented Thermoplastic Polyurethanes and Polyureas

Thermoplastic polyurethanes, polyureas (TPU) and polyurethaneureas (TPUU) are among a broad and important group of TPEs. TPU and TPUU are versatile polymers, which are used in a wide range of applications, such as coatings, fibers, adhesives, membranes and biomedical materials [3, 12]. Polyurethanes and polyureas are prepared through the step-growth addition reactions of diols (or glycols) and diamines with diisocyanates respectively. As shown in Figure 1.4., urethane groups are formed through the reactions of isocyanates with alcohols, whereas urea linkages are formed by the reaction of isocyanates with amines.

Urethane and urea linkages are capable of forming moderate to strong hydrogen bonding. The asymmetric urethane groups in polyurethanes develop linear hydrogen bonding, whereas the symmetric urea groups develop bidentate hydrogen bonding that

gives extra strength to the polyureas compared to the polyurethanes [13]. Hydrogen bonding between urethane and urea groups is schematically shown in Figure 1.3.
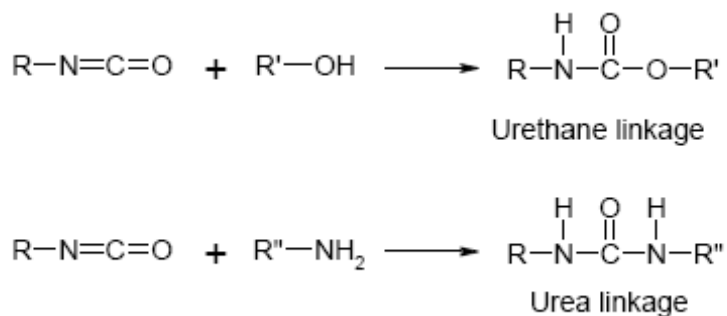
Figure 1.4. Urethane and urea formation reactions
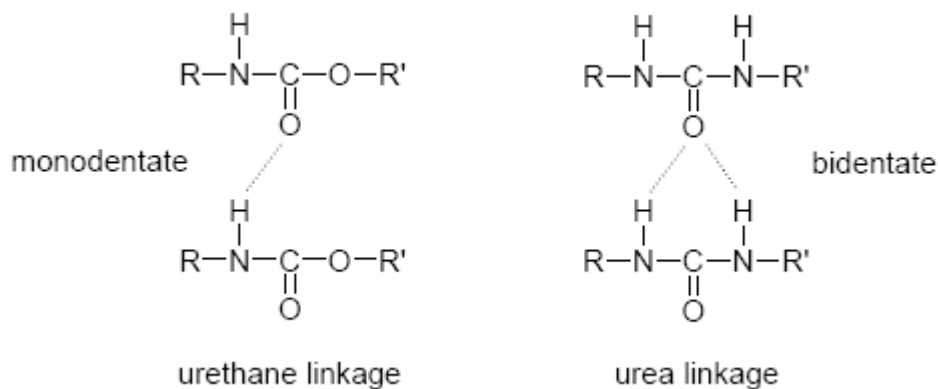
Figure 1.5. Hydrogen bonding between urethane and urea groups

As briefly explained before, the excellent mechanical and physical properties of TPUs and TPUs are due to the microphase separation. The ratio of the hard and soft segments,

type of the chain extender and molecular weight of the soft segment and also the reaction conditions determine the degree of phase separation. The physicochemical properties of TPUs and TPUUs can be modified or optimized by controlling the chemical composition, structure, molecular weight of the segments [14, 15].

1.2 Silicones and Silicone Copolymers: A brief overview

Silicones, polyorganosilicones or silicone elastomers which are composed of silicone-oxygen backbones with various alkyl substituents on the silicone [-SiRR'O-] were first commercially presented in 1940s. Silicones constitute one of the most important groups of inorganic polymers, which have a wide range of applications such as; coatings, insulators, biomaterials, surfactants, semi-permeable membranes, etc. "Siloxane" is a more scientific term than "silicone" to describe the Si-O backbone, which is partly ionic [16]. The most common and interesting silicone elastomers are poly(dimethylsiloxane) (PDMS) [-Si(CH$_3$)$_2$O-] based elastomers. Physical and chemical characteristics of siloxane bonds (Si-O) constitute the unique properties of polysiloxanes [17-19]. PDMS have weak secondary interactions, therefore it has an extremely low T$_g$ (-125 °C) compared to all other polymers. High gas permeability and low surface energy of PDMS are two other important properties for its commercial applications. Other important and unique properties of silicones include high thermal, UV and oxidative stability, hydrophobicity and biocompatibility.

The critical molecular weight, M$_e$ between entanglements for PDMS, is reported to be between 24,000 and 34,000 g/mol by different methods [20]. However, due to very weak intermolecular interactions and extremely low T$_g$, PDMS polymers do not display any mechanical integrity even at molecular weights up to 500,000 g/mol. Thus, in many

engineering applications, in order to utilize the unique properties of PDMS, extremely high polymer molecular weights are needed to reach reasonable mechanical properties. This obviously creates extremely high viscosities. Therefore, in commercial applications PDMS is always used by adding large amounts of silica fillers and chemically crosslinking the PDMS chains by using various methods.

Another feasible method to improve the mechanical properties of PDMS in order to use it in various applications, without crosslinking, is the preparation of block or segmented copolymers with other organic polymers as described by Yilgor and McGrath [16, 17, 21]. Due to its very low solubility parameter, PDMS is incompatible with most organic polymers. This gives rise to excellent microphase separation in PDMS containing copolymers, where PDMS forms the continuous matrix with organic segments forming the domains. These copolymers display good mechanical properties due to the presence of organic blocks or segments, together with the unique combination of properties of PDMS.

Preparation of segmented copolymers with end functionalized telechelic PDMS oligomers as the soft segment and polyurea, polyurethane, polycarbonate, polyacrylate, polysulfone, polystyrene, polyamide, polyimide as the hard segments have been reported in the literature [16, 22-31]. Commercially available PDMS copolymers include segmented polyurethanes, polyureas, polyesters and polycarbonates. Polyurethanes were synthesized in early 1980s, which utilized end functionalized PDMS as the only soft segment component. Mechanical properties of these copolymers were reported to be inferior compared to polyester or polyether based systems [32, 33]. The inferior performance of the copolymers was caused by their low molecular weights, due to the end-group stability problems of the starting hydroxyporpyl and hydroxybutyl terminated PDMS oligomers [30]. Yilgor et al., were able to synthesize sufficiently high molecular weight silicone-

urethanes by using α,ω−hydroxyhexyl terminated PDMS oligomers of $<M_n>$ 2300 g/mol, a cycloaliphatic diisocyanate and a diol chain extender in MEK, where DMF was utilized as a co-solvent in the chain extension step of the two-step polymerization process [30].

1.3.   Silicone-urea copolymers

Among a large number of PDMS containing segmented copolymers discussed in the literature [16, 17, 21-33] Yilgor and co-workers were the first to report the preparation of silicone-urea copolymers with excellent mechanical properties [33]. These copolymers were obtained by the stoichiometric reactions between amine terminated PDMS oligomers and various diisocyanates in ether type solvents, without using any chain extenders.

Silicone-urea copolymers, which are made of extremely non-polar and flexible polydimethylsiloxane (PDMS) soft segments and very polar and strongly hydrogen bonding urea hard segments are very interesting materials. They display unique combination of properties, such as, excellent low temperature flexibility, high UV and oxidative stability, low surface energy, high gas permeability, good electrical, thermal and mechanical properties and physiological inertness or biocompatibility [16, 34]. PDMS soft segments have very low solubility parameters of 15.6 $(J/cm^3)^{1/2}$ or 7.6 $(cal/cm^3)^{1/2}$. As a result they show almost complete microphase separation from the urea hard segments, which have solubility parameters around 45.6 $(J/cm^3)^{1/2}$ or 22.3 $(cal/cm^3)^{1/2}$ [32, 35]. This leads to very strong hydrogen bonding in the urea hard segments and excellent mechanical properties in silicone-urea copolymers.

It was shown that mechanical properties of non-chain extended PDMS based thermoplastic segmented polyurea copolymers was as good or better than silica filled

crosslinked PDMS elastomers [36]. Tensile properties of silicone-urea copolymers obtained by the stoichiometric reactions between amine terminated PDMS oligomers and diisocyanates were mainly governed by the type of the diisocyanate used, block lengths of PDMS soft segments and the resultant urea hard segment content of the copolymer [4].

Although it was fairly easy to synthesize non-chain extended silicone-urea copolymers, preparation of diamine chain extended, high molecular weight silicone-urea copolymers with good mechanical properties has not been reported until very recently [31]. The main problem for the synthesis of chain extended silicone-urea copolymers has been the selection of the proper solvent or solvent combination. In silicone-urea polymerization reactions, when no chain extenders are used, tetrahydrofuran (THF) or other ether type solvents are suitable for the preparation of high molecular weight copolymers [17, 32, 33]. THF is also a good solvent for the prepolymer formation reaction. However, when a diamine chain extender is used, a highly polar co-solvent is needed to keep the silicone-urea copolymer from prematurely precipitating out of solution. Dimethylformamide (DMF), dimethylacetamide (DMAC), and N-methylpyrolidone (NMP) are used as polar co-solvents to serve for this purpose. Although DMF, DMAC and NMP are good solvents for urea hard segments they are poor solvents for PDMS [16, 37]. Therefore, they usually lead to the formation of low molecular weight polymers with poor mechanical properties [16, 21].

Recently an unusual polymerization solvent was discovered by Yilgor and co-workers to overcome this problem [31]. They employed isopropyl alcohol (IPA) as the only solvent or a co-solvent for the preparation of aliphatic isocyanate based silicone-urea copolymers chain extended with large amounts of various diamines [31, 38, 39]. Alcohols are usually not considered as reaction solvents for polyurethane or polyurea formation reactions since

they react with diisocyanates to form urethane groups. However, for aliphatic isocyanates it has been shown that the reactivity of (NCO) group with the secondary (OH) group on IPA was much slower than its reaction with primary amine (NH_2) groups at room temperature [31, 38, 39].

As indicated before, the mechanical properties of crosslinked silicone elastomers can be improved by the addition of silica fillers. For microphase separated silicone-urea copolymers strength of the hydrogen bonding between urea hard segments determines the mechanical properties of the material, so in general there is no need to fill these copolymers with silica. It is also thought that incorporation of silica fillers to silicone-urea copolymers may decrease the strength of the copolymers because of the interaction of silica fillers with urea hard segments, which may disrupt the hydrogen bonding.

In this thesis our aim was to design, synthesize and characterize linear, thermoplastic polydimethylsiloxane-urea copolymers based on very high molecular weight amine terminated PDMS oligomers, aliphatic diisocyanates and diamine chain extenders. Our main emphasis was to study and compare the effect of system variables such as PDMS block length, structure of the chain extender, and urea hard segment content on the mechanical properties silicone-urea copolymers. In addition for the first time, we also investigated the influence of silica fillers on the tensile properties of silicone-urea copolymers.

