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EFFECT OF CHAIN LENGTH OF POLYMERIC ALIPHATIC DIAMINES ON THERMAL AND MECHANICAL PROPERTIES OF POLYUREA FILMS

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The effect of the chain length of polymeric aliphatic diamines on the final properties of polyurea films was investigated. Brittle to flexible polyurea films were synthesized by employing different polymeric aliphatic diamines with the number average molecular weight of about 230 Da, 400 Da, 2000 Da and 4000 Da. The four types of polyureas obtained were characterised by FT-IR, TGA, DSC and tensile test measurements.

Keywords: polyurea, polymeric film, polymeric chain length, thermal properties, mechanical properties

1. Introduction

Polyurea based materials present a unique combination of properties: excellent adhesion [1], abrasive resistance [1, 2], corrosive resistance [2], low flammability [2], light-weight [2], feasibility in strengthening structures as energy absorbing materials [3], which makes this material a good candidate for a wide range of applications in coating industry.

Polyurea films are microphase-separated block copolymers obtained by reacting an aliphatic or aromatic isocyanate component and an amine terminated polymer resin. The soft nanodomains (aliphatic regions) form a continuous matrix

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around the hard nanodomains (aromatic regions which are randomly dispersed in the soft matrix). Depending on the proportions between the soft and the hard regions, polyurea can display a wide range of properties, from soft rubber to hard plastic. [4] Only a 5-10% change in the chemistry of a polyurea network could lead to important changes in the mechanical behaviour of the material.[5]

According to the number of the reactants used, the synthesis of this materials can give two-component polyureas (obtained using an isocyanate component and an amine component) [4, 6, 7], or multi-component polyureas (obtained using chain extenders as the third component, besides the isocyanate and amine components) [6, 8-12].

Depending on the type of application, polyurea films with specific properties can be obtained by controlling the synthesis parameters, such as: aliphatic or aromatic reactants, monomeric or polymeric reactants, different mole ratio between the amine and the chain extender, etc.

Two-component elastomeric polyureas are extensively used as protective coating or in lining industry [6]. The synthesis of these materials presents multiple advantages like fast curing, homogenous film forming, no volatile organic compounds involved in the synthesis [6], no catalyst needed to accelerate the reaction, no foaming, and the curing process is not significantly affected by moisture or temperature [13]. The relative reactivity between isocyanate and primary amine is 1000 times higher than the one between the same isocyanate and alcohol or water. Spraying or casting are the most commonly used techniques for applying polyureas on a surface [1-3, 7, 14]. Ketones are often used for slowing down the reaction rate which allows the shaping of the materials. [13]

K. Holzworth et al. [4] have studied the effect of isocyanate content on thermal and mechanical properties of a two-component polyurea and their results indicated that a careful selection of hard segment content can have a major influence on the ultimate properties and performance of the material. Some other aspects regarding the structure-properties relationship of polyurea were mentioned in many studies [1, 3, 4, 6, 8-11, 13-16]. Most of these papers have focused on the study of the chain extenders influence on the final properties of the polyurea, but very limited research investigated the influence of the soft segment nature in the case of a two-component polyurea. Therefore, we report here for the first time a study which aims to demonstrate that the soft segment can also have a major influence on the final properties of a two-component polyurea films, depending on the chain length of the polymeric diamine used for the synthesis.

2. Experimental

2.1. Materials

Poly (propylene glycol) bis(2-aminopropyl ether) – with a number average molecular weight (Mn) of about 230 Da (PPG230, Sigma Aldrich), Poly (propylene glycol) bis(2-aminopropyl ether) - Mn≈400 Da (PPG400, Sigma Aldrich), Poly (propylene glycol) bis(2-aminopropyl ether) - Mn≈2000 Da (PPG2000, Sigma Aldrich), Poly (propylene glycol) bis(2-aminopropyl ether) - Mn≈4000 Da (PPG4000, Sigma Aldrich), diphenylmethane-4,4'-diisocyanate (MDI, technical product Desmodur® 44V20L, Bayer) and acetone (Sigma Aldrich) were used as received.

2.2. Methods - *Preparation of the polyurea films*

The polyurea films were synthesized by mixing each type of PPG (PPG230, PPG400, PPG2000 and PPG4000) with MDI, both reactants being previously solubilized in acetone. The resulting polyureas were named PU230, PU400, PU2000 and PU4000, according to the type of PPG used for their synthesis. The mole ratio between the isocyanate groups and the primary amino groups for these reactions was always 1:1.

