

Thermoplastic Polyurethane Elastomers: Synthesis, and Study of Effective Structural Parameters

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ABSTRACT

In this study two classes of polyols, a polyether and a polyester, are used for synthesizing thermoplastic polyurethane elastomers. These elastomers are prepared by chain extension of polyol/toluene diisocyanate by prepolymer method and a variety of chain extenders. The effect of polyester and polyether polyols and chain extenders on thermal stability have been investigated by studying their morphology using dynamic mechanical thermal analysis (DMTA), and thermogravimetric analysis (TGA). The physical and mechanical properties of prepared polyurethane elastomers are measured. The obtained results are investigated and discussed.

Key Words: thermoplastic polyurethane elastomer, synthesis, structural parameters, chain extender, morphology

INTRODUCTION

Thermoplastic polyurethane elastomers (TPUEs) are an important group of polyurethane elastomers. They are normally prepared by reacting a diisocyanate with a moderate weight macroglycol (2000) and a low molecular weight diol as chain extender [1]. TPUEs have excellent physical and mechanical properties such as high tensile strength, good resistance to abrasion, oil, fuels and solvents, low temperature flexibility, heat resistance and high adhesion to many substrates. These materials with Shore hardness values between 50 A and 70 D cover the whole range between rubber and plastics [2, 3]. All of these properties cause their rate of usage expand increasingly.

These materials contain two separate structural phases: the hard segment and the soft

segment. The former is related to polyol structure and the latter is related to the reaction of diisocyanate with hydroxyl groups of chain extender and polyol. Elastomeric behaviour of these polymeric systems can be attributed to microphase separation of the hard segments. The rigid domains reinforce the elastomeric matrix like covalent linkages in cross-linked elastomers. However ultimate strength is resulted from hydrogen bonds between hard segments [4, 5].

Consequently, the effective parameters on the properties of polyurethane elastomers are: soft segmental chemical construction, hard segmental chemical construction and relative size between the soft segments and the hard segments [6]. The chemical construction of segments are related to the type of polyols, the diisocyanate and the chain extenders, but the last factor changes with the

Table 1. Materials used in the synthesis of the polyurethane formulation.

| Material | Abbreviation | Functionality | Molecular weight | Supplier |
|----------------------|--------------|---------------|------------------|----------|
| Polyester polyol | Capa 255 | 2 | 2000 | Interox |
| Polyether polyol | PTHF | 2 | 2000 | BASF |
| Toluene diisocyanate | TDI | 2 | 174 | Merck |
| Ethylene glycol | EG | 2 | 62 | Merck |
| 1,3-Propane diol | PD | 2 | 76 | Merck |
| 1,4-Butane diol | BD | 2 | 90 | Merck |
| 1,6-Hexane diol | HD | 2 | 118 | Merck |
| 1,10-Decane diol | DD | 2 | 174 | Merck |

choice of different molar ratio of raw materials.

In this study, the effect of chemical soft segment constructions has been investigated by choosing two types of polyols, a polyester and a polyether. Also the role of the hard segment chemical construction in physical and mechanical properties of the elastomers has been studied with changing the chain extenders. The molar ratio of 1:3:2 for a polyol, diisocyanate and a chain extender has been used for all of the elastomers, respectively.

EXPERIMENTAL

Materials

The diisocyanate used was toluene diisocyanate (TDI) constituting the mixed 2,4: 2,6 isomers in 80/20 ratio. Polycaprolactone (CAPA 225) and polytetrahydrofuran (PTHF) with a molecular weight of 2000 were used, respectively, as a polyester and a polyether polyol. Ethylene glycol (EG), 1,3-propane diol (PD), 1,4-butane diol (BD), 1,6-hexane diol (HD) and 1,10-decane diol (DD) were used as chain extenders.

The polyols and chain extenders were dried each at 80 °C and 40 °C, respectively, and degassed under vacuum at least for 2 h before use. The materials used in this study are listed in Table 1.

Instruments and Test Methods

The instruments used in this study for TG, DMTA, tensile, tear and hardness tests were PL-STA, PL-DMTA MK II, Tensile Instron 6025 and Zwick

3123 models, respectively.

ASTM 412 test method was chosen for measuring the tensile properties. The rate for the test was 200 mm/min. The dumbbell shaped specimens for tensile tests were prepared in accordance with ASTM 412 die type C. Also, the test method for tear test was based on B.S. 903: Part A3 (1982).

Synthesis

All syntheses were carried out by prepolymer method. The diisocyanate was added to the previously dried and degassed molten polyol, and the reactants were held in a round bottom polymerization reaction vessel, equipped with a stirrer and located in an oil bath at 100 °C, and a steady flow of dry nitrogen passing continuously over the mixture forming a gas blanket. The reaction mixture was then continuously stirred for approximately 90 minutes.