This work can be divided into four sub-sections each of which explores a specific aspect of the silicone-urea copolymers. These are:

(i)   Investigation of the influence of reaction solvent and concentration of the reaction medium on the average molecular weight of the silicone-urea copolymers formed,

(ii)   Preparation of silicone-urea copolymers based on high molecular weight ($<M_n>$ 10,800 and 31,500 g/mol) PDMS oligomers and different chain extenders. Investigation of the influence of the structure of the chain extender and urea hard segment content on the tensile properties,

(iii)   Influence of the type and amount of silica fillers on tensile properties of silicone-urea copolymers,

(iv)   Investigation of the antibacterial properties of norfloxacin modified silicone-urea copolymers.

Chapter 2

EXPERIMENTAL

2.1. Materials Used

1,6-Hexamethylene diisocyanate (HDI) and bis(4-isocyanatocyclohexyl)methane (HMDI) were kindly supplied by Bayer, Germany. They were used as received. Purities of diisocyanates were higher than 99.5% as determined by the dibutylamine back titration method. α,ω-Aminopropyl terminated PDMS oligomers (PDMS-NH$_2$) with <M$_n$> values of 3,200, 10,800 and 31,500 g/mol were kindly provided by Wacker-Chemie, Germany. Molecular weights of PDMS-NH$_2$ were determined by end group titration with standard HCl in isopropyl alcohol solution. Tris(2-aminoethyl)amine (TRIS) was purchased from Aldrich. 2-Methyl-1,5-diaminopentane (DYTEK A) (DuPont), N-butylamine (NBA) (Aldrich), ethylene diamine (ED) (Aldrich), norfloxacin (NF) (Aldrich) were also used as received. Reagent grade isopropyl alcohol (IPA) (Merck), tetrahydrofuran (THF) (Merck), dimethylformamide (DMF) (LaChema), chloroform (LaChema) were used as reaction solvents without further purification. Pyrogenic amorphous silica fillers, HDK H2000 (hydrophobic) and HDK N20 (hydrophilic) were also kindly provided by Wacker Chemie. Particle sizes of these fillers are in 10-20 nm range [41] and have reported surface areas of 200±30 m^2/g.

Chemical structures of the monomers, oligomers and end-blockers are provided in Table 2.1.

Table 2.1. Chemical structures of reactants used in the synthetic studies

$$OCN-\text{(cyclohexyl)}-CH_2-\text{(cyclohexyl)}-NCO$$

HMDI

$$OCN-(CH_2)_6-NCO$$

HDI

PDMS

TRIS

DYTEK A

NORFLOXACIN
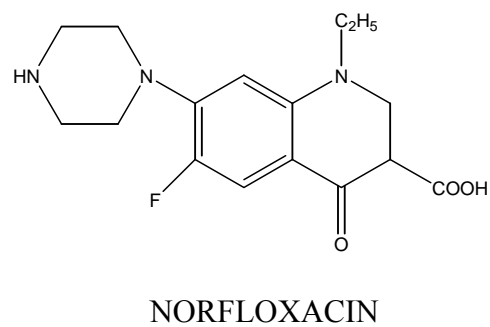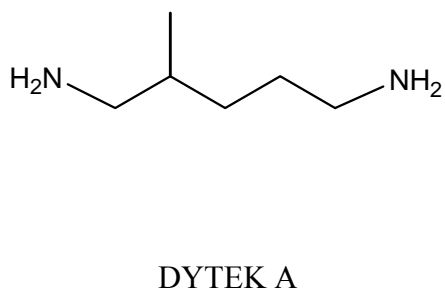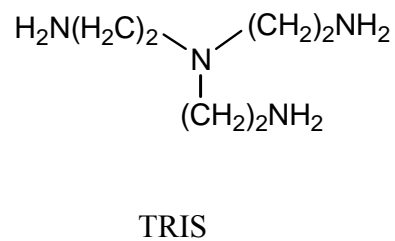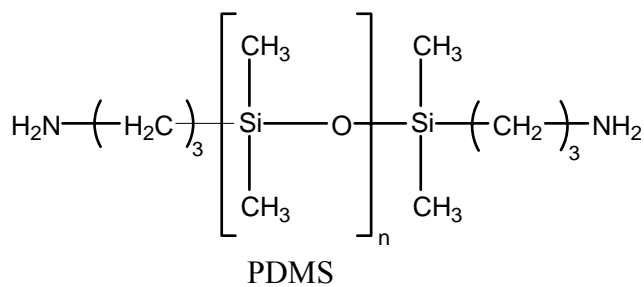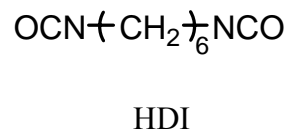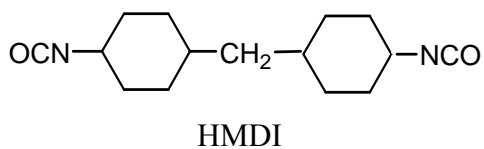
2.2. Polymer synthesis

All reactions were carried out in 250 mL, three-neck, round bottom Pyrex flasks equipped with an overhead stirrer and an addition funnel. Reactions were conducted at

room temperature. Reactions were performed by the dropwise addition of one reactant into the other in the reactor, under strong agitation. All reactions were followed by FTIR spectroscopy by monitoring the disappearance of strong isocyanate absorption peak and the formation of (N-H) and (C=O) peaks of the urea groups formed.

2.2.1. Investigation of the influence of reaction solvent and concentration of the reaction medium on the average molecular weight of the silicone-urea copolymers

In this study PDMS based segmented polyureas were synthesized through the stoichiometric reactions of HMDI and PDMS-3,200 in THF, IPA and chloroform at 10, 20 and 30% solids content. Desired amount of diisocyanate (HMDI) was weighed into the reaction vessel and dissolved in the reaction solvent at desired concentration. Stoichiometric amount of PDMS oligomer was weighed into a beaker, dissolved in the reaction solvent at the same concentration as the diisocyanate, introduced into an addition funnel and added into the reactor dropwise under strong agitation.

2.2.2. Preparation of chain extended, segmented silicone-urea copolymers

In these studies IPA and THF were used as co-solvents. Concentration of the reaction medium varied between 10-30% solids depending on the PDMS molecular weight and the urea hard segment content of the copolymer prepared. HMDI was dissolved in IPA in the reactor. Desired amount of PDMS oligomers was dissolved in IPA+THF separately and introduced into the addition funnel and added dropwise onto the HMDI solution under strong agitation. After the prepolymer was formed, stoichiometric amounts of low molecular weight diamines such as ethylene diamine or 2-methyl-1,5-diaminopentane were used as chain extender. Chain extenders were dissolved in IPA, introduced into the addition

funnel and added dropwise onto the prepolymer solution in the reactor. Reactions were followed by FTIR by monitoring the disappearance of strong isocyanate absorption peak around 2265 cm^{-1}.

2.2.3. Preparation of segmented hyperbranched polyureas

Oligomeric A_2 and B_3 approach was used during the preparation of hyperbranched polyureas, where isocyanate terminated PDMS was the oligomeric A_2. To prepare A_2, HMDI was weighed into the reactor and dissolved in IPA. Desired amount of PDMS oligomer was weighed into a beaker, dissolved in IPA+THF mixture, introduced into the addition funnel and added dropwise onto the HMDI solution. A molar ratio of [HMDI]/[PDMS]=2.0 was always used in oligomeric A_2 preparation. After the preparation of A_2, calculated amount of TRIS (B_3) was dissolved in IPA and introduced into the addition funnel. TRIS solution was added dropwise onto the oligomeric A_2 solution under strong agitation. Molar ratio of [B_3] to [A_2] was 0.55 during the reactions. Concentration of the reaction medium was kept around 10% solids to prevent gelation. Excess isocyanate end groups were capped with NBA. Completion of the reactions was again determined by monitoring the disappearance of the strong isocyanate absorption peak at 2265 cm^{-1} with the FTIR spectrometer.

2.2.4. Preparation of segmented silicone-urea copolymers containing norfloxacin

2.2.4.1. Linear silicone-urea copolymers with norfloxacin end groups

Norfloxacin is a well known antibacterial which also has reactive amine and carboxylic acid groups as shown on Table 2.1. Both of these groups can react with isocyanate, amine

group reacting faster than carboxylic acid group. As a result we wanted to incorporate norfloxacin as end groups to linear and hyperbranched polyureas with the aim of preparing polymers that may display antimicrobial properties. For this purpose first an isocyanate terminated PDMS prepolymer was prepared as discussed in 2.2.2., with a molar ratio of [HMDI]/[PDMS]=2.0 After the prepolymer was formed, stoichiometric amount of norfloxacin was dissolved in DMF and introduced into the addition funnel. Solution was added dropwise onto the prepolymer in the reactor. Reactions were again followed by FTIR by monitoring the complete disappearance of the isocyanate absorption.

2.2.4.2. Norfloxacin terminated hyperbranced silicone-urea copolymers

Since hyperbranched polymers contain very large number of end groups we thought they could display more effective antimicrobial properties if the end groups were capped with norfloxacin. Preparation of hyperbranched silicone-urea copolymers with isocyanate end groups has already been described in 2.2.3. To end cap the isocyanate terminated hyperbranched copolymer, stoichiometric amount of norfloxacin was dissolved in DMF, introduced into the addition funnel and slowly added into the reaction mixture at room temperature. Additions were continued until the complete disappearance of the isocyanate peak in FTIR spectrum.

2.2.5. Preparation of silica filled silicone-urea copolymers

PDMS-31,500, HMDI and Dytek A (as the chain extender), are used to synthesize the base polymer for silica filled systems. After the copolymer synthesis using the reaction procedure given in 2.2.2., calculated amounts of HDK H2000 (hydrophobic silica) was added into the polymer solution. Mixture was stirred for 12 hours at room temperatures to

obtain homogeneous distribution of silica in polymer solution. The solution was then poured into Teflon molds and placed in oven at 55 ^{o}C to evaporate the solvent. After reaching the constant weight molds were removed from the oven. Silica filled polymer films were peeled off the Teflon molds and stored in a sealed polyethylene bag at room temperature until further testing.

2.3. Instrumentation

FTIR spectra were recorded on a Nicolet Impact 400D FTIR spectrometer using solution cast films on KBr discs. 20 Scans were taken for each spectrum with a resolution of 2 cm^{-1}. Omnic 6.0 software was used to analyze the spectral data obtained.

Gel permeation chromatography curves of polymers were obtained on an Agilent 1100 GPC apparatus equipped with a refractive index detector and PLgel 3 μm mixed-E columns. The system was calibrated by using polystyrene standards. Samples were prepared in tetrahydrofuran (THF). Chromatograms were obtained with a flow rate of 1 mL/min at 23 ^{o}C.

