



Relaxation behavior of polyurethane networks with different composition and crosslinking density



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ABSTRACT

The relaxation behavior of a series of solvent free polyurethane model networks with variable cross-link density prepared based on different commercial diols and a diisocyanate containing component are studied by differential scanning calorimetry (DSC), dynamic-mechanical analysis (DMA) and dielectric relaxation spectroscopy (DRS). A systematic decrease of the calorimetric glass temperature T_g as well as of the softening temperatures T_{α}^{DMA} and T_{α}^{DRS} from relaxation methods is observed with increasing length of the diol sequences between neighbored diisocyanate units acting as cross-linker. This trend is explained based on an internal plasticization of the polymeric network by long, highly mobile diol units containing an increasing fraction of methylene sequences. Cold crystallization effects are only indicated for the longest diol sequence under investigation. This is understood as a consequence of a large fraction of methylene sequences in combination with weaker geometrical constraints. Two secondary relaxations, β and γ , are observed in the glassy state for all amorphous samples at low temperatures by dielectric spectroscopy indicating the existence of localized motions in the polyurethane networks. Below T_g these relaxation processes are practically unaffected by changes in the length of the diol units and the softening behavior of the polymeric model networks. Interrelations between secondary β relaxation and cooperative α dynamics are indicated. An onset of the dielectric α relaxation strength $\Delta\epsilon_{\alpha}$ is observed for all amorphous polyurethane networks. A linear extrapolation of $\Delta\epsilon_{\alpha}$ vs. $1/T$ gives onset temperatures T_{on} which are in good agreement with $\alpha\beta$ crossover temperatures $T_{\alpha\beta}$ being the temperature where the difference between α and β relaxation times $\tau_{\alpha} - \tau_{\beta}$ approaches a minimum. This finding supports an onset of the cooperative α motions in the $\alpha\beta$ crossover region as reported in the previous literature for many other glass forming materials.

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1. Introduction

Polyurethane based materials are used in various fields of application because of their unique physical and chemical properties. Prominent examples are applications in arising technology fields such as coatings, adhesives, fibres, foams and thermoplastic elastomers [1–4]. Another interesting class of related materials are biocompatible composites based on polyurethane copolymers [5–7]. It is known that the properties of polyurethane based systems strongly depend on the polymolecularity of the soft segment

as well as on the overall chemical architecture of the components. Based on this phenomenological knowledge the properties of urethane-based materials can be systematically changed by variation of chemical composition, microstructure and molecular weight of the soft and hard segments [8,9]. By changing the functional groups proportion of the components $r_H = [OH]/[NCO]$, networks with variable topology were obtained [10,11]. In general, a complex three-dimensional network is formed which can be different regarding crosslinking density, functionality of the cross links (isocyanates) and the chain length of the binding molecules (diols). The network structure was investigated in different experimental and theoretical studies [12–16] and it was demonstrated that polyurethane networks possess commonly elastomer properties since they are used above their glass transition temperature T_g .

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Many of the versatile properties of segmented polyurethanes making such materials interesting for industrial applications have been related to a nanophase separation tendency. Hence, several studies in the literature deal with the factors controlling nanophase separation and the development of experimental methods allowing to study nanophase separation in segmented polyurethanes [17–21]. Theoretical studies focusing on a statistical description of the network formation of polyurethane elastomers from soft segments and high polar hard segments are reported [22]. Dielectric studies on linear polyurethanes and polyurethane networks crosslinked using three-arm poly (propylene oxide) stars [23], molecular dynamics studies on linear and hyperbranched polyurethanes [24], as well as investigations of structure-property relations in polyurethanes with ionomers by thermoanalytical, spectroscopy or electrical methods [25–28] were performed. Structure and elasticity of model polyurethanes with well defined architecture were studied by Ilavsky and Dusek et al. [22,29] while the influence of the crosslink agent on the relaxations processes was systematically investigated by Opera [30,31].

In case of the commercially available polyurethane components Desmodur™ and Capa™, the NCO groups of Desmodur™ define the functionality of cross links, while different types of Capa™ can be used as binding agent between the polyisocyanates defining the mesh size of the network. Their length controls the distance between the cross links. The bridge length is in fact depending on molecular weight of the diol component since Capa™ contains only linear polyether diols. Hence, a high molecular weight of these diols causes a larger distance between two neighbored cross-links. It is known, that stiffness and glass transition temperature are usually systematically affected by the length of these bridges. This allows to prepare polyurethane model networks with systematically varied microstructure and network topology.

Aim of this work is to study polyurethane model networks prepared using different combinations of Desmodur™ and Capa™ by DSC and relaxation spectroscopy methods in order to learn more about the influence of network composition and topology on the overall relaxation behavior. Of special interest are (i) a better understanding of systematic changes in the softening behavior (T_g , T_{α}^{DMA} , T_{α}^{DRS}) depending on the diol units used and (ii) interrelations between the segmental dynamics (α relaxation) and localized motions seen as β and γ relaxations. Similarities to other polymeric systems containing short methylene sequences forming alkyl nanodomains will be used to explain details of the relaxations dynamics as well as the molecular origin of changes in the softening behavior. Analogies between polyurethanes model networks and many other glass forming systems regarding the relaxation behavior in the $\alpha\beta$ crossover region are discussed.