2.3. Characterization

The FT-IR spectra of the synthesized polyureas were recorded using a Bruker VERTEX 70 Spectrometer with ATR. The parameters used for the determination of each spectrum were the following: number of scans: 32; resolution: 4cm^{-1}; spectral range: 500 - 4000 cm^{-1}.

The transition glass temperatures (T_g) were measured by means of a NETZSCH DSC 204 F1 Phoenix instrument. The tests were carried out under the following conditions: nitrogen flow; samples mass: ~10mg; heating rate: 10°C/min; number of heating/cooling cycles: 2; temperature range: -80°C-200°C. T_g was determined from the inflection point obtained during the second heating cycle.

The thermogravimetric analysis (TGA) was performed using a Thermal Analysis Q500 instrument, considering the next parameters: nitrogen flow; samples mass: ~2mg; temperature range: room temperature -700°C; heating rate: 10°C/min.

Tensile tests were carried out by using a Titan - Universal Strength Tester by James H. Heal & Co. Ltd testing machine, according to the international standard ISO 37:2005. Tests were performed as following: standard dumbbell tensile specimens (width of the narrow parallel part: 5 mm; total length: 100 mm; distance between gauge marks: 20 mm); rate of extension: 500 mm/min; jaw separation (plain jaw faces): 50mm. For each type of polyurea, five tensile tests were performed and the average value was reported.

3. Results and discussions

The first step of this study consisted in obtaining different types of polyurea films by employing four types of polymeric aliphatic diamines, with different chain lengths, in order to establish the influence of this parameter on the final properties of the material.

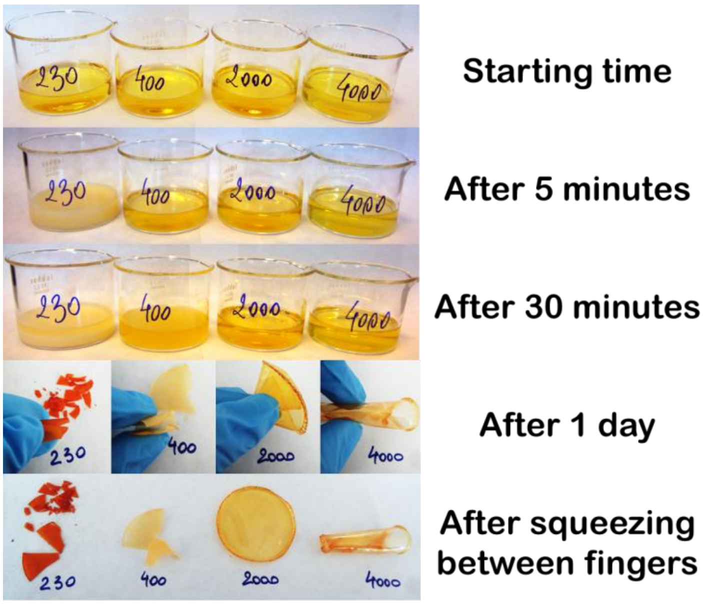

Fig. 1 – Various steps from the synthesis of polyurea

Acetone was used as solvent for both reactants (amine component and isocyanate component) in order to reduce the viscosity of the reaction mixture and to decrease the reaction rate. Fig. 1 displays some steps from the synthesis of polyurea, after mixing the isocyanate and amine solutions. It can be noticed that at the beginning of the synthesis, all the reaction mixtures were translucent. After only 5 minutes, the mixture containing PPG230 started to become opaque. After 30 minutes the mixture containing PPG400 had the same behaviour. This indicated that, unlike PU2000 and PU4000, phase separation occurred during the synthesis of both PU230 and PU400. After one day, the curing process of all the four polyureas was finished. As it can be seen from the bottom of this picture, the polyurea films obtained were very different, i.e. PU230 turned out to be brittle while PU400 seemed to have reduced flexibility. On the other side, PU2000 exhibited a high flexibility, returning to the initial shape after being squeezed between the fingers. PU4000 was more flexible and it did not return to the initial shape when squeezed.

This simple experiment showed that by varying the chain length of the polymeric diamines, a wide range of properties could be achieved, obtaining from brittle to high flexibility materials.

In order to better characterize the obtained materials FT-IR analysis was used to investigate the reaction between PPG and MDI.