Stress-strain tests were performed on an Instron model 4411 tester, controlled by Series IX software. Dog-bone shaped specimens (ASTM D 1708) were cut from solution cast films. Tests were conducted at room temperature with a 25.0 mm/min cross-head speed. For each polymer at least three samples were tested and average values of Young's modulus, ultimate tensile strength and elongation at break values were obtained. For tensile tests polymer films with final thicknesses of 0.3-0.5 mm were cast into Teflon molds from solution and kept at room temperature overnight to slowly evaporate the solvent. Then they

were transferred into a 55 °C air oven and kept there until the solvent is completely removed and the films reached to constant weight.

Hysteresis tests were also performed on the Instron model 4411 tester. Original sample length (L_o) was 24.0 mm and samples were stretched and released with a 25.0 mm/min cross-head speed. 10 Cycle hysteresis behavior of the materials were investigated by stretching them to 300% elongation.

TA model Q800 instrument was used for dynamic mechanical analysis (DMA). The specimens were cut from solution cast films described above. Measurements were performed at tensile mode, between -150 and 250 ^{o}C. The frequency was 1 Hz and the heating rate was 3 ^{o}C/min. Tests were carried out under dry nitrogen atmosphere. Tan δ and storage modulus, E', values were obtained under tension.

2.4. Antimicrobial Testing

Kirby-Bauer test method was used for testing the antibacterial activity of polymers. After preparation of agar solution, agar plates were inoculated with bacterial broth. A sterile glass rod was used to distribute agar on the surface of plates. The surface of the agar gel medium was inoculated with a suspension of a 24 hour culture of *E. Coli* containing about 10^4 cells/mL after dilution with a sterile dH_2O solution. Polymer films were placed in the plates and plates were incubated at 37 ^{o}C for 18 hours.

After 18 hours of incubation each plate were examined and inhibition zones were measured.

Chapter 3

Results and Discussion

In this study various aspects of silicone-urea copolymer synthesis and physicochemical characterization of the copolymers were investigated. A major achievement of this study is the preparation of silicone-urea copolymers using extremely high molecular weight amine terminated PDMS oligomers (M_n=31,500 g/mol), which displayed hysteresis behavior superior to that of crosslinked silicone rubber. As explained before this work can be divided into four sub-sections each of which explores a specific aspect of silicone-urea copolymers. These are:

i) Investigation of the influence of reaction solvent and concentration of reaction medium on the average molecular weight of silicone-urea copolymers,

ii) Preparation of silicone-urea copolymers based on unusually high molecular weight ($<M_n>$ 10,800 and 31,500 g/mol) PDMS oligomers and different chain extenders. Investigation of the influence of the structure of the chain extender and urea hard segment content on the tensile properties,

iii) Influence of the type and amount of silica fillers on the tensile properties of silicone-urea copolymers, and,

iv) Investigation of the antibacterial properties of norfloxacin modified silicone-urea copolymers.

3.1.   Investigation of the influence of reaction variables on the average molecular weight and the properties of the silicone-urea copolymers

During step-growth polymerization reactions of linear or hyperbranched polymers, in addition to the formation of high molecular weight polymer chains, cyclic species with different ring sizes also form due to the well known "cage effect". These phenomena have been comprehensively described by Kricheldorf [42,43] for linear polymers and Yilgor and Long for hyperbranched systems [44]. Extent of cyclization in polycondensation reactions is also closely related to the concentration of the reaction medium. Generally higher amounts of cyclic species will be forming as the concentration of the reaction medium becomes more dilute. The type and polarity (or the solubility parameter) of the reaction solvent also play an important role on the molecular weight of the polymer and the amount and size of the cyclic species formed during the reactions. Poor solvents also lead to the premature coagulation of the polymer formed, thus leading to the formation of only low molecular species.

Therefore, in this part of the study our main aims were; (1) to investigate the effect of reaction solvent and the concentration of the reaction medium on the average molecular weight of the linear silicone-urea polymers obtained and (2) to determine the amount and average sizes of the cyclic species formed. For this purpose silicone-urea copolymers were prepared through the stoichiometric reactions of aminopropyl terminated PDMS oligomers with a number average molecular weight of 3,200 g/mol and HMDI following the procedure described in section 2.2.1. Three different solvents; isopropyl alcohol (IPA), tetrahydrofuran (THF) and chloroform (CHCl$_3$) were used for these reactions, which were performed at two different concentrations of 10% and 30% by mass of solids. In order to determine the reproducibility, each reaction was performed at least twice.

FTIR spectra were taken at different stages of the reaction. Representative transmission FTIR spectra of PDMS-3200 oligomer (blue), and after half-addition (red) and complete addition (purple) of PDMS onto the HMDI are provided in Figure 3.1. Blue spectrum is for PDMS-3200, which shows strong Si-O-Si (siloxane) doublet between 1000 and 1100 cm^{-1}. Red spectrum was taken after 50% of the PDMS was added onto the HMDI, where a very strong isocyanate absorption peak at 2265 cm^{-1} due to HMDI and the Si-O-Si doublet at 1000 and 1100 cm^{-1} due to PDMS can clearly be seen. There are also well defined peaks due to the formation of urea (-HN-C(O)-NH-) linkages. The broad N-H absorption is between 3420 and 3230 cm^{-1} with peak maxima at 3335 cm^{-1}, typical for hydrogen bonded urea groups.
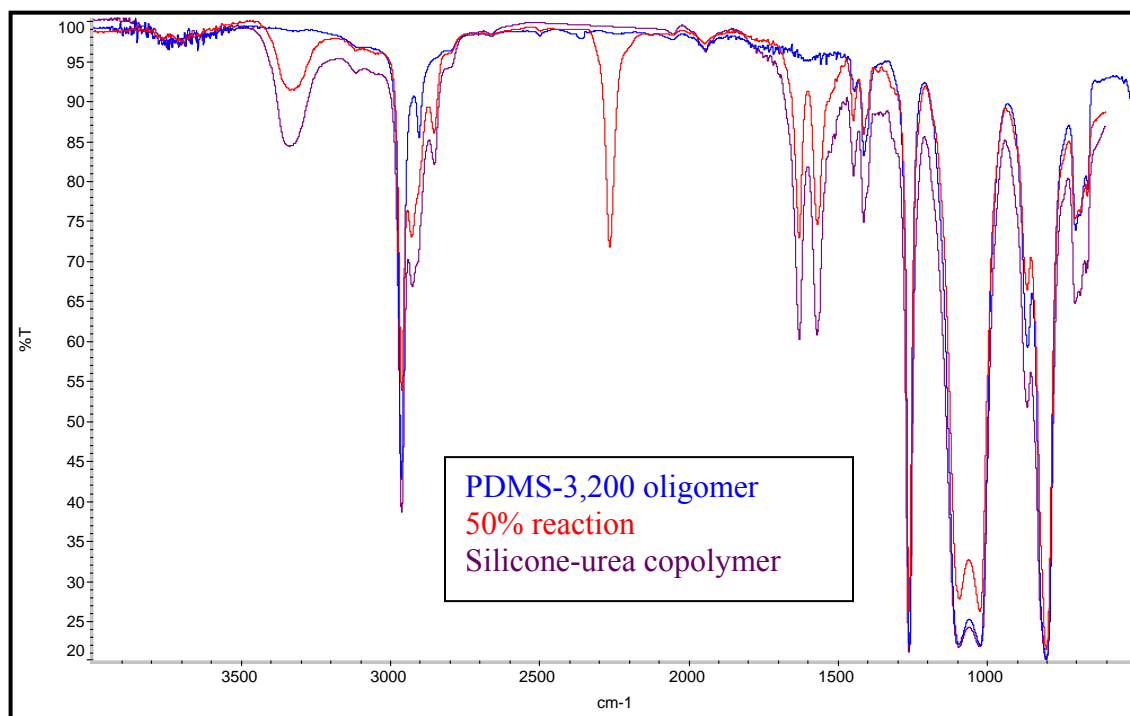
Figure 3.1. FTIR spectra of the PDMS-3200 and products at various stages of the reaction in the formation of silicone-urea copolymer from PDMS-3200 and HMDI

Two well-defined, sharp peaks in 1700-1500 range due to strongly hydrogen bonded C=O and N-C-O stretching with peak maxima at 1630 and 1571 cm^{-1}, respectively, are also clearly visible. Upon complete addition of PDMS, isocyanate peak disappears (purple spectrum). Urea peaks at 3335, 1630 and 1571 cm^{-1} become stronger. The siloxane doublet at 1000-1100 cm^{-1} is also present, clearly indicating the formation of silicone-urea copolymer.

Average molecular weight and molecular weight distributions of silicone-urea copolymers produced were determined by GPC using a calibration curve obtained using polystyrene (PS) standards, in THF. Since PDMS segments have low specific refractive index change with concentration (dn/dc) in THF, higher concentrations of silicone-urea copolymer solutions (up to 5 mg/cm^3) were used to obtain a strong signal. Comparative GPC curves for silicone-urea copolymers synthesized in CHCl$_3$, THF and IPA at 30% solids content are reproduced in Figure 3.2-a. GPC curves for THF polymerizations at 10 and 30% are also provided in Figure 3.2-b, for comparison. As can be seen from Figure 3.2-a and 3.2-b, all GPC curves are unimodal and symmetrical, indicating normal molecular weight distributions for all polymers. No peaks are observed at the low molecular weight end of the GPC curves, which is an indication of the absence of side products such as cyclic species, within the detection range of the GPC system used. This is not in agreement with the formation of cyclic species predicted by Kricheldorf in linear step-growth polymerization reactions [42,43]. As explained below, we believe this is directly related to the polymerization procedure followed in our studies compared to the procedure used in conventional polycondensation or step-growth polymerization reactions.