Conversion of the prepolymer into the final PU was carried out by stirring the prepolymer vigorously, and then adding a previously predried and degassed chain extender. When colour homogeneity was obtained in the reactant mixture, the dispersion of chain extender was considered complete and the liquid polymer was cast into a highly polished warm aluminium tray, previously coated with a release agent, to form a homogeneous sheet of 2-3 mm thickness. The cast polymer in its moulding tray was then placed in a hot air circulating oven at 110 °C and it was cured for at least 20-24 h. The cured sample sheets were then stored for at least one week at ambient temperature

Table 2. Comparison of thermal stability of synthesized elastomers by polyester and polyether, TDI and various chain extenders in N_2 atmosphere (molar ratio 1:3:2).

| Type of chain extender | Thermal stability ($^{\circ}C$) | |
|------------------------|-----------------------------------|------------------------------|
| | polyether polyol PTHF | polyester polyol CAPA 225 |
| EG | 268.82 | 269.96 |
| PD | 303.33 | 306.64 |
| BD | 312.33 | 313.23 |
| HD | 315.44 | 322.48 |
| DD | 317.25 | 332.02 |

(25 $^{\circ}C$) and 40% relative humidity before testing.

RESULTS AND DISCUSSION

After synthesizing TPUE in laboratory with various polyols and chain extenders, the effect of structural parameters were studied. Thermal stability of synthesized elastomers was investigated by using thermal gravimetry (TG). The rate of heating was 10 $^{\circ}C/min$ and the test was carried out in an N_2 atmosphere. The results of thermal stability are shown in Table 2, and they indicate that polyester based PU elastomers are more stable than polyether based PU elastomers. This phenomenon

is related to the polar nature of ester bonds.

Also in each set of elastomers, the thermal stability of TPUE is increased with the increasing length of chain extenders. There are two reasons for this, one is that, the block ratio, polyol and diisocyanate are the same in each group, and length of chain extender is the only variable parameter. The degree of polymerization of these systems is nearly equal, because polymerization conditions are constant for all of these elastomers. With longer chain extender, the longer polymer chain is obtained because polymer chain is produced from the repetition of polyol, diisocyanate and chain extender. Thermal energy distribution in longer chain is better than shorter chain and hence, the thermal stability in the former is better than the latter.

The second reason is that, the polymer chain with longer chain extender has longer hard segment. The length of hard segment has an effect on phase separation. Elastomers with higher phase separation have superior properties such as thermal stability.

The test of DMTA is used for determination of α -transition temperature. The α -transition temperature is a good criterion of glass transition temperature (T_g).

Figure 1 shows the comparison between $\tan \delta$ of two groups of synthesized elastomers. The chain extender for both elastomers is 1,4-butane diol. The glass transition temperature of polyether based elastomer is 10 $^{\circ}C$ lower than polyester based elastomer. This is due to more flexibility of etheric bond and higher phase separation in comparison with esteric bond.

Table 3 shows α -transition temperature for polyester based elastomers. There is no significant change in α -transition temperature.

The $\tan \delta$ of elastomers based on polyester polyol are shown in Figure 2. In these peaks, the sharpness of slope claims quality of phase separation [8]. The synthesized PU elastomer with 1,10-decane diol has the sharpest peak, and consequently, it has the greatest phase separation.

The effect of polyester and polyether polyols on tensile properties is important. Table 3 shows

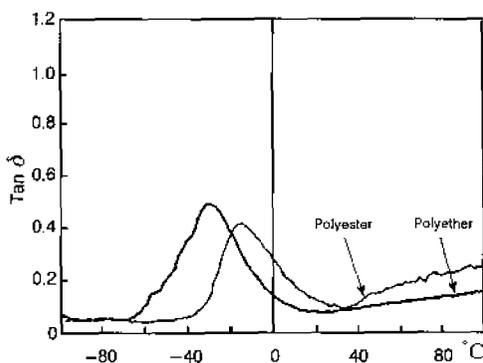


Figure 1. $\tan \delta$ for two elastomers based on polyether and polyester polyol with TDI and 1,4-butane diol (molar ratio 1:3:2).

