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Poly(urethane–oxazolidone): Synthesis, characterisation and shape memory properties

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Abstract

Poly(urethane–oxazolidone) were synthesized by reacting isocyanate-terminated oxazolidone with hydroxy-telechelic poly(tetramethylene oxide) (PTMO). The molar ratios of the reactants were varied to get polymers of varying oxazolidone and urethane compositons. The polymers were characterized by DSC, FTIR, XRD, dynamic mechanical thermal analysis and chemical analyses. An increase in the concentration of urethane and oxazolidone groups caused a decrease in tensile strength and elongation of the poly(urethane–oxazolidone). The polymers possessed crystallites of PTMO whose melting transition temperature decreased on enhancing the oxazolidone concentration. The polymers exhibited thermo-responsive shape memory properties, which was confirmed and quantified by cyclic tensile tests. The influence of oxazolidone modification and the consequent soft/hard segment variation on the thermal, mechanical, dynamic-mechanical and shape recovery properties of the resultant polymers was investigated. The oxazolidone moities conferred enhanced shape recovery and shape fixity to the polyurethane.

Keywords: Shape memory polymer; Poly(urethane–oxazolidone); Shape recovery; Shape fixity; Smart polymers; Cyclic tensile test

1. Introduction

Shape memory polymers (SMP) are smart materials, which are known to sense thermal, mechanical, electrical or magnetic changes in their surroundings and respond effectively by utilizing their distinct properties such as shape recovery, shape retention or shock absorption [1]. Specially designed polyurethane (PU), having a wide temperature range for shape recovery and possessing high recoverable strains belongs to such class of SMP [2–7]. Shape memory effect originates from the reversible phase transformations of the soft segments in a matrix constituted by phase-separated hard and soft segments [8]. The phase related to the highest temperature transition posses the physical cross-links, which determines the permanent shape of SMP. Thermal transition of the phase formed by the switching segments decides the switching transition temperature of the specific material [9]. Temporary shape is fixed by cooling the material to lower temperature. The driving force for the shape recovery is the elastic strain generated during deformation [10].

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Several PU systems are known to exhibit shape memory properties [2–6,9–16]. Recently, we reported a PTMO based PU with good shape recovery property [17], where a maximum of 92% shape recovery and 97% of shape fixity could be achieved. When the polymer is deformed at a temperature above the transition temperature and suddenly cooled to a temperature below transition, the deformed shape becomes frozen and fixed. The extent to which the shape memory polymer fixes the deformed shape on cooling below the transition temperature is referred to as the shape fixity of the polymer (see the experimental part). When it is heated above T_g, the polymer recovers its original shape [7,18–20]. The shape memory characteristics can be tuned by the way of structural modification of the PU backbone. It was of interest to investigate the impact of structural modification of PU by way of incorporation of oxazolidone moieties in their backbone on the properties of the resultant polyurethanes. In this work, we report the synthesis of oxazolidone-incorporated polyurethane and its characterization. The impact of structural variation on mechanical, thermal and the shape memory characteristics of the resultant polymers have been investigated.

2. Experimental

2.1. Materials

Hydroxy telechelic poly(tetramethylene oxide) (PTMO, Aldrich Chemicals, USA, M_n 2000 g/mole), epoxy (GY-250, diglycidyl ether of bisphenol A with epoxy value 5.4 eq/kg, Ciba Geigy, India) and tolylene diisocyanate (TDI, Aldrich Chemicals, USA) were used to synthesize poly(urethane–oxazolidone) (PUO). PTMO and epoxy were dried under vaccum in a rotavapour for 5 h at 80 °C before use. TDI of analytical grade was used without further purification.

2.2. Polymer synthesis

The synthesis was carried out in a 500 ml, 3-neck round-bottomed flask, equipped with a mechanical stirrer, nitrogen inlet and a condenser with a drying tube. In the first step, epoxy resin was dried by purging it with N_2 for 30 min at 65 °C. To this, calculated amount of TDI was added drop-wise at 100 °C and the reaction was continued at 175 °C for 1 h to get the NCO-terminated prepolymer which was characterized for the extent of reaction. During the second step, the temperature was lowered to 85 °C and the required quantity of PTMO was added and the reaction was continued for further 40 min. The resulting resin was evacuated to remove all the air bubbles and then poured on to a glass plate, heated at 120 °C/2 h to get a thin film. Chemical and spectral analyses were performed to find out the completion of epoxy-NCO and NCO–OH reactions.

2.3. Polymer characterisation

2.3.1. Differential scanning calorimetry

The DSC thermal analysis of PUOs were performed on a Mettler DSC-20 analyser. The samples were heated from −80 °C to 70 °C at a heating rate of 5 °C/min. Thermograms from the first run were taken for analysis.

2.3.2. FTIR and chemical analysis

FTIR studies of thin film samples were performed using a Perkin Elmer GX-A model FTIR spectrophotometer using ATR (attenuated total reflectance) accessory with diamond crystal. Spectrum was recorded in the range of 4000–550 cm^{-1} with a resolution of 4 cm^{-1}.

2.3.3. X-ray studies

X-ray diffraction studies were performed in a ‘X’ Pertpro (P Analytical, Netherlands) using the filter Ni and the target as Cu K radiation (of 1.5405 Å) at 40 KV and 30 mA current. The diffraction patterns of the samples of thickness 1mm were recorded with Bragg’s angle 2θ from 0 to 40°. The crystallite size L_c of the samples were determined by using Scherrer equation,

$$L_c = K\lambda/\beta\cos\theta, \tag{1}$$

where $\lambda = 1.5405$ Å, K is the instrument constant and β is the half value width in radians of the X-ray intensity vs 2θ, where θ is the angle of reflection. The analysis was done at ambient temperature (25 °C). In some cases, samples were kept cooled at 0 °C and was subjected to XRD analysis rapidly, before they attained the room temperature. The analysis temperature is around 10–15 °C.

2.3.4. Mechanical and cyclic tensile tests

Mechanical properties were determined with a tensile tester (UTM 4469). The micro tensile test specimens had the dimensions of 75 mm × 5 mm × 1 mm