Conventionally, during the preparation of linear polymers using step-growth polymerization reactions, all reactants (such as A-A and B-B) are mixed in equimolar
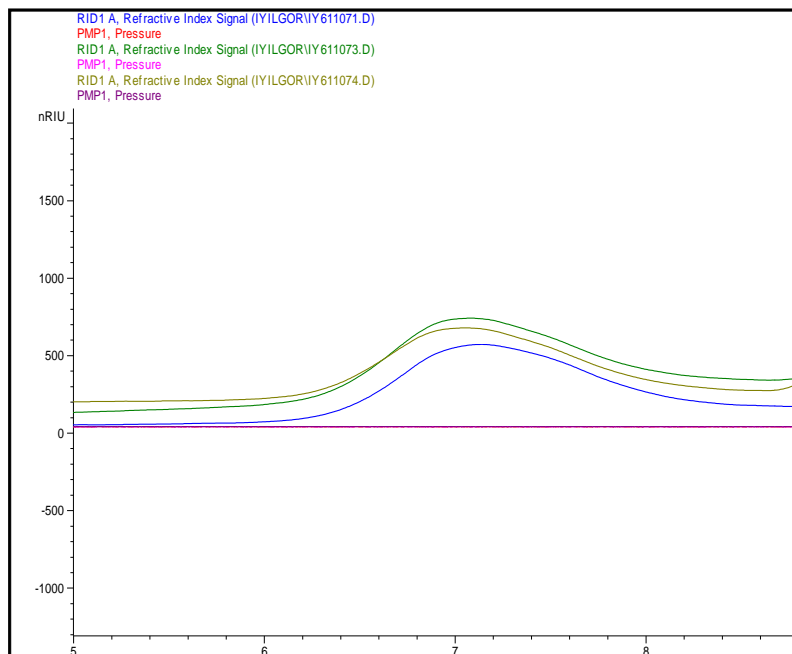
Figure 3.2-a. GPC chromatograms of silicone-urea copolymers synthesized in THF (green, top curve), chloroform (brown, middle curve),) and IPA (blue, bottom curve), all at a reaction medium concentration of 30% solids.

amounts in the reactor and reacted. As the reaction proceeds dimers, trimers and eventually oligomers with general repeat unit structure of B—(A—A—B—B)$_x$—A are formed, where (x) denotes the average number of repeat unit. Since equimolar amounts of each monomer are used, on the average one end of the growing chain is formed of (A) functionality and the other end of (B) functionality. At high conversions and dilute solutions, the probability of the (A) and (B) groups at the end of the same chain, to react with each other is fairly high, which leads to the formation of cyclic species. Nature of the reaction solvent (i. e. whether it is a good or poor solvent) may also play an important role in the extent of cyclization. -

In our system where we prepare the silicone-urea copolymers by the dropwise addition of the one reactant (A-A) (the PDMS-NH$_2$) onto the other reactant (B-B) (diisocyanate) in the reactor, we always have an excess of the (B-B) in the reactor. This means that growing chains are always terminated with (B) functionality. Since (B) groups cannot react with each other, formation of cyclic species is prevented when polymerization is performed by the dropwise addition of one reactant onto the other.
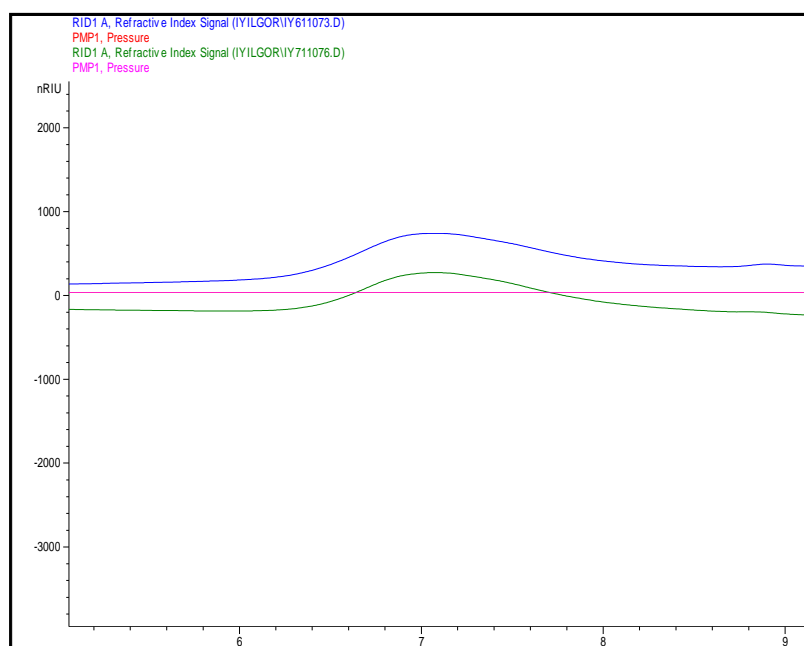
Figure 3.2-b. GPC curves of silicone-urea copolymers prepared in THF at 10% solids (green curve) and 30% solids (blue curve)

A summary of the results obtained from the analysis of the GPC data for all reactions is provided on Table 3.1, where average molecular weight and molecular weight distribution of silicone-urea copolymers as a function of reaction solvent (CHCl$_3$, THF, IPA) and concentration of the reaction medium (10 and 30% solids by weight) are provided. When

Table 3.1 is closely examined it is observed that in general $<M_n>$ values are between 13,000 and 17,000 g/mol range, whereas $<M_w>$ values are around 35,000 g/mol. Polydispersity index (or heterogeneity index) (PDI) values ($<M_w>/<M_n>$) are generally around 2.3, which is slightly higher than that predicted by step-growth theory.   Since polystyrene standards are used and its hydrodynamic behavior is different than silicone-urea systems, the molecular weight values are not absolute for silicone-urea copolymers. However, the trend indicates that the reaction solvent or the concentration of the reaction medium has no significant effect on $<M_n>$ or $<M_w>$ values and as a result also on the molecular weight distribution of the silicone-urea copolymers prepared by the slow addition of PDMS onto HMDI.

Table 3.1. Average molecular weights and molecular weight distributions of silicone-urea copolymers prepared in different solvents and concentrations

Code	Component	Rxn Solvent	Ratio	Rxn Conc. (%w)	$<Mn>$ g/mol	$<Mw>$ g/mol	PDI (Mw/Mn)
PSU1	PDMS 3,200/HMDI	IPA	(1:1)	10.0	15,300	33,500	2.19
PSU2	PDMS 3,200/HMDI	IPA	(1:1)	30.0	14,400	34,000	2.36
PSU3	PDMS 3,200/HMDI	IPA	(1:1)	30.3	15,000	36,000	2.40
PSU4	PDMS 3,200/HMDI	THF	(1:1)	10.0	13,000	33,500	2.58
PSU5	PDMS 3,200/HMDI	THF	(1:1)	14.9	15,000	34,000	2.27
PSU6	PDMS 3,200/HMDI	THF	(1:1)	32.3	16,000	37,000	2.31
PSU7	PDMS 3,200/HMDI	$CHCl_3$	(1:1)	9.7	13,000	30,500	2.35
PSU8	PDMS 3,200/HMDI	$CHCl_3$	(1:1)	10.0	15,000	35,000	2.33
PSU9	PDMS 3,200/HMDI	$CHCl_3$	(1:1)	15.0	17,000	32,000	1.88
PSU10	PDMS 3,200/HMDI	$CHCl_3$	(1:1)	25.4	17,000	39,000	2.29
PSU11	PDMS 3,200/HMDI	$CHCl_3$	(1:1)	26.4	15,000	33,500	2.23

3.2. Preparation of silicone-urea copolymers based on high molecular weight PDMS oligomers and different chain extenders

In this part of the study two different molecular weight PDMS oligomers were used in order to understand the influence of PDMS segment molecular weight on the tensile properties of the polymers. For this purpose silicone-urea copolymers were prepared using aminopropyl terminated PDMS oligomers with $<M_n>$ values of 10,800 and 31,500 g/mol. Diisocyanate used was HMDI. Two different diamines were used as chain extenders, which were ethylene diamine (ED) and 2-methyl-1,5-diaminopentane (DYTEK A). The importance of this work lies in the fact that critical entanglement molecular weight of PDMS is reported to be 24,500 g/mol and 34,000 g/mol [45,46]. If we assume the lower value to be correct, PDMS-31,500 is above this value, whereas PDMS-10,800 is below it. Therefore, the influence of soft segment entanglement on polymer properties, such as modulus-temperature behavior and tensile properties can be determined.

In order to ensure reproducibility, each polymer was synthesized at least twice, under the same reaction conditions. Polymerization reactions were performed according to the procedure given in section 2.2.2. Chemical compositions of silicone-urea copolymers synthesized using PDMS-10,800 and PDMS-31,500 oligomers and ED as the chain extender are provided on Table 3.2. Reaction solutions were crystal clear throughout the polymerization reactions. Interestingly, all of these silicone-urea copolymers displayed on Table 3.2., have very low hard segment contents, but they form nice solid films with good mechanical integrity. The abbreviation used to identify the copolymers was as follows: PSU indicates the silicone-urea copolymer; following number indicates M_n value of PDMS in g/mole; following two numbers urea hard segment content of the copolymer in weight percent and the final letter indicates the chain extender used (E = ED, D = DYTEK A). For

example PDMS-10,800, HMDI and DYTEK A based silicone-urea copolymer with 7.75% by weight hard segment content was coded as: PSU-10,800-7.8D. Stress-strain tests of the copolymers listed on Table 3.2 were investigated and the results are provided on Table 3.3.

Table 3.2. Chemical compositions of silicone-urea copolymers based on
PDMS-10,800 and PDMS-31,500
*[PDMS]/[HMDI]/[ED] ratio used during synthesis

Polymer Code	PDMS (M_n) (g/mol)	Chain Extender	Molar composition*	HS Content (wt%)
PSU-10,800-3.8E	10,800	ED	1.0/1.5/0.5	3.77
PSU-10,800-5.1E	10,800	ED	1.0/2.0/1.0	5.14
PSU-10,800-7.8E	10,800	ED	1.0/3.0/2.0	7.75
PSU-31,500-1.8E	31,500	ED	1.0/2.0/1.0	1.82
PSU-31,500-2.8E	31,500	ED	1.0/3.0/2.0	2.80
PSU-31,500-3.7E	31,500	ED	1.0/4.0/3.0	3.73
PSU-31,500-4.7E	31,500	ED	1.0/5.0/4.0	4.70

Table 3.3. Tensile properties of silicone-urea copolymers based on
PDMS-10,800 and PDMS-31,500 and chain extended with ED

Polymer Code	HS Content (wt%)	Modulus (MPa)	Tensile Str. (MPa)	Elongation (%)
PSU-10,800-3.8E	3.77	0.95	1.10	270
PSU-10,800-5.1E	5.14	1.10	1.40	210
PSU-10,800-7.8E	7.75	1.60	2.10	230
PSU-31,500-1.8E	1.82	0.50	0.80	400
PSU-31,500-2.8E	2.80	0.60	1.25	350
PSU-31,500-3.7E	3.73	0.75	2.00	450
PSU-31,500-4.7E	4.70	0.90	2.20	500

As can be seen on Table 3.3., there is a nice, increasing trend in the modulus and tensile strengths of both PDMS-10,800 and PDMS-31,500 based silicone-urea copolymers as a function of the urea hard segment content of the system. This is an expected behavior. Presence of a linear relationship between urea content and ultimate tensile strengths of silicone-urea copolymers has already been reported by Yilgor and co-workers for silicone urea copolymers based on PDMS oligomers with M_n values between 900 and 7000 g/mol [14]. Elongation at break values for PDMS-31,500 based copolymers are much higher that those of PDMS-10,800 containing copolymers, which is also expected.

