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
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 $M_n = 530$. 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 $-60$ to $+120^\circ$. The sample was aged both in the atmosphere and under vacuum after thermal treatment at $170^\circ$ for 5 min.

Young's modulus was determined at $20^\circ$ using a Tensilon UTM-II (Toyo Instruments) at a crosshead speed of 2 mm/min.

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