Synthesis and characterization of acrylate–oxetane interpenetrating polymer networks through a thermal-UV dual cure process

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Abstract

In the present work, a thermal-UV dual-cure process was performed on acrylate–oxetane systems. A 1:1 molar mixture of difunctional acrylate–oxetane mixture was prepared starting from 2,2-Bis(4-(3-acryloxy-2-hydroxypropoxy)phenyl)propane (BPADA) and 3-ethyl-3-{[(3-ethyloxetan-3-yl)methoxy]methyl}oxetane (*OXT-221*, DOX). Following a difunctional oxetane-acrylic monomer (OXAC) was synthesized.

Starting from the 1:1 molar mixture a heterogeneous IPN is generated by dual cure process: the obtained material is characterized by DMTA curves with two maximum of $\tan\delta$ peak; a broad damping effect can be expected.

In the case of OXAC dual cured system a homogeneous material with no separation domain is obtained, as evidenced by a single $\tan\delta$ peak in DMTA curves.

1. Introduction

An Interpenetrating Polymer Network (IPN's) is an intimate combination of two polymers both in the network form [1]. They can be synthesized by crosslinking polymerization of two multifunctional monomers or telechelic oligomers that polymerize by different mechanism, e.g. radical and cationic types.

As monomers polymerize, miscibility decreases, resulting in phase separation. However, since crosslink reduces phase separation, and in particular reduces domain size, it often results in finely dispersed phase domains of 10–100 nm [2].

When microheterogeneous phase domains are 10–20 nm, the whole material is essentially interphase material. Consequently, the glass transition tends to be very broad, covering the range between those of the two component polymers. This very broad glass transition leads to materials that can absorb energy; therefore they are useful as damping materials over a broad temperature and frequency range [3].

Besides sound and vibration damping materials, IPN's find potential applications in toughened plastics, in novel membrane systems and in ion-exchange resins, thanks to the very peculiar characteristics of combining the properties of the two kinds of polymer networks [4].

UV-radiation has already been used to produce IPN's [5–8]. The main interest of UV light to induce the polymerization reaction lies in high polymerization rate, which can be reached under intense illumination, together with the advantage that it can be considered an environmental friendly technique due to the solvent free process carried out at room temperature [9].

Although the use of photoinduced polymerization for IPN hybrid system formation is well known, in this work we wanted to combine thermal and UV induced polymerization methods; we have investigated a thermal-UV dual-cure process of an acrylate–oxetane mixture. The investigated systems were firstly subjected to thermal radical polymerization, which induces the acrylate double bond conversion with the formation of a polyacrylic network, and subsequently a cationic UV induced ring-opening polymerization of oxetane monomer. The properties of

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dual-cured materials were evaluated and correlated to the network structure.

2. Experimental

2.1. Materials

The acrylic resin employed was 2,2-Bis(4-(3-acryloxy-2-hydroxypropoxy)phenyl)propane (BPADA), purchased from Aldrich; the oxetane monomer employed was 3-ethyl-3-{[(3-ethyloxetan-3-yl)methoxy]methyl}oxetane (*OXT-221*, DOX) gently supplied from Toagosei, Japan; the oxetane–acrylate monomer (OXAC) was synthesized on purpose as following reported. Benzoyl peroxide was used as thermal initiator (2 wt.%) and triphenylsulfonium hexafluoroantimonate as cationic photoinitiator (2 wt.%). The structure of the employed monomers are reported in Table 1.

2.2. Synthesis of OXAC monomer

0.35 mol TOP monomer (alpha-[(3-ethyl-3-oxetanyl)-methyl]-omega-hydroxy-poly(oxy-1,2-etanedyl)] (3–6 EO) (Perstorp), 2.45 mol ethyl acrylic ester, *n*-heptane 20% on the ethyl acrylic ester, 300 ppm phenothiazine, nitrobenzene 150 ppm, Tyzor TBT (DuPont) 2% are loaded to a 3 neck round bottom flask. The blend is heated under Nitrogen flow and mechanical stirring. When the steam temperature reaches 72 °C the reflux is returned to the flask in a ratio of 10:1. The synthesis is interrupted when the steam temperature is higher than 85 °C. The product is washed with water–ethanol (1:1) to remove the un-reacted ethyl acrylate. The product is filtered and dried. A low viscosity oily liquid is obtained. Yield 97.2%. Unsaturation degree 3.0 mmol/g. Oxetane content 340 g/eq.