In this study one of our goals was to demonstrate the presence of a similar relationship for copolymers prepared from PDMS oligomers with very high molecular weights. The other, more important goal was to find out if there is any influence of the entanglements in PDMS soft segments on the tensile properties of silicone–urea copolymers.

For this purpose we plotted the ultimate tensile strengths of silicone-urea copolymers as a function of urea hard segment content separately for PDMS-10,800 and PDMS-31,500 based copolymers in Figure 3.3. It is clear that a linear relationship exists between the tensile strength and urea content for both polymers. More interestingly, the slope of the line for PDMS-31,500 based silicone-urea copolymers is much higher than that of PDMS-10,800 based systems. We believe this clearly demonstrates that in addition to the strong hydrogen bonding between urea hard segments, chain entanglements in PDMS have a synergistic effect and improves the tensile strength of silicone-urea copolymers. We believe this is the first report on the existence of such a synergistic effect of soft segment entanglements on tensile strength in segmented silicone-urea copolymers.
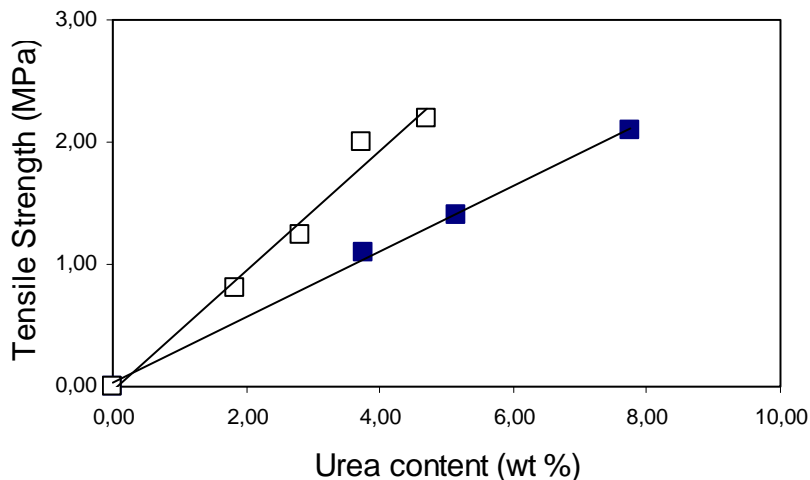
Figure 3.3. Relationship between ultimate tensile strength and urea hard segment content of silicone-urea copolymers based on PDMS-10,800 (■) and PDMS-31,500 (□) chain extended with ED

3.3. Influence of the structure of the chain extender on tensile properties of silicone-urea copolymers based on PDMS-10,800 and PDMS-31,500

It is well known that due to significant differences in the polarities of PDMS and urea groups, silicone-urea copolymers display excellent microphase separation between hard and soft segments. As a result it is not expected to have a major influence of the structure and symmetry of the diamine chain extender on the microphase morphology and physicochemical properties of these systems. In order to investigate this phenomena silicone-urea copolymers were prepared by using PDMS-31,500, HMDI and two different diamine chain extenders, which were ethylene diamine (ED) and 2-methyl-1,5-

diaminopentane (Dytek A). ED is a small and symmetric chain extender, whereas Dytek A is somewhat longer and unsymmetrical.

Chemical compositions of silicone-urea copolymers based on ED and Dytek A chain extenders are provided in Table 3.4. Due to major difference between the molecular weights of ED (60.12 g) and Dytek A (116.2 g) there seems to be a major difference in the hard segment content by weight although the molar compositions are the same.

Table 3.4. Chemical compositions of silicone-urea copolymers based on PDMS-31,500, HMDI and ED or Dytek A chain extender. (*[PDMS]/[HMDI]/[Chain extender] ratio)

Polymer Code	Molar composition*	Chain Extender	HS Content (wt%)
PSU-31,500-1.8E	1/2/1	ED	1.82
PSU-31,500-2.8E	1/3/2	ED	2.80
PSU-31,500-3.7E	1/4/3	ED	3.73
PSU-31,500-4.7E	1/5/4	ED	4.70
PSU-31,500-2.8D	1/2/1	Dytek A	2.82
PSU-31,500-3.1D	1/3/2	Dytek A	3.10
PSU-31,500-4.3D	1/4/3	Dytek A	4.32
PSU-31,500-5.4D	1/5/4	Dytek A	5.37

Table 3.5 gives the tensile properties of silicone-urea copolymers with different chain extenders. As can be seen on this table there is no significant differences between the tensile properties of homologous silicone-urea copolymers based on ED or Dytek A. Only at high levels of chain extenders ED seems to yield slightly stronger materials compared to Dytek A. However, we believe the differences are within the experimental error range.

Table 3.5. Tensile properties of silicone-urea copolymers based on PDMS-31,500, HMDI and ED or Dytek A as chain extenders (*[PDMS]/[HMDI]/[Chain extender] ratio)

Polymer Code	Molar composition*	Modulus (MPa)	Tensile Str. (MPa)	Elongation (%)
PSU-31,500-1.8E	1/2/1	0.50	0.80	400
PSU-31,500-2.8D	1/2/1	0.60	0.70	300
PSU-31,500-2.8E	1/3/2	0.60	1.25	350
PSU-31,500-3.1D	1/3/2	0.70	1.20	600
PSU-31,500-3.7E	1/4/3	0.75	2.00	450
PSU-31,500-4.3D	1/4/3	0.80	1.55	420
PSU-31,500-4.7E	1/5/4	0.90	2.20	500
PSU-31,500-5.4D	1/5/4	0.90	2.10	400

3.4. Influence of silica filler on tensile properties of silicone-urea copolymers

It is well known that high amounts of silica (up to 60% by weight) are always used in crosslinked silicone rubbers as reinforcing fillers to improve their tensile strengths. Without silica fillers PDMS rubbers display very poor tensile strengths. Since silicone-urea copolymers are inherently strong due to microphase separation and strong hydrogen bonding between urea hard segments they do not need such fillers for many applications. In fact, to our knowledge there is no information in the open literature which reports the use of reinforcing silica fillers for silicone-urea elastomers. It may be thought that

incorporation of silica fillers would interfere with the strong hydrogen-bonding in the urea hard segment and weaken them and as a result negatively influence the thermomechanical properties of silicone-urea copolymers. In order to find out whether this assumption is correct or not a hydrophobic surface treated silica filler (HDK H2000 from Wacker) was used at different levels to prepare silicone-urea/silica composites.

The base silicone-urea copolymer used in these studies was PSU-31,500-5.4D, which as shown on Table 3.4., had 5.37% by weight urea hard segment content. Tensile properties of this polymer were provided on Table 3.5.

Silica filled silicone-urea samples were prepared by adding desired amount of hydrophobic silica (HDK 2000) into the polymer solution in THF/IPA. The mixture was stirred at least for 12 hours (usually overnight) at room temperature by using a magnetic bar until the filler is homogeneously distributed in polymer solution. Silicone-urea/silica composites containing 17.0, 28.7, 37.5% and 60.0 % by weight of silica were thus prepared. To obtain the films polymer/silica solutions were cast into Teflon molds and kept in a 55 ^{o}C air oven for 12 hours to evaporate the solvent. All samples, except 60% silica containing system, yielded clear and homogenous films with good mechanical integrity.

FTIR studies on silica filled silicone-urea copolymers based on HMDI and PDMS-3200 were carried out in order to determine the presence and the extent of any interaction between silica and silicone-urea copolymers. Tensile behaviors of the composite materials were also determined to investigate and understand the effect of silica filler on properties of silicone-urea copolymers based on PDMS-31,500. Dynamic mechanical analyses of filled and unfilled silicone-urea copolymers were also performed.

3.4.1. FTIR studies on silicone-urea/silica (HDK H2000) blends

In order to find out and understand the presence of interaction between silica fillers and silicone-urea copolymers, transmission FTIR spectroscopy was used. FTIR spectra of unfilled and silica filled samples were obtained and compared. Both hydrophobic (HDK H2000) and hydrophilic (HDK N20) silica fillers were used. Base silicone-urea copolymer was obtained by the stoichiometric reaction of HMDI and PDMS-3,200 which had a urea hard segment content of 7.6% by weight. For FTIR studies films were cast from solution onto KBr discs and solvent was evaporated using an air gun. Spectra were obtained with a resolution of 2 cm^{-1}.

We were mainly interested in the presence of specific interactions between;
(i)   urea hard segments and silica and
(ii)   PDMS backbone and silica.

For this purpose we closely examined the N—H and C=O regions at 3300-3400 cm^{-1} and 1600-1800 cm^{-1} and the Si-O-Si region at 1000-1100 cm^{-1}, which are provided in Figure 3.4. In Figures (3.4.a) and (3.4.c) C-H stretching (2800-3000 cm^{-1}) and deformation (1260 cm^{-1}) peaks are also shown as reference. There seems to be no difference in the FTIR spectra of unfilled and filled systems in the N—H region at 3300-3400 cm^{-1}, where a broad symmetrical absorption peak centered at 3340 cm^{-1} is observed (Fig IV-3-a). Similarly there is no shift in the Si-O-Si doublet at 1000-1100 cm^{-1} (Fig IV-3-c). Slight broadening in the filled systems is due to the absorption of the silica fillers. However, there seems to be a change in the C=O region at 1500-1800 cm^{-1} (Fig IV-3-b). Virgin TPSC has two very sharp and symmetrical absorption peaks centered at 1630 cm^{-1} (strongly hydrogen bonded C=O peak) and 1579 cm^{-1} (amide II peak).

