Biodegradable photocross-linked polymers of glycerol diglycidyl ether and structurally different alcohols

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Structurally different alcohols, e.g. 1,4-cyclohexanedimethanol, 1,1,1-tris(hydroxymethyl)propane, hydroquinone, and bisphenol A, were used for photocross-linking of glycerol diglycidyl ether on purpose to study structure-properties relationship of the resulting polymer films. Kinetics of photocross-linking was investigated by photorheometry. Dependencies of chemical structure and amount of alcohol used on mechanical, thermal, rheological properties, and biodegradability of the synthesized polymers were studied. The addition of alcohol resulted in an increase of the rate of photocross-linking of glycerol diglycidyl ether. The amount of alcohol used had more considerable effect on properties of polymers than chemical structure of alcohol. The higher amount (> 20 mol%) of alcohol led to the easier association of alcohol molecules with released protons and thus deteriorated the properties of the cross-linked polymers. However, the addition of alcohols increased the biodegradability of resulted polymers.

1. Introduction

Usage of large quantities of polymers in household and industry has caused many problems related to waste management. Most of the conventional plastics are non-degradable and naturally occurring microorganisms can not decompose them into harmless substances. The replacement of the conventional nondegradable plastics by biodegradable [1,2] ones is the urgent task. Renewable resources are used increasingly in the production of biodegradable polymers with a wide range of properties and applications [3]. Fast increase of biodiesel production worldwide [4] leads to a huge quantity of glycerol as a by-product [5]. Converting glycerol into valuable chemicals and chemical intermediates [6] such as epoxides enables to obtain new types of biodegradable plastics.

Epoxy resins are used as thermosetting materials in the range of industrial applications, such as printing inks, matrixes for composite materials, coatings, adhesives, varnishes, insulating, and embedding materials due to their excellent engineering properties, e.g. high mechanical strength, good chemical resistance, and versatility [7–9]. Properties of such thermosetting materials depend on the final state of

the matrix obtained by curing process [10]. It is important to investigate curing kinetics in order to determine the final state of the obtained matrix and its properties. Good rheological properties, fast curing, low shinkage, and scratch resistance make epoxy resins useful in UV-curing reactions [11]. Photocationically-cured epoxy resins have considerably better thermal and mechanical properties than photopolymerized acrylates [12].

The main advantages of cationic UV polymerization is insensitivity to oxygen inhibition and low polymerization shrinkage [13–15]. Onium salts are generally used as UV-activated initiators for cationic photopolymerization [16]. Onium photoinitiators such as sulfonium salts [17] are important due to their thermal stability, solubility in most of the cationically polymerizable monomers [18]. Despite these advantages, cationically polymerized epoxy coats are often wrinkled. It was shown that this disadvantage can be avoided by using alcohols as modifiers of coating systems [19]. The effect of mono-alcohols and polymeric diols on the cationic photopolymerization of epoxides was extensively studied. However limited number of investigations of the effect of varying chemical structure and the amount of structurally different diols on cationic UV-curing of epoxides was reported [20–26].

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Two effects of diol molecules on photopolymerization kinetics of epoxides can be distinguished. The addition of diol enhances the polymerization rate due to the chain transfer reactions through an activated monomer mechanism [27]. In addition, it can associate with proton, which leads to the decrease of the effective proton concentration, and thus inhibits photopolymerization [20].

In this study, glycerol diglycidyl ether was chosen as an epoxy resin which could replace diglycidyl ether of bisphenol A, the most widely used monomer for cationic photopolymerization reactions with diols, expecting that the resulting polymers could be decomposed by naturally occurring microorganisms. To our knowledge, this is the first study of photopolymerization kinetics by photorheometry and the first study of biodegradability of the polymers obtained by photocross-linking with diols. Dependence of conversion of epoxy groups of diglycidyl ether of bisphenol A on the reaction time was studied in details [21,22]. However no studies are available on the changes of the rheological and mechanical properties when a sample undergoes a liquid to solid transition during UV-curing in real time.

In this study, four structurally different alcohols were selected for the investigation of the effect of their chemical structure and amount on the photocross-linking of glycerol diglycidyl ether and on the properties of the resulting polymers.

2. Experimental

2.1. Materials

Glycerol diglycidyl ether (technical grade, functionality – 2, weight per epoxide equivalent 138–160, molar ratio of epoxy and hydroxyl groups – 2:1), 1,4-cyclohexanedimethanol (**1**), 1,1,1-tris(hydroxymethyl)propane (**2**), hydroquinone (**3**), bisphenol A (**4**) (Fig. 1), and triarylsulfonium hexafluoroantimonate salts (mixed, 50 wt% in propylene carbonate) were purchased from Sigma-Aldrich. Tetrahydrofurane was purchased from Eurochemicals. All materials were used as received.

2.2. Photocross-linking

Different compositions (**C1–C12**, see Table 1) were prepared by mixing of 0.8 g of glycerol diglycidyl ether with the different amount (10, 20, or 30 mol%) of alcohols, 1,4-cyclohexanedimethanol (**1**), 1,1,1-tris(hydroxymethyl)propane (**2**), hydroquinone (**3**), bisphenol A (**4**), using 3 mol% of photoinitiator, mixture of triarylsulfonium hexafluoroantimonate salts, and 0.1 ml of tetrahydrofuran. The composition without alcohol (**C0**) was prepared for comparison. Compositions were poured on a plastic substrate and irradiated with Helios Italquartz, model GR.E 500 W with the intensity of 310 mW·cm^{-2} at the distance of 15 cm. The cured films were obtained after (2–4) min.