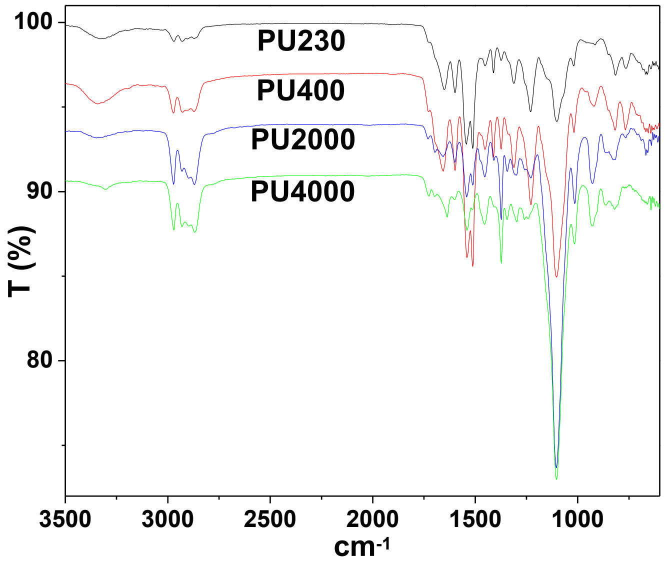

Fig. 2 – FT-IR comparative spectra of the synthesized polyureas

All the synthesized polyureas displayed similar FT-IR spectra (**Fig. 2**). This analysis confirmed the total consumption of the monomers, i.e. the peaks around 2270 cm^{-1} ($\nu_{N=C=O}$) and 3600-3400 cm^{-1} (ν_{NH2}) disappeared, and the formation of the urea linkage (R-NH-CO-NH-R) by the presence of the specific stretching vibrations: 3330 cm^{-1} (ν_{N-H}), 1655 cm^{-1}($\nu_{C=O}$) and 1105 cm^{-1}(ν_{C-N}), which increases with the length of the diamine used.

The thermal behavior of the synthesized polyureas was investigated by TGA and DSC measurements. The thermogravimetric analysis revealed that polyureas containing longer aliphatic chains were more stable than the ones containing shorter chains. In Fig. 3 and Table 1 are presented the results obtained for the decomposition process of the polyureas films. Thus, for PU230 this process started around 200°C, followed by PU400 (~240°C), while for PU2000 and PU4000 the decomposition started at higher temperatures (~290°C).

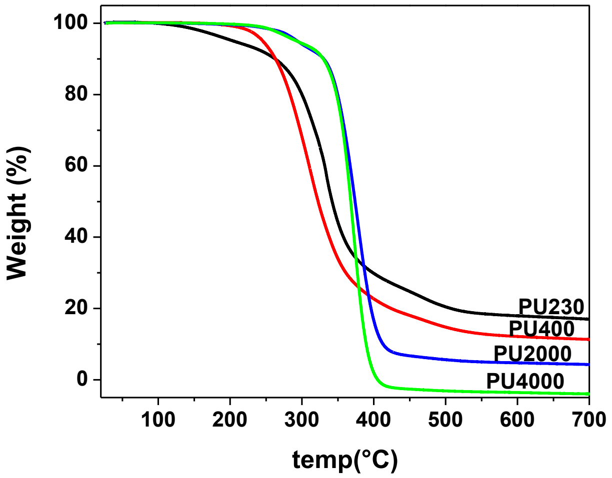

Fig. 3 –TGA curves of the synthesized polyureas

The decomposition of polyurea begins with the degradation of the hard domains, due to the relatively low thermal stability of the urea group, followed by the degradation of the soft segments [17]. Therefore, the degradation of polyureas with higher aromatic content and shorter aliphatic chains, like PU230 and PU400, started earlier.

Table 1

TGA results for the synthesized polyureas

Sample	**$T_{5\%}$ [°C]**	**$T_{10\%}$ [°C]**	**T_{max} [°C]**
PU230	205.2	262.7	335.0
PU400	245.6	263.1	314.7
PU2000	293.7	330.3	378.3
PU4000	292.9	329.6	373.2
$T_{5\%}$= onset temperature (measured at 5% weight loss) T_{max} = maximum degradation temperature			

According to literature data, polyurea films display two glass transition temperatures (Tg_1 and Tg_2) associated either with the soft polymer matrix or with the polymer chains located in the proximity of the hard nanodomains.[18]

