

Thermoplastic polyurethanes with polycarbonate soft phase: Effect of thermal treatment on phase morphology

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ABSTRACT

The thermal sensitivity of thermoplastic polyurethanes with polycarbonate soft phase (PCU) is considered. Thermal treatments were coupled with differential scanning calorimetry and infrared spectroscopy to investigate the effect of temperature on the phase morphology. PCU is characterized by a biphasic morphology: ordered hard polyurethane micro-domains are dispersed in a soft phase matrix, containing both hard and soft segments. Heating may completely destroy the short and long range order or simply change it. The infrared behaviour of the CO and NH stretching regions gives information on the organization of the segments. Thermal treatments above the processing temperature lead to an unstable monophasic morphology, that at room temperature is subjected to segregation of the hard segments, in order to recreate the biphasic morphology. Annealing treatments below the processing temperature cause reorganization in the hard micro-domains, inducing changes in their amount and dimensions. The result of the annealing depends on the temperature and on the exposure time. The thermal sensitivity also involves the chemical properties, given the thermal lability of the urethane bonds in the range of the processing temperature.

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1. Introduction

The interest in polyurethanes arises from their heterogeneity in chemical and physical properties. Thanks to the opportunity to incorporate other functional groups in the polymer network, producing varied copolymers, polyurethanes properties may range from rigid hard thermosetting materials to softer elastomers. Thermoplastic polyurethanes (TPUs) combine elastomeric behaviour with the possibility to be processed with conventional thermoplastic machinery. Thanks to the large range and exceptional mechanical properties, TPUs have many uses that cover medical technology, shoe manufacturing, car industry and many others [1].

TPUs are linear block copolymers consisting of two building blocks: hard segments (HSs) and soft segments (SSs). The HSs are polyurethane blocks, based on diisocyanate and chain extenders, commonly diols, while SS blocks are based on macrodiols, such as polyester, polyether and more recently polycarbonate [2,3]. The introduction of polycarbonate blocks extended the application to long-term implants in the biomedical field, thanks to their higher biostability and biocompatibility [4].

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Depending on the thermodynamic incompatibility between HSs and SSs, TPUs are characterized by phase separation into a soft phase (SP) and a hard phase (HP). In block copolymers characterized by complete immiscibility, a complete phase separation occurs leading to different morphologies of the bulk, exhibiting a characteristic glass transition temperature (T_g) for each phase [5]. In TPU the phase separation is not complete because of the restriction imposed by the topology of the block copolymers that causes a certain degree of mixing [6]. In addition, the shorter HSs proved to be soluble in the soft phase [7], so the SP contains both HSs and SSs. Consequently, the T_g of the SP will depend on the relative amount of the two different segments and can be predicted with equations such as the Fox equation, in which the T_g of the mixed phase is determined as a combination of the T_g and the weight fractions of the single components of the phase [5,6].

The hard phase is constituted of polyurethane blocks, ordered in a three dimensional network of hydrogen bonds among the stacked chains, segregating from the soft phase in hard micro-domains [8]. Those micro-domains being linked to the soft phase they act as physical crosslinks, causing a typical elastomeric behaviour at room temperature, while retaining thermoplastic processability, on heating.

As a consequence of this complex morphology TPUs show multiple thermal transitions in differential scanning calorimetry (DSC) [9]. In addition to the T_g of the SP, other endothermic signals

are observed and associated to the short and long range order in the HP [10]. The endotherm at lower temperature (generally referred with T_i) is related to the disordering of the hard micro-domains [11]. Some authors correlated the value of this temperature to the number of polyurethane units in the blocks involved in the micro-domain [12,13]. The short range order, which depends on the thermal history of the polyurethane, can be increased by annealing without affecting any long-range order which may be present [10,14]. The second endotherm (T_{ii}), that is detected at temperature higher than T_i , depends on the copolymer composition and is due to the micro-phase mixing transition, in which the HSs dissolve completely in the SP creating a unique and homogeneous phase [6]. This temperature is independent of the thermal history of the TPU [15].

Some of the transformations observed during thermal treating in DSC can be observed even in FT-IR [16,17]. Urethane bonds show different carbonyl stretching ($1800\text{--}1650\text{ cm}^{-1}$): the absorption peak at lower frequency is referred to strongly hydrogen-bonded carbonyls, while the absorption band at high frequency is assigned to free (not involved in hydrogen bonding) carbonyl groups [18,19]. Between these two signals are located the vibration of the loosely hydrogen-bonded carbonyls located in the soft phase. On the other hand, hydrogen bond formation can be even observed in the NH stretching region ($3450\text{--}3250\text{ cm}^{-1}$), where a broad band belongs to the stretching of hydrogen bonded N–H groups. Monitoring of the infrared behaviour of these species during thermal treatments allows evaluation of the change in their chemical environment and then in the interaction among the segments.

In the literature, several morphological models have been proposed to describe the morphology of TPUs [9,20,21]. However, these models are often contradictory, since the morphology of the phases is not universally described, but rather strongly dependent on the amount, size and chemical nature of the different blocks.

