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Water diffusion in a crosslinked polyether-based polyurethane adhesive

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ABSTRACT

Crosslinked polyurethanes (PU) are employed as structural adhesives. Research has been done extensively on the interaction of water with thermoplastic PU but is still largely unexplored in the case of PU networks. A chemically simple but well-defined PU is utilized here as a starting point to understand the influence of water in this kind of polymer. For up to 15 days of immersion in water, no changes in the chemical composition of the PU were observed in the IR spectra. Depending on temperature, water saturates the PU samples much earlier. Plasticization is the result as a significant decrease of the mechanical modulus and a glass transition shift to lower temperature is observed in the polymer. Interestingly, only some 70% of the water saturation is sufficient for maximum plasticization. It is concluded from the IR spectra that water debilitates the interactions between polymer chains within the network. The bridging of at least a part of the originally hydrogen-bonded urethane groups is substituted by hydrogen bonds between water and the urethane moieties.

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1. Introduction

Polyurethanes (PU) made by the polyaddition of two or more components often have to stick as bulk or coating to another material or are employed as structural adhesives for many substrates such as metals, concrete, wood or other polymers [1]. Their long-term performance determines the usability of such material combinations and adhesive joints. Therefore it has to be known how suitable PU adhesives are affected when they are exposed to environment. The presence of water is one of these environmental factors which may change their properties and thus impair the performance of the adhesive. Many analyses report on the diffusion of water and other solvents in polyurethane matrixes [2–16]. They mostly refer to linear thermoplastic polyurethanes. Only few chemically crosslinked systems were studied [8]. Moreover, the research on water diffusion in polyurethane adhesives is limited to commercial systems [17,18] or patents on formulations [19]. Some spectroscopic analysis was done on how water is absorbed in a varnish based on a polyester–urethane copolymer and its effect on the ester groups which later may break and blister the coating [15]. In another poly(ester urethane) the infrared bands assigned to water were examined. It was concluded that at the beginning of diffusion into the polymer, water forms double hydrogen bonds

with the carbonyls from two urethane groups as an intermediate step to bridge hydrogen bonds between C=O and N–H groups [20]. Infrared spectroscopy was also applied to a thermoplastic poly(ether urethane) in order to determine the influence of the soft segments on the water absorption ability of the polymer: an increasing ratio of soft to hard segments leads to a higher hydrophilicity in the polymer, since water was easily bridged to more urethane groups by hydrogen bonds [21]. The plasticizing effect of water on the molecular mobility of poly(ester-urethane) was also concluded from a decrease of the calorimetric glass transition temperature, T_g , of the polymer [3,22,23] and from a shift of the dielectric loss peak to lower temperatures [7]. On the other hand, a polyurethane made from a polyether with hydroxyl-terminated groups and 4-4'-methylene diphenyl isocyanate (MDI) showed no change in the position of dynamic T_g determined by mechanical relaxation spectroscopy. A redistribution of hydrogen bonds between ether and urethane groups triggered by water was offered as an explanation of this behavior [24].

In summary, most of the work on polyurethanes is related to semi-crystalline thermoplastics for membranes or coatings. The field of cross-linked adhesives is still largely unexplored and, in particular, no sufficient research is available on systems where additives and their influence on the properties are excluded.

In this paper, a crosslinked polyether–polyurethane synthesized only from polyols and diisocyanate is considered as a basic model for reactive polyurethane adhesives. A model of the mechanical behavior of that adhesive under the influence of moisture has been published recently [25]. Now, it is studied how water interacts with the network

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of this polyurethane. The results give the starting point for further investigations about the aging in PU adhesive joints in contact with water.

2. Experimental

2.1. Sample preparation

All preparation steps are carried out in dried air (dew point: $-60\text{ }^{\circ}\text{C}$ to $-50\text{ }^{\circ}\text{C}$) as an inert atmosphere for the polyurethane curing reaction. The resin component of the adhesive consists of two polyether alcohols with a ratio of 90 mol% of hydroxyl groups from a triol (Bayer Baygal K55) and 10 mol% hydroxyl groups from a diol (Bayer Desmophen 3600Z, see Fig. 1). The MDI isomer mixture (Bayer Desmodur VP.PU 1806, Fig. 1) serves as the isocyanate component. Diol and triol are mixed at room temperature (ca. $23\text{ }^{\circ}\text{C}$). Then, under permanent stirring, the isocyanate mixture is added to the equimolar ratio of isocyanate and hydroxyl groups. The reactive mixture is evacuated for 15 min at 0.01 mbar in order to remove air bubbles. After that the mixture is poured onto flat polystyrene plates to produce bulk samples with a thickness from 1 to 5 mm. The plates are cured for 7 days at room temperature and then post-curing at $60\text{ }^{\circ}\text{C}$ completed the reaction after another 7 days. Rectangular samples of about $90\text{ mm} \times 35\text{ mm}$ are cut from the plates for the water diffusion measurements.

