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RESEARCH ARTICLE

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Synthesis and surface properties of polyurethane modified by polysiloxane

Abstract A series of polyurethanes modified by polysiloxane (Si-PU) were synthesized based on 2,4-toluene diisocyanate (TDI), dihydroxybutyl-terminated polydimethylsiloxane (DHPDMS), polytetramethylene glycol (PTMG) and 1,4-butanediol (BDO). Fourier transform infrared spectroscopy analysis showed that DHPDMS had been incorporated into the polyurethane chains. With the increase of DHPDMS content, the water contact angle increased while the surface tension decreased. As the DHPDMS content increases above 5%, both the contact angle and the surface tension tend to approach a constant. The contact angle increases with increasing temperature, and it tends to approach a constant when the temperature is higher than 50°C. The result indicates that Si-PU exhibits good surface and mechanical properties when the DHPDMS content is 5%.

Keywords dihydroxybutyl-terminated polydimethylsiloxane, polyurethane modified by polysiloxane, contact angle, surface tension

1 Introduction

Polysiloxane materials are well known for their hydrophobicity, thermal stability and biological consistency [1–3], but some defects in tensile strength and adhesion property restrict their application in some areas. The polysiloxane modified polyurethane (Si-PU) obtained by incorporating siloxane units into the main chain of polyurethane possesses both the properties of polysiloxane and polyurethane. These properties do not only include good thermal stability, freeze resistance, hydrophobicity and insulativity, but also adequate flexibility, cohesiveness, wear resistance and surface property [4–13]. However, more siloxane components are needed to improve the surface property for this main chain type of Si-PU. A recent sudy has focused on the effect of polysiloxane content on the surface property at ambient temperature [14]; however, there is limited material about property influence at variable temperatures.

In this work, a series of Si-PUs was synthesized by using the self-made DHPDMS. The effects of DHPDMS content on the properties of Si-PU such as surface property and tensile strength were investigated using the measurement of contact angle, the analysis of surface tension and the determination of stress-strain. The influence of temperature on surface property was also studied.

2 Experimental

2.1 Materials

A mixture of 2,4-toluene diisocyanate (TDI, Shanghai Chemical Reagent Co., Ltd.) and *n*-hexane (50% volume ratio) was distilled under vacuum and used after filtration. Polytetramethylene glycol (PTMG, $M_n = 1000$ g/mol, Tianjin Petrochemical Co., Ltd.) and dihydroxybutyl-terminated polydimethylsiloxane (DHPDMS, $M_n = 2000$ g/mol, self made [15]) were desiccated at 110°C at vacuum for 1 h before use. 1,4-butanediol (BDO, Shanghai Chemical Reagent Co., Ltd.) was used as received.

2.2 Synthesis of Si-PUs

TDI, PTMG and DHPDMS were first added into a three-necked flask reactor fitted with a mechanical stirrer, a thermometer and a reflux condenser according to stoichiometric proportion (OH/NCO = 1/5; TDI/PTMG/DHPDMS = 5/1/0–5/0.9/0.1, mole ratio) and reacted at 90°C for 3 h under N_2 atmosphere. After the

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system temperature was dropped to room temperature, BDO (TDI/BDO = 5/3.5, mole ratio), a catalyst (di-*n*-butyltin dilaurate, 2–3 drops) and suitable butanone (as solvent) were added and then reacted at 80°C for 2 h until the NCO content reached the theoretical value, and the polyurethane modified by polysiloxane (Si-PU) was obtained. A series of Si-PUs with different DHPDMS content were synthesized by regulating the feed ratio of DHPDMS (0%, 1%, 3%, 4%, 5% and 9%, mass percent) in the total amount of original materials. The samples were named as Si-PU-0, Si-PU-1, Si-PU-3, Si-PU-4, Si-PU-5 and Si-PU-9, respectively.

2.3 Preparation of Si-PU films

A film with thickness of about 1 mm was prepared for further measurements and analyses of the contact angle, the surface tension and the stress-strain. This was done by casting the butanone solution of Si-PU on a leveled polytetrafluoroethylene Petri dish at room temperature for 7 days until the solvent was evaporated, and then dried at 60°C for 2 days in a vacuum system.

