Mechanical and Underwater Acoustic Properties of the Polyurethane Elastomers with Different Hard Segment Contents

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Abstract: Polyurethane elastomers with different hard segment contents were synthesized by one-step method, using polypropylene glycol (PPG) as soft segment, toluene diisocyanate (TDI) and triethanolamine (TEA) as hard segments. The effects of hard segment content on the molecular structure, mechanical properties and underwater acoustic properties of polyurethane elastomers were studied. The results showed that hard segment contents have a great impact on mechanical and underwater acoustic properties of the PUs obtained, the tensile strength, hardness and compressive strength increased with the growth of the hardness segment contents, and sample with 20 wt% has the best underwater acoustic properties, whose α can reach at 0.7.

1. Introduction

Polyurethane (PU) elastomers are generally formed by the reaction of isocyanates with polyols, and different specific chemical structures or synthesis process in PU can result in different properties [1].

Polyurethane elastomer can be regarded as a block copolymer composed of soft and hard segments, and the hard segment includes the isocyanate and the chain extender, while the soft segment is contributed to polyol. The good mechanical properties are due to the hard segment region, which has lots of hydrogen bonding in there, while the soft segment portion provides high elastic properties [2, 3]. Polyurethanes can be formed in different types from soft rubbers to plastics with hardness by changing the ratio of soft and hard segments [4]. Hard segment content has a great impact on the performance of the PUs, therefore, it is important to investigate the effect on the properties of polyurethane elastomer with different hard segment contents.

In this study, polyurethane elastomers with different segment contents were synthesized, and the thermal, mechanical and underwater properties were studied.

2. Experimental

2.1. Main materials

The Poly propylene glycol with a molecular weight of 2000(PPG2000) was provided by Shanghai Macklin Biochemical Co., Ltd. 2,4-tolylene diisocyanate(TDI) and triethanolamine(TEA) were purchased from XiYa Regent Co., Ltd and Tianjin Fuyu Fine Chemicals Co., Ltd., respectively. All raw materials need to be dehydrated before being used.

2.2. Procedure for composite Preparation

The PUs with different hard segment contents were obtained by one-step polyaddition process, and the molar ratio of NCO/OH is 1.7.

The polyurethane elastomers were fabricated according to the following steps : (i) Poly propylene glycol was added to a 250-mL beaker with a stirrer; then, TEA was added to the beaker under stirring by a high speed for 5 mins; (ii) TDI was added to the beaker, then, the mixtures were stirred by a high speed for 1min;(iii) the mixtures after stirring well were pumped for approximately 0.5-1.0 h to remove air bubbles at 80℃; (iiii) finally , the mixtures were cast in a mold ,and the polymerization was performed at 80℃ for 10 h and at 110℃ for 3 h. Figure 1 shows the step of synthesising PUs.

2.3. Measurement methods

Attenuated total reflection-Fourier transform infrared spectra were obtained with a ThermoFisher ISO10 (USA) spectrophotometer using thin films. Spectra were recorded from 400-4000cm^{-1} averaging 16 scans with a reflection mode.

Differential scanning calorimetry (DSC) was performed on a Netzsch DSC 204 F1 thermal analyser (Germany). The temperature range used was from -80℃ to 120℃ in N_2 atmosphere and the heat rate was 20℃/min.

Thermogravimetric analysis (TG) was measured by a Netzsch TG 209 F1 thermal analyser in the range of room temperature to 800℃ in N_2 atmosphere at the heat rate 20℃/min.

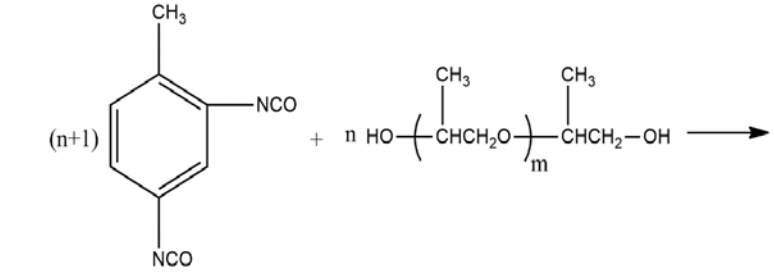
Dynamic mechanical analysis (DMA) was carried out with a Perkin-Elmer DMA 8000 thermal analyser (USA). The temperature range was from -100℃ to 100℃ at a fixed frequency 1 Hz and the heat rate was 3℃/min.

