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The influence of montmorillonite and bentonite addition on thermal properties of polyurethanes based on aliphatic polycarbonate diols

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ABSTRACT

Segmented polyurethanes based on hexamethylene-diisocyanate, aliphatic polycarbonate diol and 1,4-butanediol as chain extender were prepared in a bulk by one-step procedure. The structure of elastomeric materials obtained in the form of films and sheets was varied eighter by polycarbonate diol type or chain extender content. The organically modified particles of montmorillonite and bentonite were used as reinforcing fillers. The glass transition temperatures of prepared hybrid materials were determined by modulated differential scanning calorimetry MTDSC. Thermal stability of obtained materials has been studied by thermogravimetry coupled with DSC from an engineering perspective to determine service temperature of prepared elastomeric composites.

1. Introduction

Due to the wide range of compositions possible, polyurethanes have found extensive use in numerous commercial applications such as coatings, foams, adhesives, sealants, synthetic leathers, membranes, elastomers as well as in many biomedical applications. Although these materials contain repeating urethane groups, other moieties such as urea, ester, ether and aromatic may also be present in the structure. The flexibility available in the selection of raw material components such as di-/tri-isocyanates, polyols, as well as chain extenders have made it possible to custom tailor the properties to a large extent [1]. A correct design of the segmented polyurethane structure becomes crucial as it provides the desired properties that meet customers' needs. The mass fraction, molecular mass, polydispersity of hard and soft segments, as well as manufacturing conditions are affected on morphological factors, such as degree of hard/soft macro- and micro-phase separation, crystallinity, and domain size. All these factors define properties, such as hardness, stiffness, tensile strength, and clarity of materials [2]. The high polar nature of the urethane linkages is responsible for the thermodynamic micro-heterogeneous phase separation and often in combination with the crystallization of both segments leads to the formation of hard and soft domains, which in turn regulates the behavior of materials [3]. Soft segments are generally derived from polyether or polyester polyol, whereas diisocyanate via conversion to urethane linkage NHCOO forms the hard segment. The aliphatic segmented polyurethanes are very promising materials due to their suitable end-use properties, and hence, they can be used for various applications [4–6]. Manufacturing of polyurethanes is often based via crosslinking of network precursor (prepolymer) prepared in the first step. The urethane linkage is a result of the reaction between an NCO group from isocyanate component and hydroxyl group OH from polyol. If a stoichiometric excess of isocyanate is used, the resulting urethane chains are NCO terminated and the product is called NCO terminated precursor. In general, these materials derive their specific properties from the thermodynamic incompatibility of the polymer segments and their consequent micro-phase separation on a length scale comparable to the dimensions of the chain segments. Hard segment packing is affected by some structural factors: the isocyanate size and symmetry; the chain extender length and functionality, the polyol type, molecular mass, and functionality [7]. Other factors influencing the phase separation are crystallinity, and tendency for soft segment–hard segment hydrogen bonding [8]. In industry, considerable attentions have been devoted to new polycarbonate-based polyurethane elastomers due to their improved mechanical performances [9] and their better anti-hydrolyzation and anti-oxidation properties compared to

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the traditional polyurethanes [10,11]. The aliphatic polycarbonate polyurethane can be used for industrial parts, building materials, sports goods, medical equipment [7,12,13], and even artificial tissues [14]. According to publication of Tetsushi et al. [15] new types of polycarbonate diols, which are liquid at room temperature, are easy for handling, and improved in flexibility and chemical resistance when changing to polyurethane, compared with conventional commercially available (solid at laboratory conditions) polycarbonate diols. Dispersing nanometer-scale inorganic particles in a polymer networks offers the potential of creating new materials, the properties of which arise from the synergies between the components. Using polyhedral oligosilsesquioxane nanobuilding blocks can be used to create a wide variety of hybrid materials, where precise control of nanostructures and properties is required. In polyurethane/polyhedral oligosilsesquioxane nanohybrids, the degradation temperatures are shifted toward higher temperatures that can be determined using thermogravimetry [16]. The polymer nanocomposites based on minerals with a layered structure that are used as fillers are systems containing reinforcing elements in the form of plates approximately 1 nm thick with different ratios of the length to the crosssection size [17]. It was shown that the rigid amorphous fraction of the polyurethanes increases with increasing volume fraction of organically modified montmorillonite [18]. The knowledge of thermal properties and the interplay of the constituents' phases make it possible to manufacture polyurethane materials having properties combinations that are better than those found in other polymeric materials, specifically biodegradable elastomeric materials with high stiffness and tear resistance [19]. Upon thermal excitation, the covalent bonds in polyurethane chains undergo complex vibration and rotation within their local space. With further excitation, these bonds can break to form a variety of fragment radicals or small molecules, which may further mutually recombine or undergo further fragmentation [20]. Ultimately, the resulting fragments may be vaporized, diffused out, or carbonized. The decomposition process ends with the loss of all volatile material and with the formation of char that does not change further above the char temperature. A number of investigations have been made to determine the effect of the chemical structures of chain extender on the thermal stability of polyurethanes. The chain length, molecular volume, functionality and the conformational arrangement can influence hard segment packing, crystallinity and thus the thermal stability of the hard domains. This paper presents our results on thermal stability investigation of polycarbonate-based segmented polyurethanes which structure has been varied either by polycarbonate diol type or aliphatic chain extender content. The additional goal has been focused to the influence of organically modified montmorillonite and bentonite on the thermal properties of hybrid materials obtained in the form of films and sheets.