In silica filled silicone-urea copolymers, a small but a fairly well defined peak (shown by bold red arrow) is observed at 1735 cm^{-1}, which may be an indication of the presence of non-hydrogen bonded C=O groups. This may indicate presence of an interaction between silica and urea groups, which seems to be leading to a slight break-up in the hydrogen bonding between urea groups.
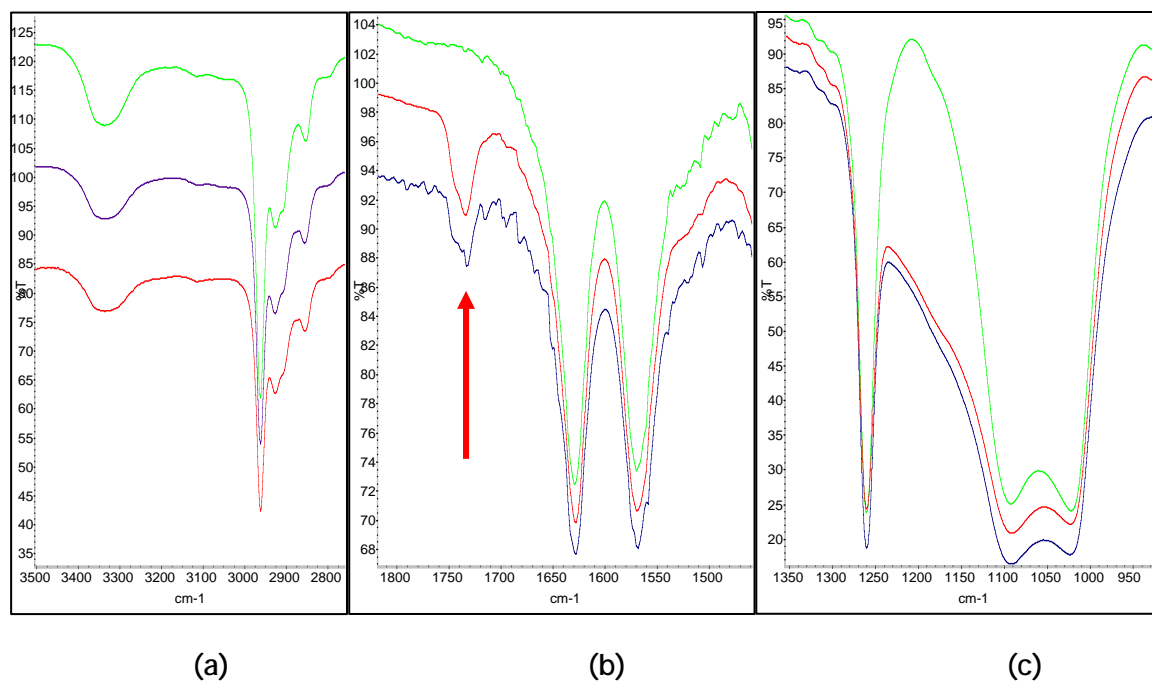

Figure 3.4. Comparative FTIR spectra of virgin and silica filled silicone-urea copolymers: (a) N-H and C-H stretching region (2800-3500), (b) Amide I and Amide II region (1500-1800), (c) Si-O-Si and C-H bending region (950-1350)
[Silicone-urea copolymer (green spectrum), Silicone-urea with 20% H2000 (blue spectrum), Silicone-urea with 20% N20, (Red spectrum)]

3.4.2. Tensile properties of silicone-urea/silica blends based on PSU-31,500-5.4D copolymer

Stress-strain curves for virgin, 17.0 and 28.7% hydrophobic silica (HDK H2000) filled silicone-urea (PSU-31,500-5.4D) copolymers are reproduced in Figure 3.5. It was a very pleasant surprise to observe dramatic improvements in the tensile properties of silicone-urea copolymer through the incorporation of hydrophobic silica. Interestingly, modulus, tensile strength and elongation at break values all showed dramatic improvements as a function of the silica incorporation.
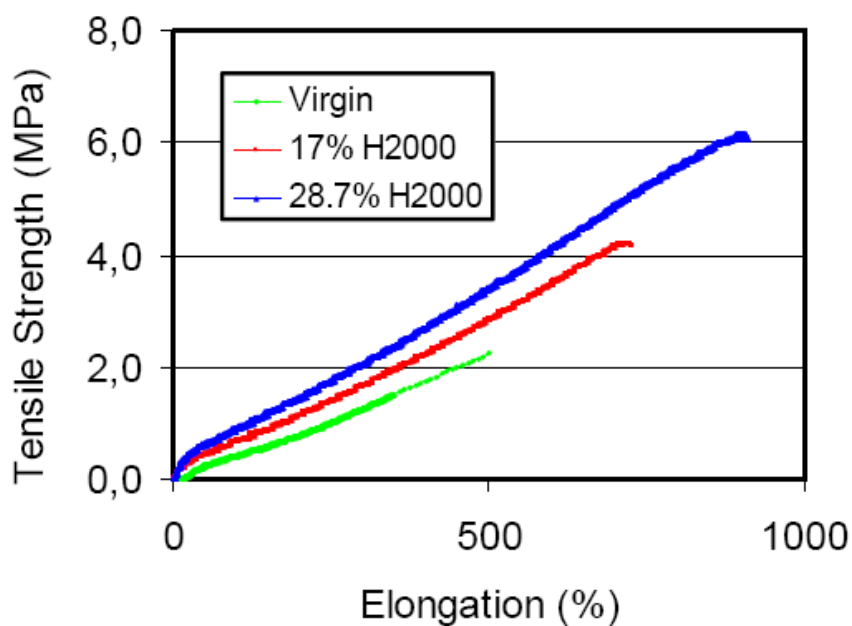

Figure 3.5. Stress-strain behavior of unfilled and silica filled PSU-31,500-5.4D copolymer

This may indicate that one or more of the following phenomena may be effective or have an influence on the system:

(i) hydrophobic silica (HDK H2000) is homogeneously and well distributed in the system,

(ii) HDK H2000 acts as a truly reinforcing filler for the system,

(iii) silica filler does not have any adverse effect on the microphase separation between urea and siloxane and/or it does not interfere with the hydrogen bonding between the urea hard segments,

(iv) silica filler mainly interacts with the PDMS soft segments,

(v) failure mechanism of the system changes.

Comparative results on the tensile properties of unfilled and HDK H2000 silica filled silicone-urea copolymers are provided in Table 3.6. From this table it can very clearly be seen that incorporation of silica filler considerably improves the tensile properties of silicone-urea copolymers similar to that of silicone rubber.

Table 3.6. Tensile properties of HDK H2000 silica filled PSU-31,500-5.4D copolymer

Polymer code	HS Content (wt%)	Filler (wt %)	Modulus (MPa)	Tensile Str. (MPa)	Elongation (%)
PSU-31,500-5.4D	5.31	0	0.9	2.20	500
PSU-31,500-5.4D-17	5.31	17.0	1.2	4.15	730
PSU-31,500-5.4D-29	5.31	28.7	2.6	6.10	900
PSU-31,500-5.4D-38	5,31	37.5	5.0	5.50	880

3.4.3. Dynamic Mechanical Analysis

Dynamic mechanical behavior (storage modulus versus temperature curves) of virgin and 28.7% silica filled silicone-urea copolymers are reproduced in Figure 3.6. DMA results indicate that the modulus of silica filled systems (6000 MPa) in the glassy state is much higher than that of the unfilled silicone-urea copolymer (2000 MPa). This is expected from truly reinforcing fillers.

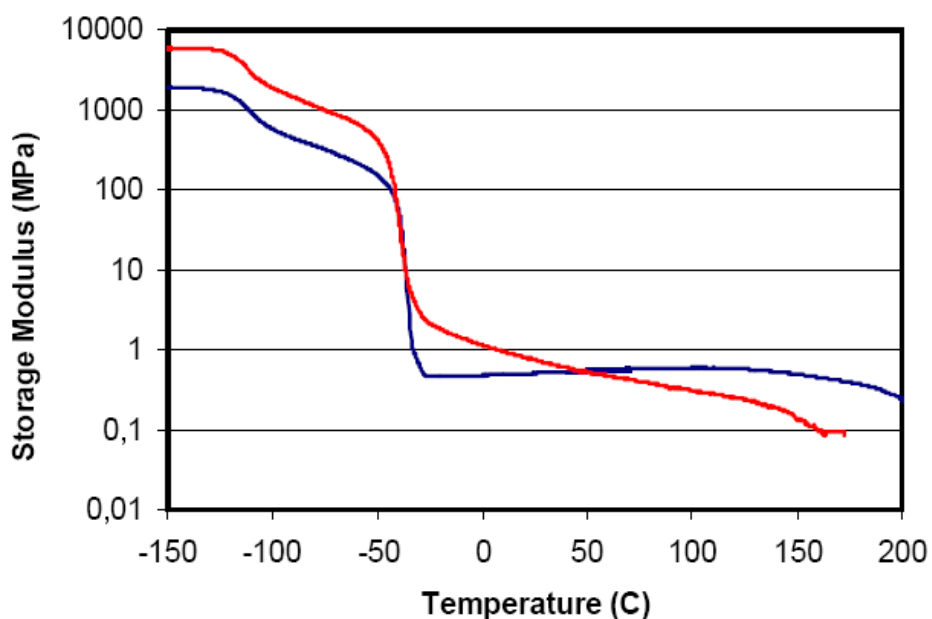**Figure 3.6**. Dynamic mechanical behavior of unfilled PSU-31,500-5.4D (blue curve) and 28.7% silica filled PSU-31,500-5.4D-29 (red curve) silicone-urea copolymers

After the glassy region both (filled and unfilled) polymers show a small PDMS glass transition around -120 °C and a sharper PDMS melting transition around -40 °C, typical for high molecular weight PDMS. Interestingly, these results indicate that the

presence of 27.8% by weight of silica filler does not seem to influence the crystallinity or crystallization behavior of PDMS-31,500. PDMS melting transition is followed by a fairly long rubbery plateau extending from -40 $^{\circ}$C to 150 $^{\circ}$C. The rubbery plateau of the unmodified copolymer, which contains 94.7% by weight of PDMS is fairly flat between in this region and shows only a slight drop up to 200 °C. This clearly demonstrates the power of the hydrogen bonding in the system even with very low urea hard segment content. Rubbery plateau of 28.7% silica filled material initially has a much higher modulus value compared to unfilled material however, with temperature rubbery modulus decreases slightly. This may indirectly indicate some interaction between urea groups and silica particles at these temperatures reducing the strength of the hydrogen bond network of hard segments.

3.5. Hysteresis behavior of silicone-urea copolymers

In addition to their overall tensile properties and mechanical strengths one of the most important performance characteristics of elastomers (both thermoplastic and thermoset) is their hysteresis behavior. When an elastomer is stretched and released it is expected to recover its original shape, preferably instantaneously. For most elastomers this is not the case. This is due to loss or dissipation of energy during the extension and recovery process. However, in many cases the original shape will be recovered completely with time or temperature. As shown in Figure 3.7., hysteresis (energy dissipated) for an elastomer is equal as the area difference between the loading (stretching) and unloading (recovery) curves. From these curves it is possible to calculate the percent hysteresis of the sample by comparing the area under the stretching curve and recovery curve.
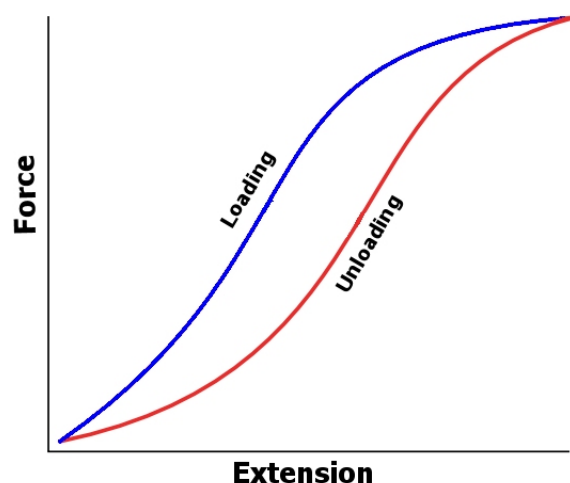
Figure 3.7. Elastic hysteresis of an idealized elastomeric material. The area in the centre of the hysteresis loop is the energy dissipated as heat.