2. Experimental

2.1. Materials and sample preparation

Polyurethane networks with variable cross-link density are prepared based on different commercial Capa™ (Perstorp Group) and Desmodur™ (BayerMaterials Science) components. Capa™ components being polyols with variable average lengths are used in combination with Desmodur™N3300 being a 1,6-hexamethylene diisocyanate-based system acting as crosslinking agent.

ϵ -caprolactone based systems of the Capa™2000 series exhibit a practically linear structure terminated with primary hydroxyl groups and have defined molecular weights (Scheme 1). The OH-values of the used Capa™2000 types were determined by titration. Their molecular weight correlates with the net bridge length of polymer networks if cross-linked with 1,6-hexamethylene diisocyanate. Capa™2043 is derived from 1,4-butanediol while all

other diols such as Capa™2054, Capa™2085, Capa™2125 and Capa™2205 are derived from diethylene glycole. Molecular weight M_w as well as average number of caprolacton units per diole n are systematically varied in the chosen diol series (Table 1) [32].

As cross linkers 1,6 hexamethylene diisocyanate (HDI) based mixtures from trimers, pentamers and heptamers are used. Main component in the used Desmodur™N3300 system (Scheme 1b) is the trimer of HDI [33]. The average functionality F specifying the mean number of free functional groups, in this case NCO-groups, per cross-linker molecule is $F = 3.5$ for Desmodur™N3300.

The set specification of Capa™ and Desmodur™ was used for getting suitable mixtures with well defined molar ratios of the functional groups. In order to obtain a homogenous film, small amounts (0.2–0.5 wt%) of the additive BYK™332 (BYK Additives & Instruments) is added dropwise to the Capa™, followed by addition of Desmodur™ during stirring at 50 °C. This mixture was poured in preheated dishes of glass or Al-foil, which were heated within 30 min to 120 °C. After 24 h at 120 °C the preparation of the desire film was complete. The samples were than cooled down to 23 °C and investigated within two days.

2.2. Methods

Dielectric spectroscopy is used to study the frequency-temperature behavior of relaxation processes in the investigated polyurethane series. Dielectric measurements are performed with an impedance analyzer (Hewlett Packard HP 4282 A) covering the frequency range from 0.1 Hz to 1 MHz at sample temperatures ranging from –100 °C to 100 °C. Polyurethane films with a thickness of about 200 μm kept between two gold-plated stainless-steel electrodes (diameter 20 mm) are used as sample capacitors. The samples are exposed to a temperature-controlled nitrogen gas stream. The sample temperature is measured with a PT100 sensor directly at the lower electrode and a Quatro Cryosystem from Novocontrol GmbH is used as temperature controller. The dielectric measurements are performed with the following steps: The sample (i) was annealed at –100 °C, (ii) ramped with a rate 10 K/min to 100 °C measuring four frequencies in order to find relevant relaxation processes, (iii) cooled down and annealed again at –100 °C, and (iv) heated in steps of $T = 5$ K or $T = 2$ K (depending on the temperature region) from –100 °C to 100 °C. In the latter case, the samples are annealed at least 15 min at each temperature in order to make sure that the control temperature was constant within an interval of ± 0.02 K.

Dynamic-mechanical measurements were carried out using a DMA242c dynamic mechanical analyzer (Netzsch GmbH). Oscillatory tests at a frequency of 1 Hz are performed in tensile mode with a strain amplitude of 70 μm and a prestrain of 70 μm . Stripes with a dimension of $40 \times 5 \times 0,1$ mm³ were cut from the prepared films. The dynamic modulus E^* was measured in the range from –120 °C to 50 °C, at a heating rate of 3 K min^{–1} under nitrogen atmosphere. The variation of storage modulus (E'), loss modulus (E'') and loss tangent ($\tan\delta = E''/E'$) as a function of temperature was recorded. Before measuring, the samples have been pretreated in an oven at 60 °C for at least 24 h to minimize the influence of humidity.

Differential scanning calorimetry (DSC) measurements were performed using a DSC200 (Netzsch GmbH). Measurements are carried out according a standard program. Samples with a mass of about 10 mg were (i) cooled from 25° to –120 °C at a rate of –10 K/min, (ii) held at –120 °C for 10 min, (iii) heated from –120 °C to 100 °C at a rate of +20 K/min, (iv) annealed at 100 °C for 10 min, (v) cooled to –120 °C with a rate of –10 K/min, (vi) held at that temperature for 10 min and finally (vii) reheated at a rate of +20 K/min to 100 °C. This second heating scan has been further evaluated. The glass temperature is determined based on a midpoint construction.

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