2.4 Measurements

Fourier transform infrared (FTIR) spectroscopy was done, with the FTIR spectrometer (VECTOR-22, Bruker) set in the range of 4000 to 400 $\mathrm{cm^{-1}}$. The measurement was carried out by casting the Si-PU diluted solution onto a NaCl pellet and then drying under vacuum.

The contact angle and the surface tension were measured by the sessile-drop method using a contact angle goniometer (JC 2000C1, Shanghai Zhongchen Digital Technical Equipment Ltd.) with a temperature control system. The contact angles at different temperatures were obtained by the variation of testing temperature, and the whole measuring process was monitored by an imaging apparatus. The result reported was the mean value of 3 times for each sample. Surface tension of the Si-PU film was calculated by the geometric-mean method [16], and water and *n*-octane were used as test liquids.

The stress-strain curves were obtained using a tensile tester (Instron 4466) with a cross head speed of 100 mm·$\mathrm{min^{-1}}$ at 25°C. The dumbbell-shaped specimen was 2 cm in length and 0.4 cm wide at the extension part.

3 Results and discussion

3.1 Analysis of FTIR spectra of Si-PUs

FTIR spectra of Si-PUs are shown in Fig. 1. All typical absorption peaks of polyurethane such as those at 3330 $\mathrm{cm^{-1}}$ (NH stretching vibration), 1710 $\mathrm{cm^{-1}}$ (C=O stretching vibration) and 1107 $\mathrm{cm^{-1}}$ (C–O–C stretching vibration) for urethane are displayed clearly, showing the existence of urethane in synthesized Si-PUs. It can be seen from Fig. 1 that the asymmetric stretching vibration of NCO group at 2270 $\mathrm{cm^{-1}}$ appears for all samples, which illustrates that there are NCO groups in Si-PUs. These groups remaining in Si-PUs will react further and cure during the application to enhance their properties. In addition, the absorption peaks at 1260 $\mathrm{cm^{-1}}$ (Si–CH_3 symmetry bending), 1060 $\mathrm{cm^{-1}}$ (Si–O–Si stretching vibration) and 803 $\mathrm{cm^{-1}}$ (CH_3–Si rocking vibration) illustrate that DHPDMS has been incorporated into polyurethane chains. Moreover, it can be seen that the variation of absorption strength at 803 $\mathrm{cm^{-1}}$ reflects changing DHPDMS content in the samples of Si-PUs.

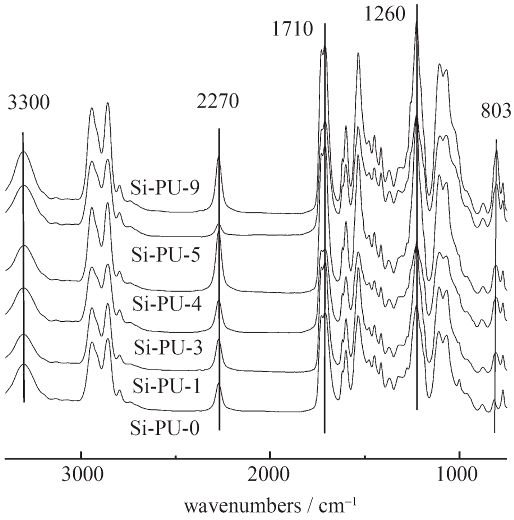

Fig. 1 FTIR spectra of Si-PUs

3.2 Water contact angle of Si-PU films

Water contact angle reflects the property of the unimolecular layer on the film surface. The relationship between the water contact angle and DHPDMS content is shown in Fig. 2. It can be seen that the contact angle increases with rising DHPDMS content when DHPDMS content is lower than 5%. This may be ascribed to the migration tendency of DHPDMS molecules caused by lower surface energy [17,18], which results in the reduction of surface tension and increase of contact angle from 73° for the sample Si-PU-0 to 103° for the sample Si-PU-5. But when the DHPDMS content increases above 5%, the water contact angle reaches the maximum of 103° and remains a constant even though the DHPDMS content increases continuously. Therefore the surface property can be improved significantly when the DHPDMS content is over 5%, but the water contact angle cannot be raised with a continuous increase in DHPDMS content. This can be