2. Experimental

2.1. Materials

The primary materials were polycarbonate macrodiols with molecular mass ca. 1000 (PCDL T5651 and T4671), kindly provided by Asahi Kasei Chemical Corporation. All characteristics of macrodiols were given by the supplier. For PCDL T5651: OH value: 111.4 mg KOH/g; water content: 0.0052 wt.%; viscosity at 50 °C: 1619 mPa. For PCDL T4671: OH value: 109.9 mg KOH/g; water content 0.0072 wt.%; viscosity at 50 °C: 2388 mPa. The hexamethylene-diisocyanate (HMDI), 1,4-butane diol (BD) and the catalyst, dibutyltin dilaurate (DBTDL), all Fluka, were used. The catalyst solution was prepared in oil Marcol (20%). As fillers, organically modified montmorillonite (Cloisite®15A produced by Southern Clay Products, Inc.) and organically modified bentonite (Bentonite for organic systems, BO, Fluka) were used.

2.2. Polyurethane film preparation

The films were prepared by one-step technique. The ratio of NCO and OH groups, called isocyanate index ($r = [\mathrm{NCO}]/[\mathrm{OH}]$) was kept constant: 1.05. In this contribution, the ratio of OH groups from polycarbonate diol and chain extender ($R = [\mathrm{OH}]_{\mathrm{diol}}/[\mathrm{OH}]_{\mathrm{extender}}$) was eighter 1 or 10. Catalyst concentration, c_{DBTDL}, was 0.05 m/m%. One serie was prepared without chain extender. The chain extender (1,4-butane diol) mixed with catalyst was added to diol, and the reaction system was degassed. In the final step, diisocyanate was put to the reaction vessel. Then, the reaction mixture was degassed again, in order to remove the residual bubbles. Such prepared reactive system was spread on polypropylene sheet. The constant layer thickness (500 μm) was obtained using a ruler. Prepared samples were kept in an oven under nitrogen atmosphere at 90 °C for 24 h. The filled samples were obtained by the same procedure, except that the filler particles were left to be dispersed in polycarbonate diol over the night.

2.3. Polyurethane sheet preparation

The chain extender and catalyst were placed into the reaction vessel containing diol and blended at room temperature. After that, the reaction mixture was degassed during 5 min. Hexamethylene-diisocyanate was added as the last component. Finally, reactive system was placed to the teflon molds. The molds were transferred to an oven and left there at 90 °C during 24 h. The thickness of prepared sheets was 2 ± 0.1 mm.

2.4. Modulated differential scanning calorimetry

Thermal behavior of chosen samples was estimated by modulated differential scanning calorimeter (MTDSC, Q1000 TA Instruments). The measurements were done in sealed aluminum pans from −80 to 200 °C with a heating rate of 3 °C/min. The sample masses were about 3 mg. A purge gas was nitrogen. The instrument was calibrated using an indium standard. A modulation period was 40 s with modulation temperature amplitude of ±0.5 °C. MTDSC results were obtained from the first scan.

2.5. Thermogravimetry coupled with differential scanning calorimetry (SDT analysis)

Thermal stability of the synthesized materials was determined by thermogravimetry instrument coupled with DSC (SDT Q600 TA Instruments). The measurements were performed from room temperature to 500 °C in flowing nitrogen atmosphere (100 cm^3/min), with a heating rate of 20 °C/min and sample masses of about 3 mg, employing open alumina crucible and a corresponding empty referent crucible.

3. Results and discussion

3.1. Polycarbonate-based polyurethane structure

Segmented polyurethanes have chains composed of alternating low glass transition (soft) segments and more rigid polar hard segments which soften much above room temperature. The morphology of prepared segmented polyurethanes is influenced by structure of chains given in Fig. 1.

The hard domains in obtained polyurethane samples consist of segments formed from hexamethylene-diisocyanate (HMDI) and chain extender (1,4-butanediol), while the soft segment is based on