Hysteresis behavior of unfilled and silica filled silicone-urea copolymers based on PDMS-31,500 were investigated at room temperature. All samples were stretched to 300% of their original length with a crosshead speed of 25.00 mm/min or approximately about 100% per minute and released with the same rate. Every sample was subjected to 10 hysteresis cycles. Areas under the curves were obtained and compared with the initial stretching curve and the amount of cumulative hysteresis at each cycle was calculated. Hysteresis curves for the unfilled PSU-31,500-5.4D and 17.0, 28.7 and 37.5% silica filled systems are provided in Figures 3.8, 3.9, 3.10 and 3.11 respectively.

When the hysteresis curves in Figures 3.8, 3.9, 3.10 and 3.11 are examined one can easily see that unfilled silicone-urea copolymer has lower hysteresis when compared with the filled systems. Another simple observation is that as the amount of silica filler increases the hysteresis also increases.
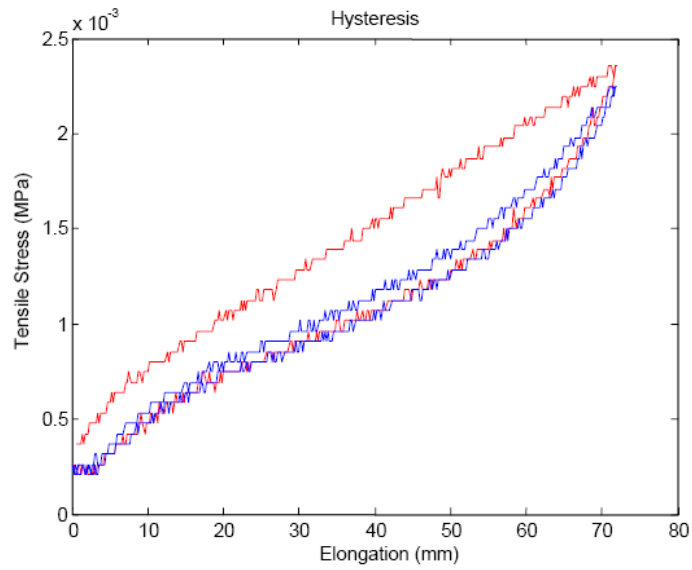
Figure 3.8-a. Hysteresis curves for unfilled PSU-31,500-5.4D
(Cycles 1 (red curve) and 2 (blue curve))
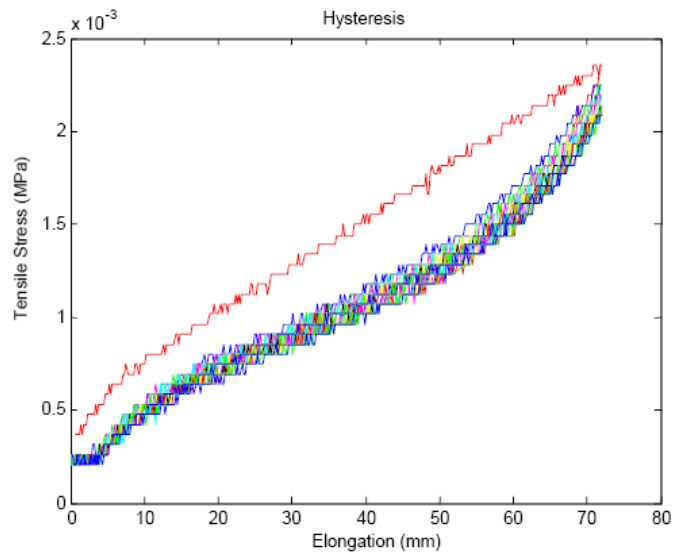
Figure 3.8-b. Hysteresis curves for unfilled PSU-31,500-5.4D (Cycles 1 to 10)

Figure 3.9-a*. Hysteresis curves for PSU-31,500-5.4D-17 (17.0% silica) (Cycle 1-5)

Figure 3.9-b*. Hysteresis curves for PSU-31,500-5.4D-17 (Cycle 6-10)
(*) Unit on the X-axis will be Elongation (mm) for both figures (L_o =24.0 mm)

Figure 3.10-a*. Hysteresis curves for PSU-31,500-5.4D-29 (28.7% silica) (Cycle 1-5)

Figure 3.10-b*. Hysteresis curves for PSU-31,500-5.4D-29 (Cycle 6-10)

(*) Unit on the X-axis will be Elongation (mm) for both figures (L_o=24.0 mm)
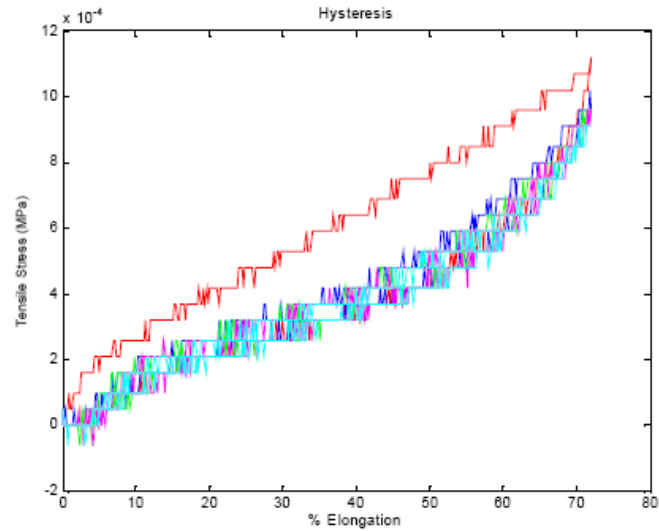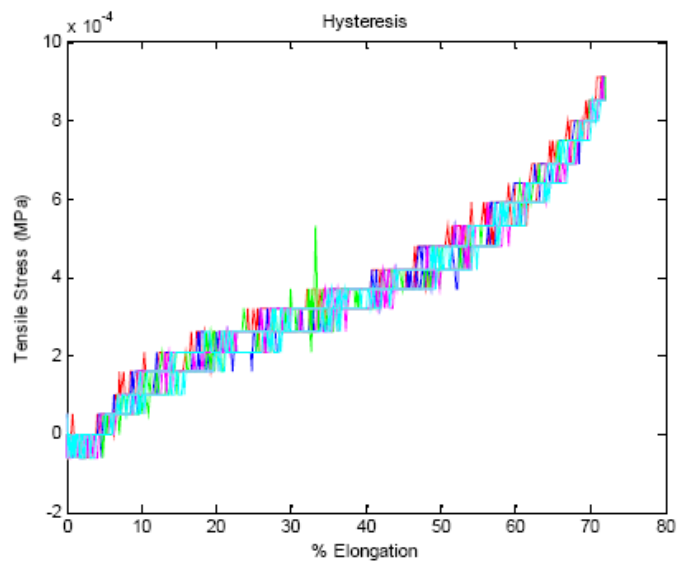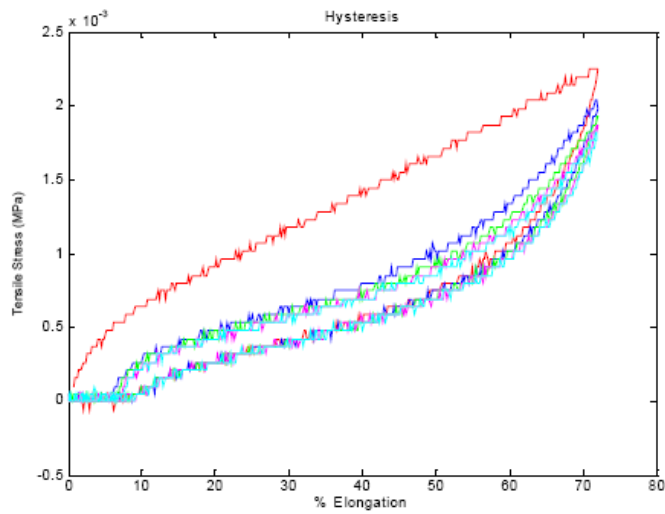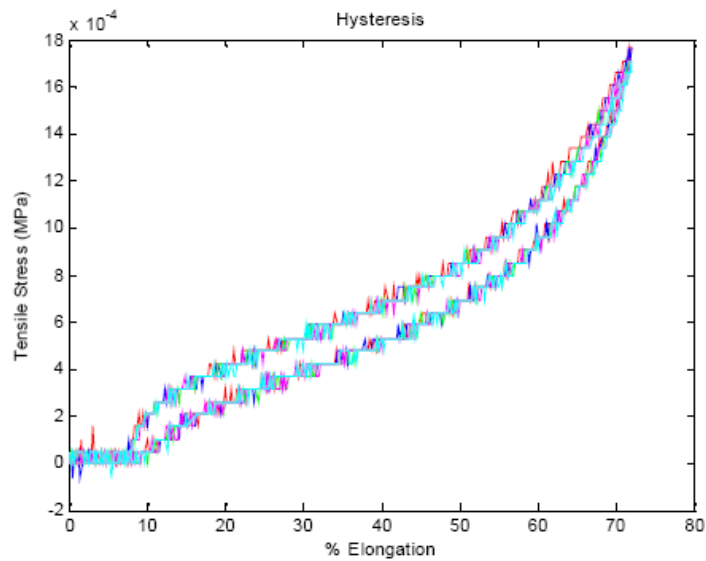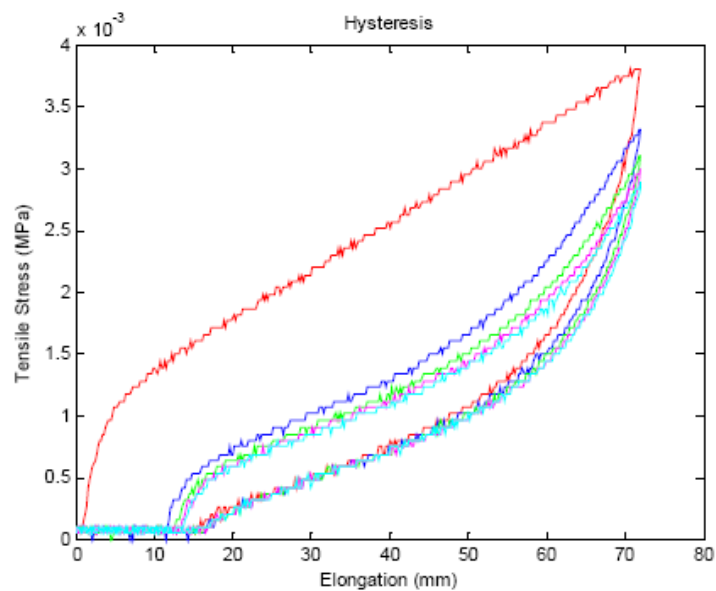
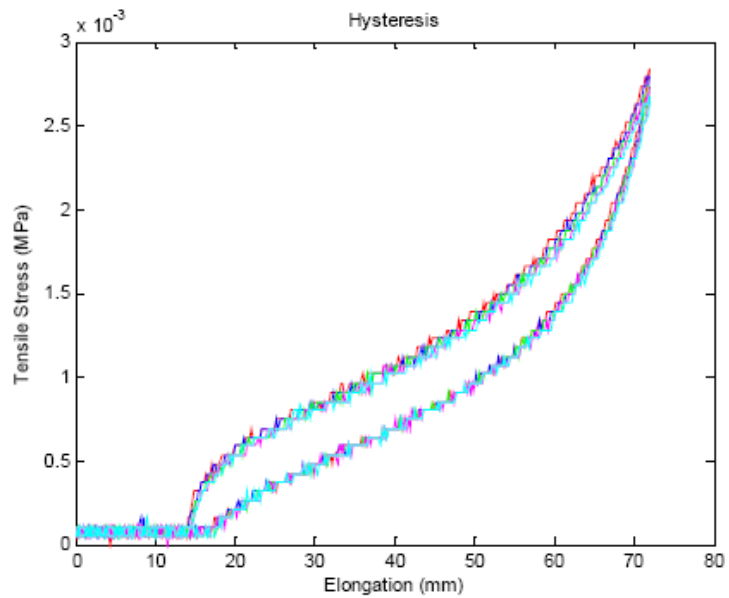**Figure 3.11-a.** Hysteresis curves for PSU-31,500-5.4D-38 (37.5% silica) (Cycle 1-5)