Obviously, the phase morphology of a TPU will influence the mechanical behaviour of the material, thus the aim of this work was the study of the effects of thermal treatments on the phase morphology of a PCU developed for medical application, in order to prevent the phase morphology degradation during the medical device production. Taking into account the thermal stability of polyurethanes [22–24], thermogravimetric measurements have been performed on PCU to evaluate the thermal stability.

2. Experimental

2.1. Materials

The block copolymer commercialised under the trade name of Bionate[®] is a polyurethane, containing a polycarbonate macrodiol as soft segments. The hard segments are based on 4,4'-diphenylmethane-diisocyanate (MDI) and 1,4-butanediol (BD) as chain extender, whereas the soft segments are poly(1,6-hexyl 1,2-ethyl carbonate) diols (PHECD). The chemical structure of this polyurethane is schematized in Fig. 1. The polycarbonate urethane is produced by DSM PTG (The Polymer Technology Group Inc.,

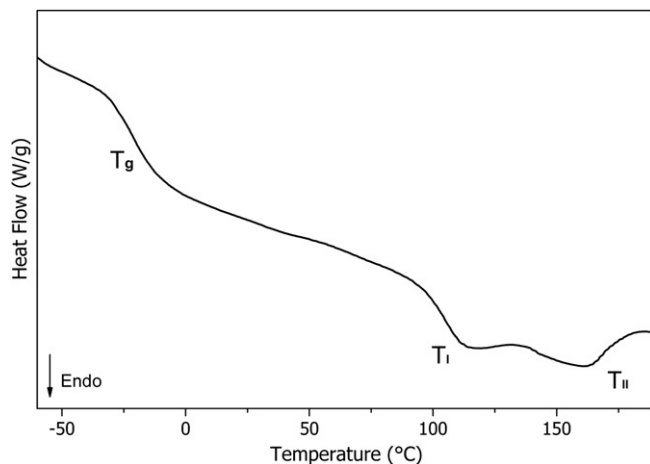


Fig. 2. DSC curve of Bionate 80A, first heating from $-75\text{ }^{\circ}\text{C}$ to $220\text{ }^{\circ}\text{C}$ at $20\text{ }^{\circ}\text{C}/\text{min}$.

Berkley, CA) and commercialized in form of pellet in different hardness grades. The Bionate[®] studied was an 80A grade.

2.2. Methods

Thermal degradation was measured in a Hi-Res thermogravimetric analyser (TGA Q500 balance, TA Inc.) on 10–15 mg sample contained in alumina pans, with a $10\text{ }^{\circ}\text{C}/\text{min}$ heating ramp from $50\text{ }^{\circ}\text{C}$ up to $800\text{ }^{\circ}\text{C}$ under a $100\text{ cm}^3/\text{min}$ nitrogen flow ($60\text{ cm}^3/\text{min}$ sample purge and $40\text{ cm}^3/\text{min}$ balance purge). Thermo-oxidation was determined in the same way using a $60\text{ cm}^3/\text{min}$ air flow in the sample purge.

A differential scanning calorimeter (DSC Q200, TA Inc.), provided with a cooling system RCS90, was used to collect DSC thermograms. The DSC measurements were performed with closed aluminium pans under nitrogen atmosphere ($50\text{ cm}^3/\text{min}$) and with a $20\text{ }^{\circ}\text{C}/\text{min}$ heating rate, from $-75\text{ }^{\circ}\text{C}$ up to $220\text{ }^{\circ}\text{C}$ cyclically.

To analyse the effect of the temperature on the morphology of the material, annealing experiments were carried out in situ in the DSC apparatus in closed aluminium pans. To evaluate the effect of processing on Bionate, samples were heated at different temperatures between $80\text{ }^{\circ}\text{C}$ and $220\text{ }^{\circ}\text{C}$ and then the morphology was checked.

The infrared measurements were performed with a Perkin Elmer Instruments. An FT-IR microscope Spectrum Spotlight 300 was used to collect spectra in reflection-absorption mode on samples held on an aluminium support, with a 4 cm^{-1} resolution, 16 scans and area of analysis of $100 \times 100\text{ }\mu\text{m}$. In situ FT-IR were collected during heating in a THMS600 heating/cooling stage (Linkam Scientific Instruments Ltd.) with heating ramp between $30\text{ }^{\circ}\text{C}$ and $200\text{ }^{\circ}\text{C}$ and $5\text{ }^{\circ}\text{C}/\text{min}$ heating rate.

ATR-FTIR spectra were recorded on an FT-IR spectrometer Spectrum 100 in the attenuated total reflectance (ATR) mode with a diamond crystal, using 16 scans per spectrum and a resolution of 4 cm^{-1} .

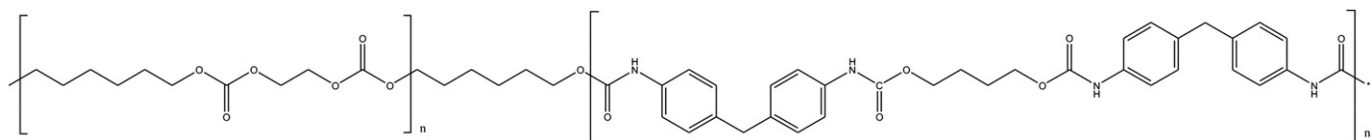


Fig. 1. Chemical structure of Bionate 80A.

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