^{1}H NMR (400 MHz, CDCl$_3$, δ): 6.41, 6.13, 5.83 (CH$_2$=CH); 4.43, 4.37 (CH$_2$–oxetane); 4.31, 3.71, 3.60 (OCH$_2$); 1.73, 0.84 (CH$_2$CH$_3$).

^{13}C NMR (100 MHz, CDCl3, δ): 166.07, 130.99, 128.23, 78.37, 73.75, 69.23, 63.38, 43.35, 26.62, 8.12.

2.3. Cured sample preparation

The 1:1 molar ratio of the monomers BPADA and DOX or the OXAC monomer were added of 2 wt.% of the thermal initiator benzoyl peroxide and 2 wt.% of the cationic photoinitiator triphenylsulfonium hexafluoroantimonate.

After 2 h treatment at 80 °C, under nitrogen atmosphere, the sample was irradiated for 1 min at room temperature with a light intensity on the surface of the sample of 30 mW/cm^2. Transparent cured polymer network were obtained.

2.4. Characterization technique

The polymerization conversion was followed after thermal treatment and subsequently after UV irradiation by FT-IR investigation employing a Thermo-Nicolet 5700 instrument. The liquid formulations were coated onto a SiC wafer and FT-IR spectra recorded after thermal treatment at 80 °C, under nitrogen atmosphere, and than after following UV irradiation. Because the IR absorbance is proportional to the monomer concentration, acrylic double bond (peak centred at 1635 cm^{-1}) and oxetane group (peak centred at 980 cm^{-1}) conversion can be calculated with reference to the spectra recorded at time zero.

The gel content was determined on the cured films by measuring the weight loss after 24 h extraction with chloroform at room temperature.
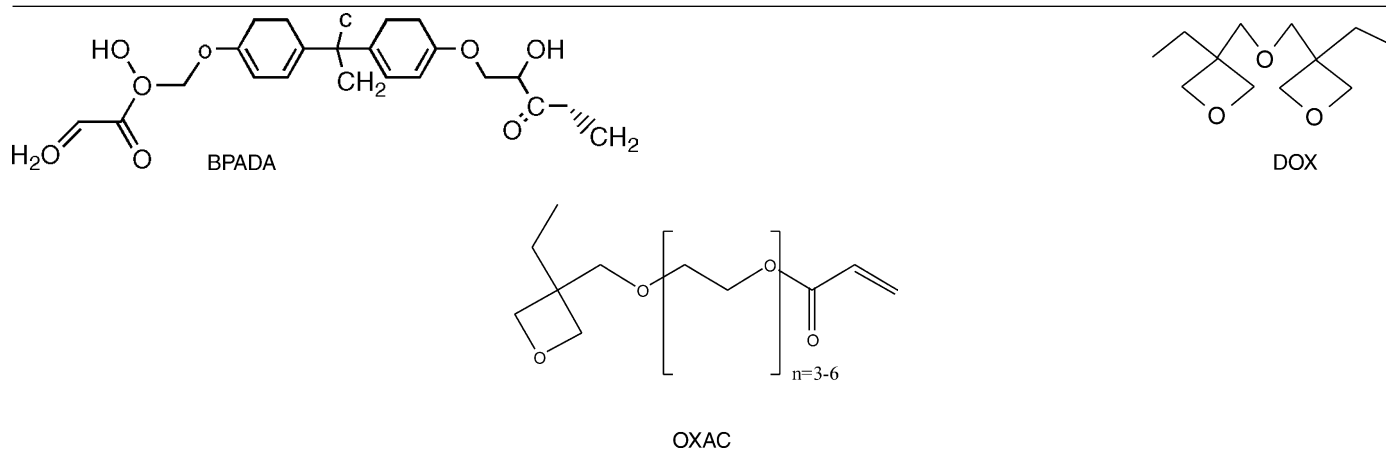
DSC measurements were performed with a DSCQ 1000 of TA Instruments equipped with a low temperature probe, under nitrogen flux, in the range between −80 and 150 °C.

Dynamic mechanical thermal analyses (DMTA) were performed with a Rheometric Scientific MKIII (UK) instrument, at a frequency of 1 Hz in the tensile configuration.

The pencil hardness was evaluated on photocured films according to the standard test method ASTM D 3363.

The AFM measurements were done on the films coated on glass substrates in the tapping mode using a Dimension 3100 Nanoscope IV (Veeco, USA). A Pointprobe silicon-SPM-sensor (Nanosensor, Germany) with spring constant of ca. 3 N/m and resonance frequency of ca. 75 kHz was used.

Table 1
structure of monomers employed

OXAC