Photocross-linked product of **C0** IR (KBr): 3430 (ν O–H), 2911 (ν CH$_2$ aliph.), 2869 (ν C–H aliph.), 1083 (ν C–O–C) cm^{-1}.
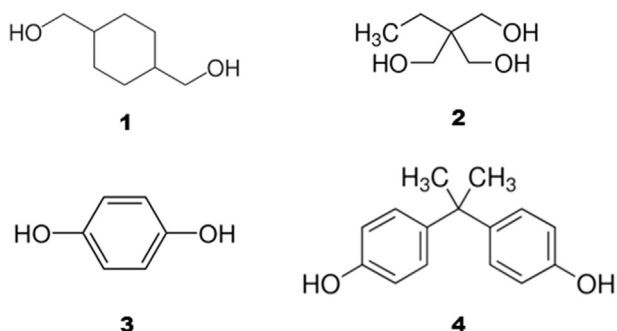

Fig. 1. Structures of alcohols used in this study: 1,4-cyclohexanedimethanol (**1**), 1,1,1-tris (hydroxymethyl)propane (**2**), hydroquinone (**3**), and bisphenol A (**4**).

Photocross-linked products of **C1–C3** IR (KBr): 3457–3421 (ν O–H), 2913–2911(ν CH$_2$ aliph.), 2867–28,764 (ν C–H aliph.), 1085–1084 (ν C–O–C) cm^{-1}.

Photocross-linked product of **C4–C6** IR (KBr): 3439–3397 (ν O–H), 2913–2911 (ν CH$_2$ aliph.), 2870–2869 (ν C–H aliph.), 1086–1084 (ν C–O–C) cm^{-1}.

Photocross-linked products of **C7–C9** IR (KBr): 3398–3378 (ν O–H), 3041–3039 (ν CH$_2$ ar.), 2913–2911 (ν CH$_2$ aliph.), 2872–2869 (ν C–H aliph.), 1512–1511 (ν C=C ar.), 1085–1084 (ν C–O–C) cm^{-1}.

Photocross-linked products of **C10–C12** IR (KBr): 3426–3376 (ν O–H), 3042–3040 (ν CH$_2$ ar.), 2913–2911 (ν CH$_2$ aliph.), 2869–2868 (ν C–H aliph.), 1512 (ν C=C ar.), 1089–1086 (ν C–O–C) cm^{-1}.

2.3. Chemical structure analysis

Fourier Transform Infrared Spectroscopy (FT-IR) measurements of the photocross-linked polymers were performed on a Perkin Elmer Spectrum BX II FT-IR spectrometer, using KBr pellets. The spectra were acquired from 10 scans. The range of wavenumber was (400–4000) cm^{-1}.

Real-time FT-IR monitoring was performed using Bruker Vertex 70 spectrometer. The samples were irradiated by UV/Vis radiation in a wavelength range of (250–450) nm using UV/Visible spot curing system OmniCure S2000, Lumen Dynamics Group Inc. Intensity of radiation was 9.3 W·cm^{-2} (high pressure 200 W mercury vapor short arc).

2.4. Soxhlet extraction

The amount of insoluble polymer fraction was determined by Soxhlet extraction. The samples of the cross-linked polymers (0.2 g) were put into a filter package and placed in a Soxhlet apparatus. Extraction was performed with chloroform for 72 h. Insoluble fractions were dried under vacuum to constant weight. The amount of insoluble fraction was calculated as a difference of the sample weight before and after extraction.

2.5. Kinetics of photocross-linking

UV/Vis curing tests were carried out with MCR302 rheometer from Anton Paar equipped with the plate/plate measuring system. Peltier-controlled temperature chamber with the glass plate (diameter of 38 mm) and the top plate PP08 (diameter of 8 mm) was used. Measuring gap was set to 0.3 mm. The samples were irradiated at room temperature by UV/Vis radiation in a wavelength range of (250–450) nm through the glass plate of the temperature chamber using UV/Visible spot curing system OmniCure S2000, Lumen Dynamics Group Inc. Intensity of the UV radiation was 9.3 W cm^{-2} (high pressure 200 W mercury vapor short arc). Shear mode with the frequency of 1 Hz was used. Strain of 2% was used in all cases. Storage modulus G′, loss modulus G″, loss factor tanδ (tanδ = G″/G′), and complex viscosity ŋ* were recorded as a function of irradiation time. Storage modulus G′, loss modulus G″, complex viscosity ŋ* values were taken after 10 min of sample irradiation by UV/Vis irradiation.

2.6. Differential scanning calorimetry

Glass transition temperatures (T$_g$) of the photocross-linked polymers were estimated by differential scanning calorimetry (DSC). The measurements were performed on a Perkin Elmer DSC 8500 apparatus with the heating-cooling-heating rate of 10 °C·min^{-1} under nitrogen atmosphere (nitrogen flow rate 50 ml·min^{-1}).

2.7. Thermogravimetrical analysis

Thermal decomposition temperatures of polymers were determined