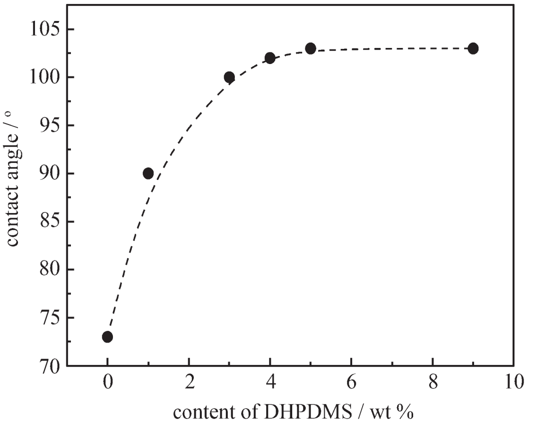

Fig. 2 Water contact angle increases with increasing DHPDMS content at room temperature

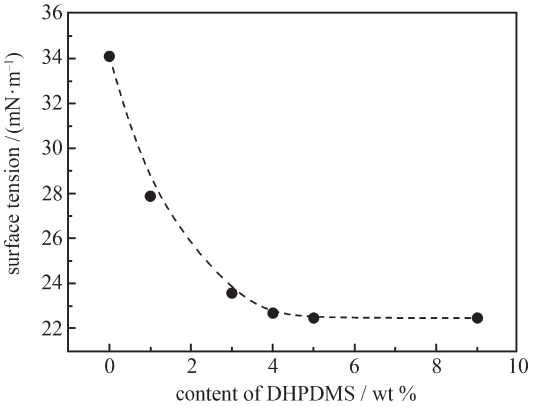

Fig. 3 Surface tension decreases with increasing DHPDMS content at room temperature

ascribed to the restriction for the migration of siloxane blocked in Si-PU chains and the limitation for the enrichment of DHPDMS on the surface layer of the film.

3.3 Surface tension of Si-PU films

The surface tension of solid film can be calculated by the geometric-mean method using the following equation [16,19]

$$\begin{aligned}\gamma_{L1}(1+\cos\theta_1)&=2\left(\gamma_{L1}^{d}\gamma_{S}^{d}\right)^{1/2}+2\left(\gamma_{L1}^{p}\gamma_{S}^{p}\right)^{1/2}\\ \gamma_{L2}(1+\cos\theta_2)&=2\left(\gamma_{L2}^{d}\gamma_{S}^{d}\right)^{1/2}+2\left(\gamma_{L2}^{p}\gamma_{S}^{p}\right)^{1/2}\end{aligned}\qquad(1)$$

where γ_S is the surface tension of solid film and composed of two components of the dispersion: $\gamma_S{}^d$ and the polarity $\gamma_S{}^p$. γ_{L1} and γ_{L2} represent the surface tension of two testing liquids, and are also divided into the dispersion components $\gamma_{L1}{}^d$, $\gamma_{L2}{}^d$ and the polarity components $\gamma_{L1}{}^p$, $\gamma_{L2}{}^p$ respectively. These symbols follow the relationships $\gamma_S=\gamma_S{}^d+\gamma_S{}^p$, $\gamma_{L1}=\gamma_{L1}{}^d+\gamma_{L1}{}^p$, $\gamma_{L2}=\gamma_{L2}{}^d+\gamma_{L2}{}^p$. In this way, if the value of $\gamma_{L1}{}^d$, $\gamma_{L1}{}^p$, $\gamma_{L2}{}^d$ and $\gamma_{L2}{}^p$ for two testing liquids are known, $\gamma_S{}^d$ and $\gamma_S{}^p$ can be calculated according to Eq. (1) by measuring the contact angles θ_1 and θ_2 of two testing liquids on the solid surface, which can further give the surface tension γ_S of solid film. Here the two testing liquids are water (L1) and *n*-octane (L2); corresponding $\gamma_{L1}{}^d$, $\gamma_{L1}{}^p$, $\gamma_{L2}{}^d$ and $\gamma_{L2}{}^p$ are 21.8, 51.0, 21.8 and 0 mN/m, respectively.

The relationship between surface tension and DHPDMS content is shown in Fig. 3. It can be seen that tension of Si-PU films decreases sharply with the increase of DHPDMS content. The surface tension approaches a constant when the DHPDMS content reaches 5%. This may be ascribed to the migration of siloxane units to the surface layer of Si-PU film [20–21]. But the surface tension of the film does not change clearly further when DHPDMS content reaches 5% because the migration is limited by the main chain movement.