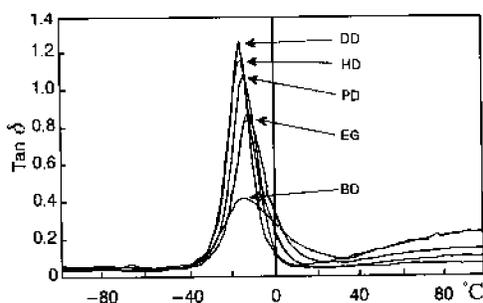
Table 3. α -Transition temperatures for synthesized elastomers: CAPA 225/TDI by various chain extenders (molar ratio 1:3:2).

| Type of chain extender | α -Transition temperature ($^{\circ}$ C) |
|------------------------|--|
| BG | -11.5 |
| PD | -13.5 |
| BD | -15.0 |
| HD | -15.5 |
| DD | -15.5 |

that the ultimate tensile strength of polyester based elastomers is higher than polyether based elastomers due to polarity of polyesters and significant amount of hydrogen bonding.

In both groups, elastomers with 1,6-hexane diol and 1,10-decane diol have high strength, respectively. The length of the employed chain extender has two opposite effects, with decreasing length, high density of urethane bonds and hydrogen bonds are produced, but they are accompanied with weaker phase separations. The tensile properties are resultant of two opposite effects. In both elastomers, the loss tangent peaks are with approximately the same sharpness, but the density of hydrogen bonds in 1,6-hexane diol is higher than 1,10-decane diol and hence, the tensile strength of TPUEs synthesized with 1,6-hexane diol is higher than 1,10-decane diol.

Elongation at break of the synthesized

**Figure 2.** Comparison of $\tan \delta$ for synthesized elastomers with CAPA 225/TDI by various chain extenders (molar ratio 1:3:2).**Table 4.** Ultimate strength of synthesized elastomers: CAPA 225 and TDI by various extenders (molar ratio 1:3:2).

| Type of chain extender | Ultimate strength (N/mm ²) | |
|------------------------|--|----------|
| | PTHF | CAPA 225 |
| EG | 5.993 | 8.281 |
| PD | 3.544 | 7.719 |
| BD | 3.199 | 5.488 |
| HD | 4.853 | 13.47 |
| DD | 3.319 | 11.21 |

elastomers are shown in Table 5. In both, polyether and polyester based urethanes, elongation at break is increased with increasing chain extenders molecular weight. Obviously the longer the chain length the longer the hard segment would be. Thus, during final stage in tensile tests, the chains slip over each other and the probability of urethane group to remain adjacent and repack in longer intervals is greater, and therefore, the elastomers show higher elongation at break.

The results of hardness test for both groups are presented in Table 6. The hardness of polyether based elastomer is slightly higher than polyester one. The data obtained show variation from 57 Shore A to 60 Shore A for polyester based elastomer. Thus it is deduced that the effect of chain extenders molecular weight on the hardness data is not considerable.

Tear test on the synthesized elastomers was

Table 5. Elongation at break of synthesized elastomers: CAPA 225 and PTHF/TDI and different chain extenders (molar ratio 1:3:2).

| Type of chain extender | Elongation at break (%) | |
|------------------------|-------------------------|----------|
| | PTHF | CAPA 225 |
| EG | 375 | 412 |
| PD | 430 | 448 |
| BD | 501 | 539 |
| HD | 506 | 575 |
| DD | 893 | 748 |

Table 6. Hardness (Shore A) for synthesized elastomers with CAPA 225 and PTHF/TDI by various chain extenders (molar ratio 1:3:2).

| Type of chain extender | Hardness (Shore A) | |
|------------------------|--------------------|----------|
| | PTHF | CAPA 225 |
| EG | 64.85 | 60.41 |
| PD | 59.99 | 58.43 |
| BD | 61.81 | 59.43 |
| HD | 62.83 | 59.8 |
| DD | 60.45 | 56.64 |

Table 7. Tear strength of synthesized elastomers with CAPA 225 and PTHF/TDI by various chain extenders (molar ratio 1:3:2).

| Type of chain extender | Tear strength (kN/m) | |
|------------------------|----------------------|----------|
| | PTHF | CAPA 225 |
| EG | 16.176 | 22.387 |
| PD | 10.465 | 54.920 |
| BD | 15.390 | 43.973 |
| HD | 28.308 | 58.612 |
| DD | 5.504 | 34.86* |

* It should be noted that, since slippage occurred during test carried out on this sample and no complete tear resulted, thus it should be treated with caution.

also carried out. The samples were in a strip form with 35×12 mm dimensions and with a 2 mm notch in the middle. By stretching the sample with testing machine, the maximum force of tear is reported, and tear strengths are calculated by $T=kN/m$, in which m is thickness in meter. From Table 7 it is shown that the data for tear strength of polyester based urethanes group are higher than polyether based.

CONCLUSION

Polyester based TPUEs have higher tensile strength, tear strength and thermal stability than

polyether based elastomer, but the polyethers based urethanes are slightly harder.

DMTA studies for both groups of elastomers show that an elastomer with larger chain extender has a larger hard segment, and a better phase separation. By increasing the phase separation, good physical and mechanical properties are expected.

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