DSC analysis provided very different values for the synthesized polyurea films (Fig. 4). As previously described, all synthesized polyurea exhibit two glass transition temperatures [19], denoted as Tg1 at lower temperature and Tg2 at higher temperature. The first inflection point (Tg_1), located between -56°C and -58°C was very similar for all the synthesized polyureas. Tg_1 corresponds to the transition from glassy- to rubbery- state of the polypropylene glycol sequences which were relatively far from the hard phase, therefore having a higher mobility. The second inflection point (Tg_2) was different for each type of polyurea, and it was ascribed to the glass transition of the lower mobility polymer chains located in the proximity of the hard nanodomain. Polyureas with longer aliphatic chains displayed negative Tg_1 values and low Tg_2 values. The soft polymer matrix of PU4000 contains the longest aliphatic chains therefore it displayed the lowest Tg_1 value (-62.8°C). Even if PU 2000 contained shorter aliphatic chains, these were still long enough to lead to a high mobility, therefore it presented a glass transition temperature (Tg_1) with only 10°C higher than PU4000. The higher Tg of PPG2000 block compared with that of PPG4000 block, may be explained through a stronger influence of the rigid domain connected to both ends of the PPG chains, despite the lower molecular weight of PPG2000. In the case of shorter chains, this influence should be larger, leading to a higher Tg value. Tg_1 values for the soft matrix of PU400 and PU230, were much higher because the aliphatic chains involved in their synthesis were much shorter.

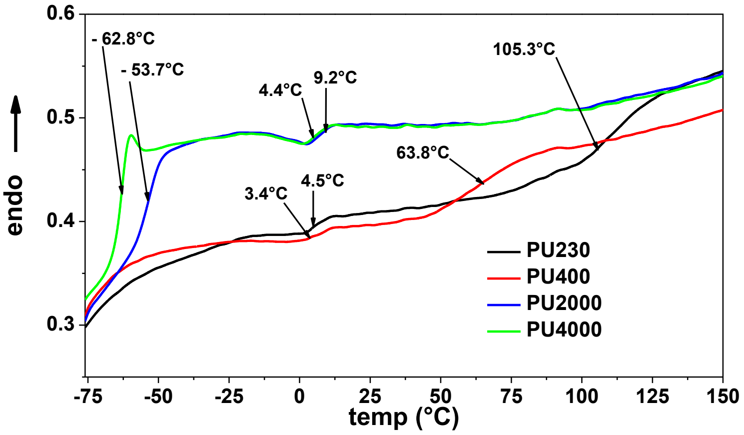

Fig. 4 –DSC curves of the synthesized polyureas

Tensile tests were performed only in the case of PU2000 and PU4000 samples. Dumbbell specimens could not be cut from the other two polyureas (PU230 and PU400) because they were brittle and they cracked when cut to the necessary dimensions.

Table 3

Tensile test results

Sample	Tensile stress at break (MPa)	Tensile strain at break (%)	Young modulus (MPa)
PU2000	6.89 ± 0.40	118 ± 6	4.98 ± 0.2
PU4000	0.25 ± 0.02	1029 ± 40	0.324 ± 0.06

Table 3 presents the stress and strain values of the flexible polyureas. A dramatically decrease of the tensile strength and, at the same time, a significant increase of elongation, can be noticed in the case of PU4000 due to the high amount of aliphatic chains existing in the structure of this material. On the other side, a shorter aliphatic chain leads to higher tensile stress values but also to lower tensile strain values. Even if the length of PPG4000 chain is twice the one of PPG2000, the mechanical properties of the resulting polyureas (PU2000 and PU4000) differ by one order of magnitude. PPG4000 has a lower Young Modulus than PPG2000 due to the high flexibility of the amine aliphatic chain; therefore, PPG2000 needs higher loads to be deformed.

4. Conclusions

The effect of the chain length of polymeric aliphatic diamines on the thermal and mechanical properties of polyurea films was studied. Four types of polyurea, with different degrees of flexibility, were synthesized. FT-IR analyses confirmed the formation of the urea group and the total transformation of the monomers. The thermal stability of the polyurea films varied with the length of the aliphatic chain, the ones with longer aliphatic chains having a higher onset temperature. All the synthesized polyureas presented two transition glass temperatures, the first one being associated with the soft nanodomains and the second one to the polymer chains situated in the proximity of the hard nanodomains. Tg_1 varied between -62.8°C and 4.5°C due to the different length of the aliphatic chain and Tg_2 varied between 4.4°C and 105.3°C depending on how the polymer chains surrounded the hard nanodomains. The stiffness of the polyurea films varied from brittle to flexible according to the polymeric aliphatic diamines used for their synthesis. Mechanical analysis could be performed only on the flexible polyureas. The mechanical properties of these polymeric films differed by one order of magnitude, the one with longer aliphatic chains leading to higher deformation but lower mechanical strength.

Therefore, polyurea films can have a specific design, achieved by adjusting the length of polymeric aliphatic diamines, in order to satisfy the requirements of a certain type of application.

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