Generally, the surface tension is influenced not only by the surface state (such as component and structure) but also the environment temperature. Although the temperature coefficient of surface tension of a polymer is not very large, the effect of temperature on the surface property is crucial in some conditions. The water contact angles of Si-PU films at different temperatures are shown in Fig. 4. It can be seen that the contact angle of all Si-PU films increases with increasing temperature from 20°C to 50°C, and the contact angle remains a constant when the temperature is over 50°C. Fig. 4 also shows that the contact angle increases with an increase of DHPDMS content at different temperatures, but this phenomenon is not distinct when the temperature is higher than 50°C. It is considered that as the migration speed of siloxane units increases at the elevated temperature, the contact angle increases rapidly. When the temperature reaches a definite value, the migrated siloxane component on the surface layer remains a constant while the migration of siloxane segments at the deep layer is limited by the main

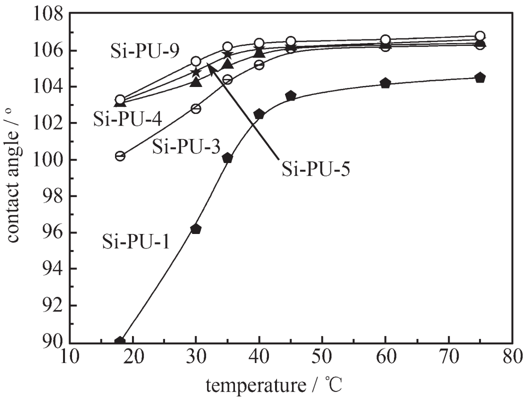

Fig. 4 Water contact angle of Si-PUs at different temperatures

chain movement, resulting in a constant contact angle. Moreover, it was found that the higher the DHPDMS content, the lower the temperature, at which the contact angle reached a constant. For the Si-PU samples with higher DHPDMS content, the surface formed a compact hydrophobic layer, so that the effect of siloxane enrichment on the contact angle becomes smaller. For lower DHPDMS content, the migration of siloxane segments has a relatively large effect on the formed surface hydrophobic layer.

3.4 Tensile strength and extension at break of Si-PU films

Generally, the mechanical strength of polysiloxane is much lower than that of polyurethane; the incorporation of polysiloxane into the polyurethane chain will decrease the mechanical property of polyurethane. The stress-strain curves of Si-PU films are shown in Fig. 5. It can be seen that the tensile strength of Si-PU samples has a little increase when the DHPDMS content is below 5%. The elongation increases from 370% to 440% when the DHPDMS content is higher than 5%. Combining the results of contact angle with the surface tension, it is concluded that the Si-PU can exhibit good surface and mechanical properties when the DHPDMS content is about 5%.

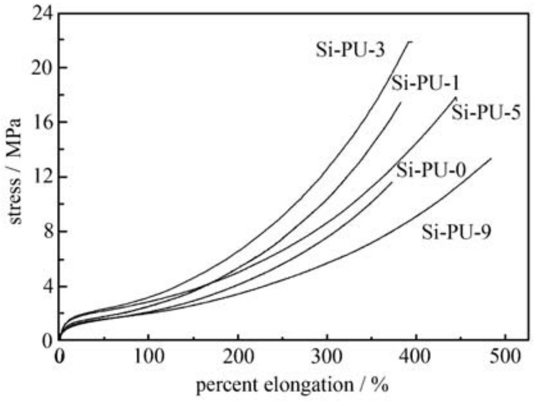

Fig. 5 Stress-strain curves of Si-PU films

4 Conclusion

A series of polyurethanes modified by polysiloxane (Si-PU) were synthesized with the DHPDMS content varying from 0% to 9%. The results show that the contact angle increases and the surface tension decreases with increasing DHPDMS content, and both remain a constant when DHPDMS content is over 5%. The contact angle of Si-PU increases with rising temperature and reaches a constant when temperature exceeds 50°C. It was found that the higher the DHPDMS content, the lower the temperature at which the contact angle reached the constant. In a word, synthesized Si-PUs can exhibit both good surface and mechanical properties when DHPDMS content is about 5%.

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