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EFFECT OF WATER VAPOUR ON THE AGING OF A POLYURETHANE ELASTOMER

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An analysis of differential scanning calorimetry and elastic modulus data for a polyester-based polyurethane elastomer is presented. The material was annealed at 170°C for 5 min. The DSC curves were recorded at different times following thermal treatment, with different aging conditions. In particular, aging in the presence of humidity and under vacuum has been analyzed and the results are discussed in terms of the Wilkes model based on disruption of the domain structure with thermal treatment and the restoration of the previous situation at room temperature.

Polyurethanes are block copolymers in which there are sequences of soft and hard segments [1, 2]. Soft segments are blocks with the glass transition below the normal operating temperature and are therefore rubbers, while hard segments are blocks with softening temperature (glass transition or melting point) above the normal operating temperature. Soft segments are usually polyether or polyester macroglycol, while hard segments are formed with an aromatic diisocyanate and a low molecular weight diol. The polar nature of the isocyanate group produces a strong molecular association between the hard segments, that causes the polymer to undergo phase separation in hard-segment and soft-segment-rich domains [3–6]. The hard domains act as physical crosslinks and as filling particles for the flexible soft segment phase and provide the material with high modulus and elastomeric properties. These materials behave like crosslinked elastomers at the temperature of use, but at high temperature they soften and flow like thermoplastics.

Materials with different properties can be obtained by changing the chemical nature of the soft segment, the molecular weight of the macroglycol, the percentage of the hard segment and the reaction conditions [6, 7]. The present paper deals with the time-dependence of the thermal and mechanical properties in a polyester-based polyurethane first investigated by Wilkes et al. [8–10]. They observed changes in the soft segment T_g, degree of phase separation and Young's modulus as a function of the time after thermal treatment. The results were explained by assuming a model in which the thermal treatment partially destroys the domain structure. At high

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temperature, although the incompatibility between the hard and soft regions still exists, a partially mixed state is possible as a consequence of the high molecular mobility. At lower temperature, even though the domain texture is thermodynamically favoured, the demixing process is not instantaneous because of the high viscosity of the bulk at room temperature. Therefore, the thermal treatment leads to a transitory state characterized by a partial mixing of more polar and less polar sequences. The first effect is a decrease of the elastic modulus for the reduced filling action of the partially destroyed hard domains, and the second is a shift to higher values of the soft phase T_g, as a consequence of partially mixed rigid polar sequences. The slow demixing that takes place at room temperature after thermal treatment produces a modulus recovery, and a T_g decrease with a rate depending on the domain formation kinetics. In order to verify and to give further support to this model based on the mixing and demixing of the hard and soft phases, in the present paper we have investigated the thermal and mechanical behaviour following thermal treatment in a polyester-based polyurethane with 40% hard segments. We attempted to influence the mechanism and the kinetics of domain formation by changing the aging conditions at room temperature. In particular, we have analyzed the transitory state under two different conditions, in the presence or in the absence of humidity, assuming that the polar molecules of water diffusing in the sample can effect the mixing and demixing process via polarity and mobility phenomena.

Experimental

Material

The sample was a polyester-based polyurethane, prepared by one-stage polymerization, in which the hard segment was 4,4'-diphenylmethane diisocyanate (MDI) extended with 1,4-butanediol (BDO), and the soft segment was polycaprolactone diol (PCL) with molecular weight $Mn = 530$. The content of hard segments was 40%. Further details are reported elsewhere [6, 7].

DSC traces were obtained on a Mettler differential scanning calorimeter in the range -60–$+120°$. The sample was aged both in the atmosphere and under vacuum after thermal treatment at 170° for 5 min.

Young's modulus was determined at 20° using a Tensilon UTM–II (Toyo Instruments) at a crosshead speed of 2 mm/min.

Results and discussion

Figure 1 shows a series of DSC traces obtained on the same sample with different aging conditions after thermal treatment at 170° for 5 min. Curve *a)* relates to the control (sample not treated thermally). The glass transition of the soft segments is at − 13°, and an endothermic peak is found at about 60°. This peak is to be ascribed to the short-range ordering of hard segment domains according to Cooper *et al.* [11, 12] and Samuel and Wilkes [13]. Curve *b)* relates to the sample immediately after thermal treatment. T_g is shifted upward (+8°) and the endotherm at 60° has disappeared. This behaviour is consistent with the Wilkes model. In fact, at high temperature there exist the thermodynamic conditions that favour disruption of the domain structure and time is needed to restore the original situation. Curve *c)* related to the sample aged for 2 days in the atmosphere. The value of T_g is restored, even though the endotherm is slightly below the original value, indicating that short-range ordering is not completely restored. In curve *d)* (aging for 1 week in the atmosphere), the DSC trace is perfectly identical to the control trace, indicating that the short-range ordering has been completely restored. Curve *e)* relates to the sample aged for 2 days under vacuum. The value of T_g is − 5°, that is higher than the T_g in the control trace, and the endothermic peak is decreased both in temperature and in size, indicating that aging for 2 days in the atmosphere produces a different effect compared to aging for 2 days under vacuum. This means that, although the amount of humidity absorbed is modest, the water accelerates the attainment of the