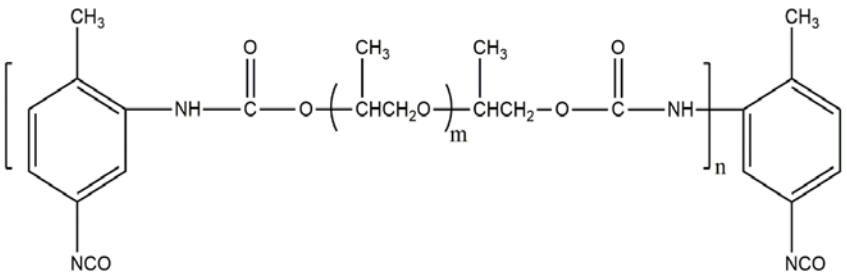
The hardness was obtained using the Shore A method on a LX-A hardness tester (China), according to Chinese Standard GB/T 531.1-2008.

The resilience was performed with an elastic meter according to Chinese Standard GB/T 1681-2009.

Mechanical testing (tensile testing, compression testing) were measured by the MTS GDX300 testing machine (USA) according to Chinese Standard GB/T 528-2009 and GB/T 7757-1993. The speed of tensile testing and compressive testing were 500mm/min and 10mm/min, respectively.

The underwater acoustic properties were obtained on a pulse tube according to Chinese Standard GB/T 14369-2011. The frequency was from 2-25 kHz. The temperature of the water was 28℃, and the sample needed to be soaked in water for 24 h before experiment.





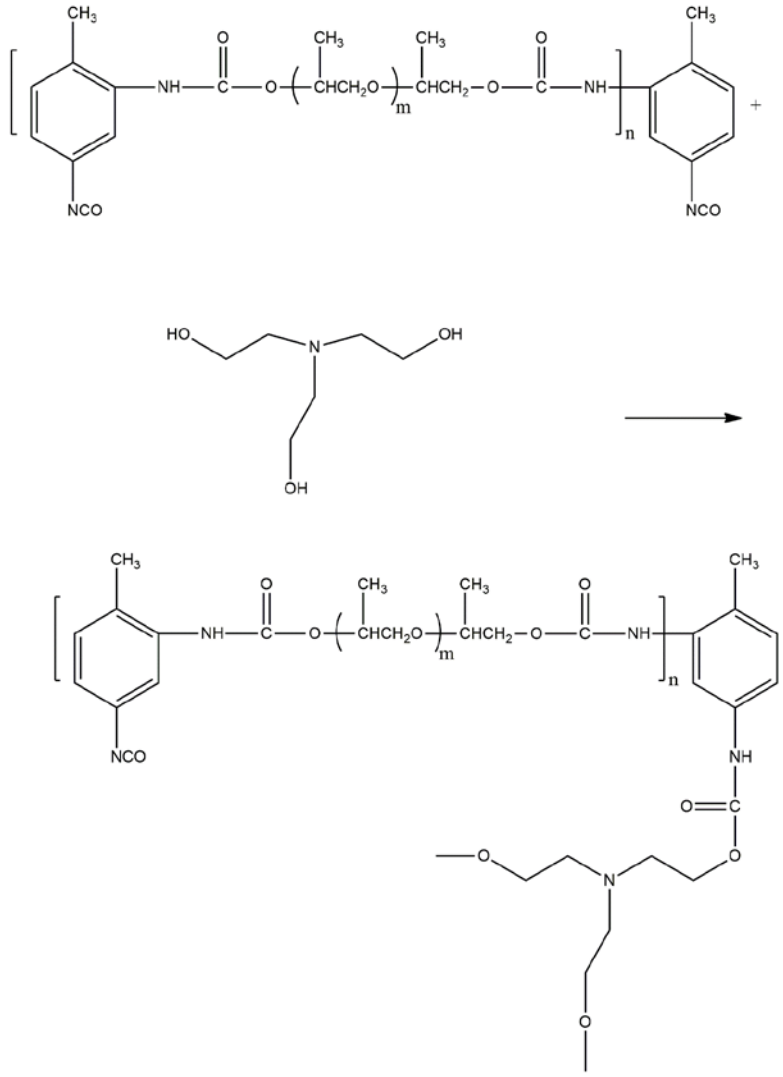


Figure 1. Synthesis of PUs

3. Results and discussion

3.1. Morphology

Figure 2 shows the photo morphologies of the PUs samples with the hard segment contents of 15, 20, 25, 30 mass%. It can be seen from the photo that PUs were transparent and colorless, and the color gradually deepens as the hard segment content increases.