2.2. Aging conditions and gravimetric test

Two environments were investigated for the water diffusion: immersion in bi-distilled water at $25\text{ }^{\circ}\text{C}$, $45\text{ }^{\circ}\text{C}$ and $60\text{ }^{\circ}\text{C}$ and air at 90% relative humidity and $60\text{ }^{\circ}\text{C}$. The measurements at $60\text{ }^{\circ}\text{C}$ will be used in future experiments as a reference for the aging of PU adhesive joints mentioned in Section 1.

For the immersion experiments the samples were stored in a closed recipient maintaining a constant water level during the experiment. The humid air is produced in another closed container by means of a saturated solution of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, analytical grade, Fluka) at the test temperature. The samples were weighed periodically with the help of an analytical balance (Kern ABJ320-4NM) until a constant mass was maintained.

2.3. Glass transition by modulated differential scanning calorimetry (MDSC)

Small bulk samples (ca. 5–6 mg) were cramped in an aluminum pan. Calorimetry is done in a Q100 (TA Instruments) under nitrogen gas (flow rate = 20 ml/min) with three cycles of cooling to $-70\text{ }^{\circ}\text{C}$ at -10 K/min and subsequent heating at 10 K/min to $80\text{ }^{\circ}\text{C}$. An underlying modulation rate of $\pm 1\text{ K/min}$ was used.

2.4. Uniaxial tensile stress test

Dog-bone samples of type 5 A (ISO 527-2:1996, ca. 1 mm thickness) were punched out of the PU plates. Before mechanical testing, the fresh samples were annealed in an oven at $60\text{ }^{\circ}\text{C}$ in ambient atmosphere for 15 min. After immersion in water at $60\text{ }^{\circ}\text{C}$, they were stored in a water bath at the same temperature until testing. Tensile stress tests were performed on a Kappa100 testing machine (Zwick, Germany) at 10^{-3} s^{-1} elongation rate and $25\text{ }^{\circ}\text{C}$ to a maximum elongation of $\epsilon = 0.35 \dots 0.4$ (i.e. well below any irreversible deformation).

2.5. Fourier-transform infrared microspectroscopy

Dry and water-saturated polyurethane blocks similar to those used for the measurement of water diffusion were cut and measured point by point from the edge to the center of the cut (see Fig. 2) to analyze how water affects the state of the polymer. Therefore the cut face was placed under the Ge crystal tip (truncated cone) of a μ -ATR-FTIR spectrometer (Bruker IFS 66 v/s with Hyperion 2000 microscope, p-polarized light, spectral resolution 4 cm^{-1}). 500 spectra were accumulated at each point (diameter ca. $100\text{ }\mu\text{m}$) on the cut.

3. Results and discussion

3.1. Water diffusion

The diffusion of water in the adhesive is modeled with the help of the Fick's second law of diffusion. The samples considered here have a thickness which at least is one order of magnitude smaller than the width and the length of the slabs. Hence, Fick's law can be written for one dimension as [26]:

$$\frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial x^2} \right) \quad (1)$$

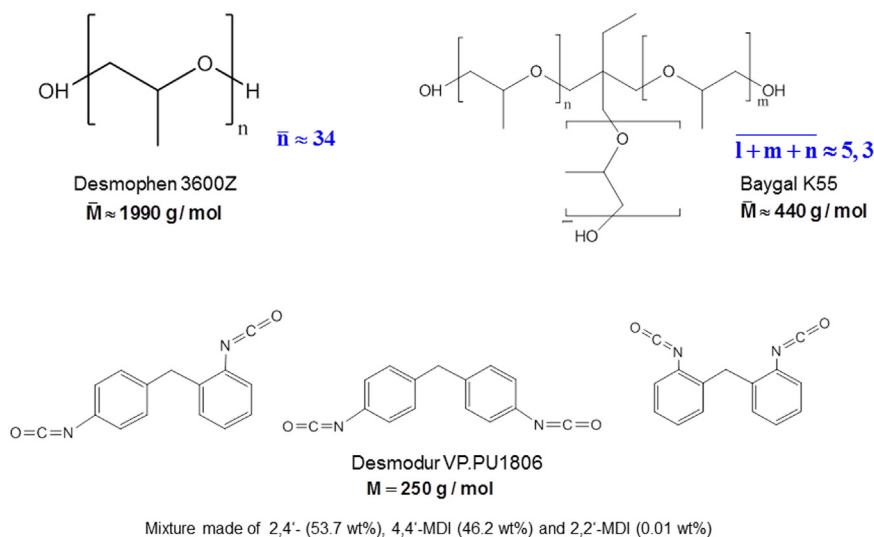


Fig. 1. Reactants used in the synthesis of the polyurethane adhesive.

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