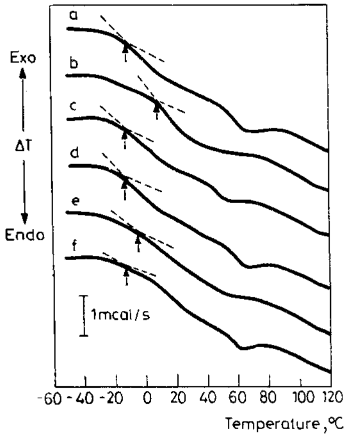

Fig. 1 DSC traces following a 5 min thermal treatment at 170°C with different aging: a) control; b) immediately after thermal treatment; c) aged 2 days in the atmosphere; d) aged 1 week in the atmosphere; e) aged 2 days under vacuum; f) aged 1 week under vacuum

original situation. A possible explanation of this is the decreased viscosity due to the absorption of water (plasticizer effect) and at the same time the formation of hydrogenbonds, that facilitates the aggregation of polar segments (hard-segment domains). Finally, in curve *f*) relating to the sample aged for 1 week under vacuum, the original situation is restored. This means that under vacuum too it is possible to reach equilibrium, but with slower kinetics. Other DSC traces have been recorded, but here only the more significant are reported.

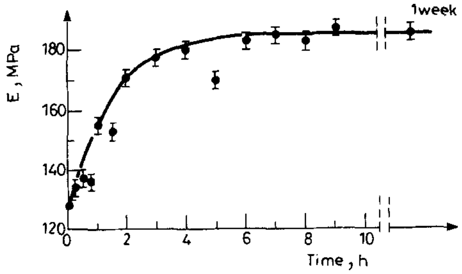

Fig. 2 Young's modulus *vs.* time following a 5 min thermal treatment at 170°C

Figure 2 shows Young's modulus as a function of the time following thermal treatment. The modulus increase is about 45% and the maximum is reached after about 5 hours. The lack of the filler effect due to the disruption of the hard domains produces a decrease of the modulus, and the restoration of the original value for the effect of phase separation is perfectly in agreement with the results of thermal analysis.

Conclusions

In the light of this experiment, we can say that water plays a relevant role in the kinetics of restoring thermal behaviour after heat treatment. We believe that water decreases the viscosity, and therefore promotes the transport of segments of chains, and also aggregates polar groups that produce hard-segment-rich domains.

References

1 A. Noshay and J. E. McGrath, Block Copolymers, Academic Press, 1977.

2 J. H. Saunders and K. C. Frisch, Polyurethanes Chemistry and Technology, Krieger Publishing, 1978.

3 S. L. Cooper and A. V. Tobolsky, J. Appl. Polym. Sci., 10 (1966) 1837.

4 G. M. Estes, S. L. Cooper and A. V. Tobolsky, J. Marcomol. Sci., C4 (1970) 313.

5 R. R. Lagasse, J. Appl. Polym. Sci., 21 (1977) 2489.

6 R. Russo and E. L. Thomas, J. Macromol. Sci., 22 (1983) 553.

7 C. G. Seefried, J. V. Koleske and F. E. Critchfield, J. Appl. Polym. Sci., 19 (1975) 2503.

8 G. L. Wilkes, S. Bagrodia, W. Humphries and R. J. Wildnauer, J. Polym. Sci., Pol. Letters, 13 (1975) 321.

9 G. L. Wilkes and R. J. Wildnauer, J. Appl. Phys., 46 (1975) 4148.

10 S. Abouzahr, G. L. Wilkes and Z. Ophir, Polymer, 23 (1982) 1077.

11 R. W. Seymour and S. L. Cooper, Marcomol., 6 (1973) 48.

12 H. N. Ng, A. E. Allegrezza, R. W. Seymour and S. L. Cooper, Polymer, 14 (1973) 255.

13 S. L. Samuels and G. L. Wilkes, J. Polym. Sci. Polym. Phys., 11 (1973) 807.

Zusammenfassung — Es wird eine Analyse von DSC-Daten und elastischen Modulwerten von Polyurethanelastomeren auf Polyesterbasis ausgeführt. Das Material wurde bei 170° 5 min getempert. DSC-Kurven wurden zu unterschiedlichen Zeiten nach der unter verschiedenen Alterungsbedingungen ausgeführten thermischen Behandlung aufgenommen. Insbesondere wurde die Alterung in Gegenwart von Feuchtigkeit und im Vakuum untersucht. Die Ergebnisse wurden dem Wilkes-Modell entsprechend diskutiert, das auf einer bei thermischer Behandlung eintretenden lokalen Zerstörung der Struktur und der Wiederherstellung der ursprünglichen Situation bei Raumtemperatur basiert.

Резюме — Представлен анализ данных ДСК и модулей упругости для полиуретанового эластомера на полиэфирной основе. Кривые ДСК были измерены в различные периоды после термической обработки эластомера при различных условиях его старения. Подробно изучено старение эластомера в вакууме и влажной атмосфере и полученные результаты обсуждены на основе модели Вилкса, основанной на разрушении при термической обработке доменной структуры эластомера и восстановлении ее при комнатной температуре.