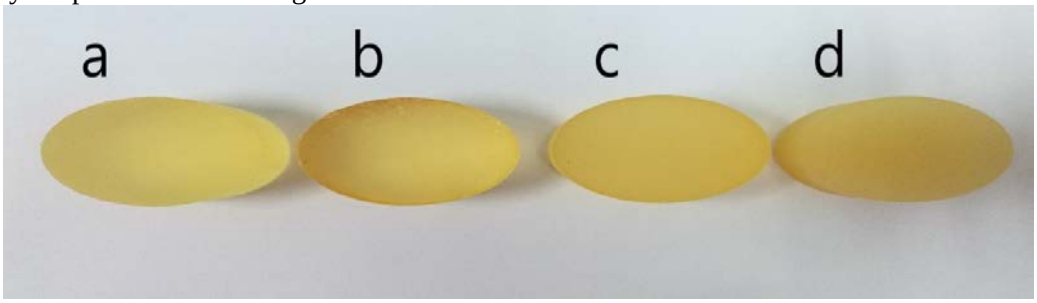


Figure 2. Photos of the samples with different hard segment contents: (a) the sample of 15 wt%, (b) the sample of 20 wt% and (c) the sample of 25 wt%, and (d) the sample of 30 wt%. (wt% represents the hard segment content, which is the mass ratio of hard segment and soft segment. Same as below)

3.2. FTIR

In order to analysis the chemical structure of the polymers obtained, FTIR analysis was conducted for PUs.

Fig.3 shows the absorption peaks of the PUs with different hard segment contents. The peaks at 2969 cm^{-1} and 2685 cm^{-1} were associated with asymmetric and symmetric C-H stretching of CH_2, respectively. In addition, the peaks at 1373 cm^{-1} and 1087 cm^{-1} were attributed to symmetric C-H bending of the CH_3 group and C-O stretching of the ether group, respectively. Further, the peaks at 1727 cm^{-1} and 3295 cm^{-1} were associated with stretching of C=O and N-H, respectively. It is significant that the peak at 2265 cm^{-1} of –N=C=O group was disappearing, which indicates that the reaction between TDI, PPG and TEA was completed.

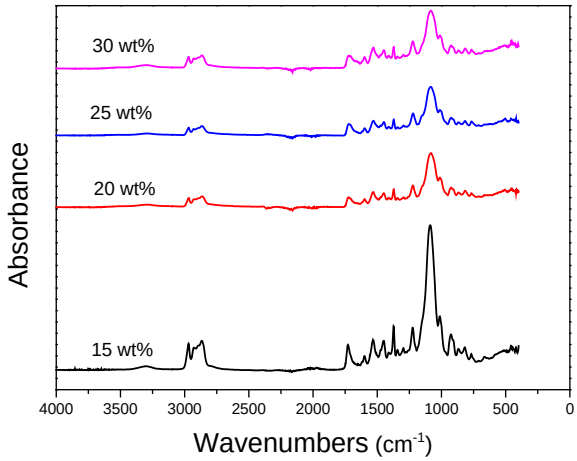


Figure 3. FTIR spectra of PUs with different hard segment contents

3.3. DSC

DSC measurements can analysis the glass transitions of PUs, which can indicate the flexibility of the molecular chain.Fig.4 shows the DSC curves of the PUs with different hard segment contents, and the temperature ranged from -80 to 120 ℃. In addition, numerical data determined from DSC curves was shown in Table 1. It can be seen from the Fig.4 that the curves of PUs with different hard segment contents were similar. The numerical data analysis of the T_g in Table 1 indicated that T_g increased with the growth of hard segment contents, and the T_g values of PUs with different hard segment from 15 wt% to 30wt% were -46.3℃ to -39.8℃. Further, the T_g values of all PUs obtained were below 0 ℃, which indicated the PUs were in high elasticity used in water.

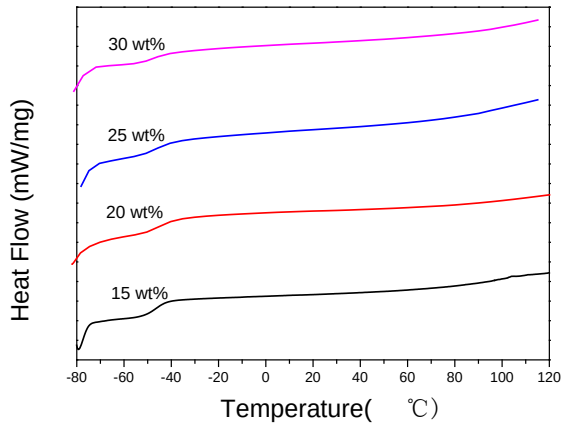


Figure 4. DSC curves of the PUs with different hard segment contents

3.4. TG

TG is a kind of measurement that can reveal the stability of the samples. Fig.5 and Fig6 shows the curves of TG of the samples and the curves of DTG of the samples, respectively. The temperatures of 5% (T5), 15% (T15) and 50% (T50) of mass loss can be found from DSC curves, and the temperatures of maximum rates of mass loss (T_{max}) can be found from DTG.