Figure 3.11-b. Hysteresis curves for PSU-31,500-5.4D-38 (Cycle 6-10)

Comparative hysteresis data obtained from the analysis of the hysteresis experiments on unfilled PSU-31,500-5.4D and silica filled systems are provided on Table 3.7. Percent hysteresis for each cycle is calculated as follows:

$$\% \text{ Hysteresis for a cycle} = \frac{\text{Area under the stretch curve} - \text{Area under recovery curve}}{\text{Area under the stretch curve}} \times 100$$

In order to calculate the total hysteresis after desired number of loading/unloading cycles, denominator is taken as the area under the first stretch curve.

Table 3.7. Hysteresis data on silica filled silicone-urea (PSU-31,500-5.4D) copolymer

TOTAL HYSTERESIS AFTER CYCLES (%)							
Polymer Code	Silica (wt %)	Ext (%)	Cycle 1	Cycle 2	Cycle 3	Cycle 5	Cycle 10
PSU-31,500-5.3D	0	300	25.67	27.00	27.63	28.85	30.52
PSU-31,500-5.3D-17	17.0	300	38.13	39.48	41.63	42.62	46.73
PSU-31,500-5.3D-29	28.7	300	53.62	55.68	56.84	58.03	59.53
PSU-31,500-5.3D-38	37.5	300	62.91	65.87	66.90	67.72	69.38

It is well known that for elastomers most of the energy is dissipated, or the highest hysteresis is observed at the end of the first loading/unloading (or stretching/recovery) cycle. This is mainly because the equilibrium chain configuration of the system is substantially disturbed at the end of this process and a new configuration is achieved. After the second cycle the hysteresis becomes much smaller. As can be seen on Table 3.7, this expected behavior is observed for all the samples investigated in this study. For unfilled

PSU-31,500-5.4D, fairly substantial hysteresis (25.67%) is observed after the first cycle of 300% stretch, which is quite high. On the other hand the hysteresis in the second cycle is only 1.37%! In fact total hysteresis in 9 cycles following the first cycle is only 4.85%. Same trend is also observed for the silica filled systems, although overall hysteresis observed is higher than the unfilled material. For PSU-31,500-5.4D-17, hysteresis after the first cycle is 38.13%. For the second cycle, hysteresis is only 1.50%, very similar to the unfilled material. Total hysteresis for the last 9 cycles is 8.6%, higher that the unfilled system but still fairly small.

As discussed above, silica filled silicone-urea copolymers display substantially higher hysteresis values when compared with the unfilled host polymer. This is understandable, because in addition to the disruption in the equilibrium configuration of the base polymer (such as its microphase morphology, hydrogen bonding between urea groups, and chain entanglements), in filled systems the equilibrium distribution/configuration of the fillers will also be permanently disrupted.

In Figure 3.12, percent hysteresis after the first and the tenth cycles are plotted as a function of the silica content of the system. It is interesting to note that there seems to be a linear relationship between the filler content of the system and percent hysteresis it experiences. At this point we do not have a reasonable molecular level explanation for this phenomenon.
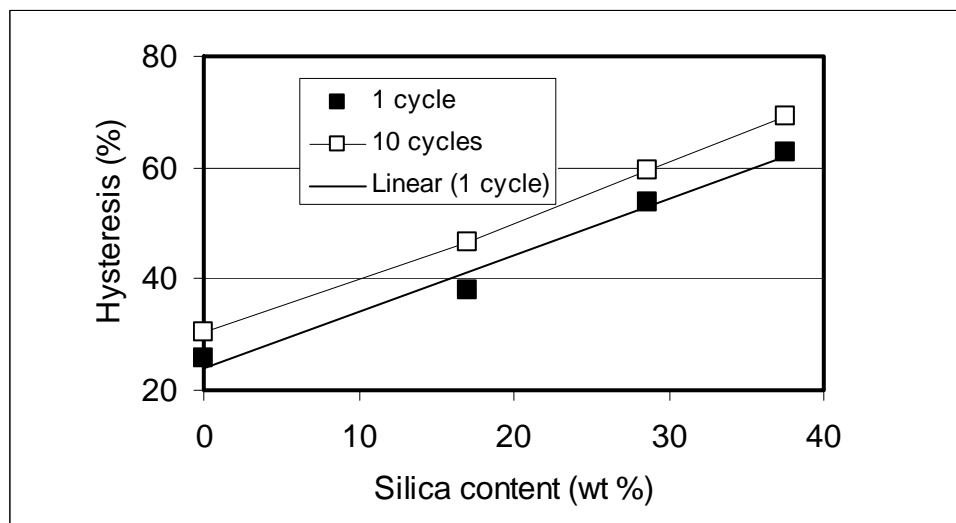
Figure 3.12. Percent hysteresis for the first and the tenth cycles as a function of the silica content for PSU-31,500-5.4D.

3.6 Investigation of the antibacterial properties of norfloxacin modified silicone-urea copolymers

Norfloxacin is an effective antibacterial agent which contains amine type reactive groups. Norfloxacin has a secondary amine and a carboxyl group, both of which can react with isocyanate groups on a polyurethane or polyurea prepolymers and provide antibacterial activity to the polymer produced against Gram-positive and Gram-negative aerobic pathogens.

Linear and hyperbranched silicone-urea copolymers with isocyanate end groups were prepared and the end groups were then capped with norfloxacin. Blends of silicone-urea copolymers and norfloxacin were also prepared. Activities of these materials towards gram negative *Escherichia coli* (E. Coli) were investigated. Bacteria were spread on nutrient agar

plates and the polymer film was then placed on plate. Zone of inhibition is measured after 18 h of incubation at 37 °C. Table 3.8 gives a list of norfloxacin containing copolymers and their antibacterial activities.

Table 3.8 Chemical compositions of norfloxacin containing silicone-urea copolymers and their antibacterial activities.

Polymer backbone	Molar Composition	HS (wt %)	NF (wt %)	Activity
PDMS 3,200/HMDI/NBA	1.0/2.0/2.0	18.8	Control	-
PDMS 3,200/HMDI/NF	1.0/2.0/2.0	28.3	15.5	++
PDMS 3,200/HMDI/NF	1.0/2.0/2.0	28.4	15.5	-
PDMS 3,200/HMDI/NF	1.0/2.0/2.0	28.5	15.5	-
PDMS 3,200/HMDI/NF	1.0/2.0/2.0	28.6	15.5	-
PDMS 3,200/HMDI/NF/NBA	1.0/2.0/1.0/1.0	24.0	8.30	-
PDMS 10,800/HMDI/ED	1.0/2.0/1.0	5.14	Control	-
PDMS 10,800/HMDI/NF	1.0/2.0/2.0	9.40	5.05	-
HMDI/PDMS-3,200/TRIS/NBA	2/1/0.55/0.35	17.0	Control	-
HMDI/PDMS-3,200/TRIS/NF	2/1/0.55/0.35	19.0	3.12	++

From the data provided on Table 3.8 it is not possible to draw any conclusions regarding the antibacterial activities of these norfloxacin modified silicone-urea copolymers. Out of four identical norfloxacin modified linear silicone-urea copolymers (PDMS 3,200/HMDI/NF) with norfloxacin contents of 15.5 weight percent, only one shows fairly high activity against E. Coli. Interestingly, hyperbranched silicone-urea copolymer containing only 3.12 percent by weight of norfloxacin (HMDI/PDMS-3,200/TRIS/NF) also seems to show antibacterial activity. Our research efforts in order to better understand this behavior is continuing.

Chapter 4

CONCLUSIONS

Novel silicone-urea copolymers based on fairly high molecular weight aminopropyl terminated polydimethylsiloxane (PDMS) soft segments ($<M_n>$ 10,800 and 31,500 g/mole) were prepared and characterized. Although they had fairly low urea hard segment contents all polymers formed films, showed very good microphase separation as indicated by dynamic mechanical analysis, and displayed reasonably good mechanical properties.

Ultimate tensile strengths of the copolymers showed a linear dependence on their urea hard segment contents, which has previously also been demonstrated by our group [32]. Interestingly, when silicone urea copolymers with identical urea hard segment contents were compared, those based on PDMS-31,500 showed higher tensile strengths than those based on PDMS-10,800. Critical entanglement molecular weight of PDMS is reported to be 24,500 g/mol. Therefore, we believe this synergistic effect on tensile properties is a result of the chain entanglement in PDMS-31,500, which is not present in PDMS-10,800. In addition, PDMS-31,500 based silicone-urea copolymers also displayed very low hysteresis values, which is also very interesting.

For the first time we also prepared silica filled silicone-urea copolymers, containing up to 37.5% of silica by weight. Although high levels of fumed silica are commonly used in PDMS elastomers as reinforcing fillers, to date no report on their use in silicone-urea copolymers have been available. We have demonstrated that incorporation of hydrophobic silica into silicone-urea copolymers based on PDMS-31,500 dramatically increases the

modulus, tensile strength and elongation at break values of these copolymers. In order to find out the presence of any interaction between silica and the urea groups we also investigated the FTIR spectra of the blends. Interestingly, no significant changes in the positions or intensities of hydrogen bonded urea peaks in 3200-3400 and 1500-1700 cm^{-1} region of the FTIR spectra were observed.

Silica filled silicone-urea copolymers displayed slightly higher hysteresis values when compared with the virgin copolymer.

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