The temperature of a 5% mass loss of the samples ranged from 308 to 269℃， the temperature of a 15% mass loss of the samples ranged from 362 to 355℃ and from 393 to 402℃ for a 50% mass loss of the samples. The temperature of the decomposition increased with the growth of hard segment contents may be due to the improvement of the hydrogen bond and rigidity in PUs.

It can be easily seen from the DSC curves that the decomposition of the samples can be divided into two-step process. The first step (temperatures ranged from 250 to 350 ℃) of the decomposition was contributed to the di-isocyanate and chain extender, and the decomposition of PPG may be responsible for the second step (temperature is at approximately 400 ℃).

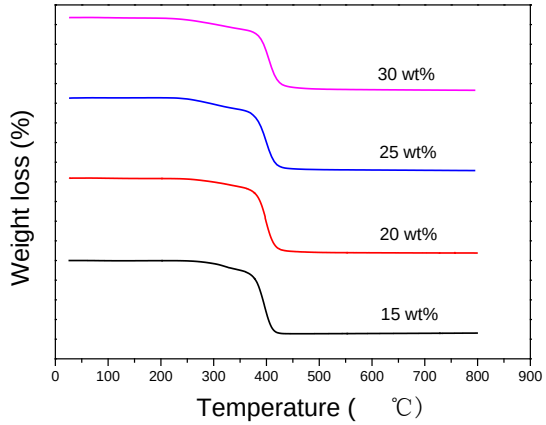


Figure 5. TG curves of the PUs with different hard segment contents

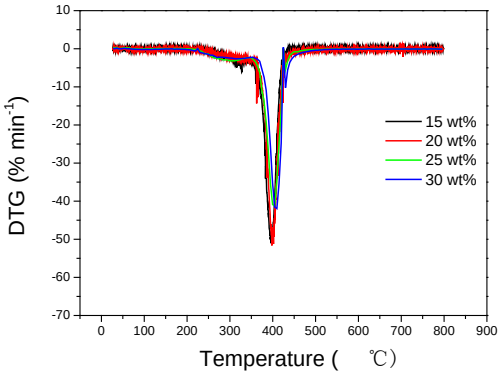


Figure 6. DTG-temperature curves of the PUs with different hard segment contents

Table 1. TG and DSC data of the PUs with different hard segment contents

Hard segment content/%	T_5 /℃	T_{15}/℃	T_{50}/℃	T_{max}/℃	T_g /℃
15	308	362	393	396	-46.3
20	300	369	397	399	-46.1
25	279	354	396	400	-43.6
30	269	355	402	404	-39.8

3.5. Mechanical properties

The mechanical properties such as hardness of Shore A, tensile strength, elongation at break, resilience and compression modulus are listed in Table 2, while the stress-strain curves are presented in Fig.7.

It can be seen from the Table 2 that hardness increased in Shore A with the growth of the hard segment contents, and the hardness value of 20 wt. % was 32% more than that of 15 wt%, while the hardness value of 25 wt% and 30 wt% were 113% and 227% more than that of 15 wt%, respectively. The great improvement of hardness performance in Shore A was due to the increased contents of hard segment, which resulted in the crystallization and cross-linking in PUs obtained.

As shown in Table 2, the tensile strength of the samples ranged from 1.20 to 4.18 MPa, while the elongation at break was in the range of 874 to 121 %. The tensile properties of the PUs were contributed to soft segments, which provided stretching and retracting properties for PUs.

We further studied the resilience properties of the PUs. Looking at Table 2, it is apparent that the resilience values decreased with the increasing of the hard segment contents.

As can be seen from the Table 2, the compression modulus values significantly increased with the growth of the hard segment content, and the compression value of 30 wt% was 228% more than that of 15 wt%, indicating that the hard segment content may be the key factor to improve the compression properties of the PUs.

Table 2. Mechanical properties of the Pus with different hard segment contents

Hard segment content/%	Hardness/Shore A	Tensile strength/MPa	Elongation at break/%	Resilience/%	Compression modulus/MPa
15	48	1.20	874	61	5.51
20	57	1.98	384	55	7.29
25	70	2.98	208	45	11.77
30	79	4.18	121	40	18.06

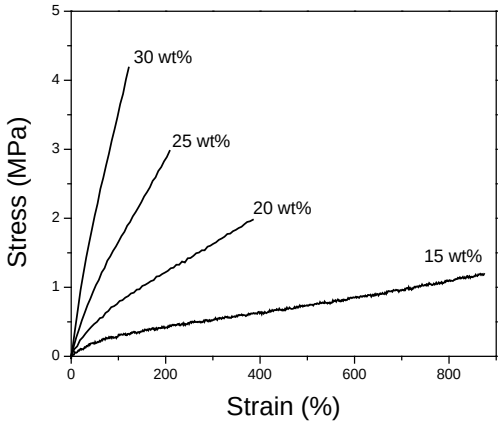


Figure 7. Stress-strain curves of the PUs with different hard segment contents

3.6. Underwater Acoustic Properties

Fig.8 shows the underwater acoustic coefficients with different hard segment contents, while $\tan\delta$ - temperature curves for the PUs with different segment contents are presented in Fig.9.

It can be seen from the Fig.8 that the α (underwater acoustic coefficient) of all PUs obtained increased with the growth of the hard segment contents, but there are differences between these curves. The curves of the PUs of 15 wt% and 30 wt% were similar, and the α of them were under 0.2, which indicated the underwater acoustic properties of the samples were not idea. The curve of the PUs of 20 wt% was above other curves in Fig.8, indicating that the PU of 20 wt% obtained had the best underwater acoustic properties. Looking at Fig.9, the $\tan\delta$ (damping factor) of PU of 20 wt% was

0.87, while the tanδ of 15 wt%, 25 wt% and 30 wt% were 1.35, 0.69 and 0.49, respectively. Tanδ revealed the properties of the loss of sound waves of the materials, and the higher the Tanδ, the better the sound absorption performance of the PUs. However, the values of tanδ need to be with a certain range due to the equation (1). The relationship between the reflection coefficient and tanδ of a material is given as follow [5-8]:

$$|\gamma| = (\frac{\eta^2}{4}) / (\frac{4+\eta^2}{4}) \approx \frac{\eta}{4} \quad (1)$$

Where γ is the reflection coefficient, η is tanδ. It can, therefore, be seen from the equation that reflection depends on its tanδ, indicating that the tanδ of a material too high or too low is not suitable for getting high α.

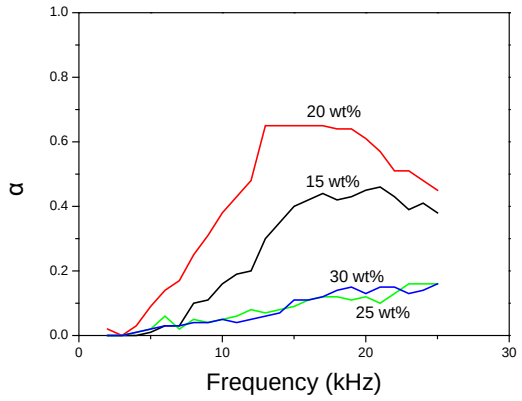


Figure 8. Acoustic absorption coefficient-frequency curves of the PUs with different hard segment contents

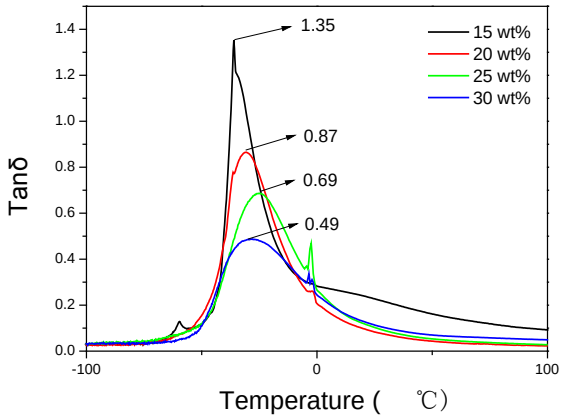


Figure 9. Tanδ -temperature curves of the PUs with different hard segment contents

4. Conclusion

(1) The elongation at break and resilience of the PUs obtained decreased with the increasing of the hard segment contents, while the tensile strength, hardness and compressive strength increased with the growth of the hardness segment contents.

(2) Hard segment contents have a great impact on underwater acoustic properties, and the sample with 20 wt% has the best underwater acoustic properties, whose α can reach at 0.7.

Acknowledgments
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