



Network dynamics in cationically polymerized, crosslinked epoxy resins and its influence on crystallinity and toughness



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ABSTRACT

Crystallinity in crosslinked epoxy resins is a rarely observed phenomenon. If crystallinity is properly adjusted, it can lead to enhanced toughness in cationically polymerized epoxy resins. This work demonstrates the controlled crystallization of partially crystalline poly(ϵ -caprolactone) (PCL) in a model system based on a cycloaliphatic epoxy matrix polymerized with a thermo-latent, cationic initiator. Samples with the same composition were polymerized under varied conditions leading to different degrees of crystallinity and furthermore to differences in morphology and mechanical behavior. Mild curing conditions lead to a sufficient flexibilization of the epoxy matrix and the epoxide consumption is caused mainly by the activated monomer mechanism. On the other hand, more intense polymerization conditions result in a higher amount of transesterification compared to mild conditions which is evidenced by decreasing crystallinity and higher gel content despite a complete polymerization reaction. The PCL chains are shortened by transesterification while the smaller PCL chains are integrated into the network. Additionally, stress relaxation experiments measured with DMA and deformation-fixation-relaxation experiments reveal a type of flowing and stress reduction of the crosslinked polymers caused by rearrangement reactions. SEM micrographs show that increasing crystallinity leads to a raised roughness of fracture surfaces. Examination of the mechanical properties shows that enhanced crystallinity leads to higher stiffness, mechanical strength and also to superior toughness even if the network density does not significantly change. This work shows how the morphology and properties of the epoxy resin can be adjusted by just small variations in the polymerization conditions.

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1. Introduction

Crosslinked epoxy resins are well established materials that are used for example as adhesives, printing inks, coatings, fiber matrices, or electrical insulators. They exhibit high thermal stability, good mechanical properties, and furthermore possess outstanding chemical resistance [1]. Drawbacks including brittleness can be overcome by adjustments in flexibilization and morphology. For that reason, a huge number of articles has been published dealing with different toughening methods for epoxy resins including plasticization with polyesters, polyethers, polyetherimides, and polysulfones [2–5], reaction with copolymers

[6–8], incorporation of rubber or inorganic particles [9–13], reaction with a twin monomer [14], and reaction with hyperbranched polymers [15–17]. These methods are suitable for thermosetting epoxy resins showing high glass transition temperatures T_g and moduli but in the case of strongly flexibilized epoxy resins (low T_g polymers), other concepts are needed for enhancing toughness and strength. For this reason, flexibilized crosslinked epoxy resins can be further toughened by the presence of segregated crystalline domains as observed by Lützen et al. [18,19], whereby this is strongly influenced by the degree of branching of the polymers forming the domains [20].

Polyisoprene, known as natural rubber, and polyethylene show strain-induced crystallization [21–25] whereby the crystals formed act as a filler, leading to increased reinforcement and stiffness of the respective rubber [26]. The influence of crystallinity on the strength of thermoplastics is also well known [27]. The occurrence of crystallinity in thermosetting materials such as epoxy resins,

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unsaturated polyester, or novolaks has already been described in the literature but has so far remained an extremely rarely documented phenomenon [3,20,28–34]. This is also the case for the toughening of epoxy resins by crystalline domains [18–20,35,36]. In contrast to strain-induced crystallization, known from rubbers, crystallinity in epoxy resins forms prior to stretching. Lützen et al. demonstrated that an increase in mechanical moduli, tensile strength, and deformation energy can be achieved by recrystallization in epoxy resins after polymerization on a time scale of days to weeks [18]. Crystallization is supposed to be the driving force for phase separation, which may be responsible for toughness. These observations indicate the vital role of crystalline phases in flexibilized epoxy resins. The appearance of crystallinity in amorphous crosslinked networks may be the result of arrangements of poly(ϵ -caprolactone) (PCL) chains to crystalline domains after and during polymerization. This might be possible due to the cleavage of chemical bonds or because of transesterification reactions. Transesterification in epoxy resins is a phenomenon already known in specific systems [37–40]. Montarnal and Capelot et al. did pioneering work on Vitrimers[®] that revealed the importance of dynamic processes in crosslinked epoxy resins. A thermally stimulated exchange reaction, known as transesterification, enables a crosslinked system to flow to some extent, opening up new applications such as self-healing and stress relaxation. Under consideration of the dynamic processes in epoxy resins, partially crystalline thermoplastics, especially polyesters, seem to be promising materials for introducing crystallinity into crosslinked epoxy resins. Polyethers and polyesters bearing hydroxyl functions are well known for toughening cationically polymerized epoxy resins [2,11,18,20,35,36]. Thereby, the hydroxyl groups react with the epoxide groups leading to an integration into the polymer network due to a chain transfer reaction, known as activated monomer mechanism (AM) [41–43]. Recently, it has been pointed out that cationically polymerized thermosetting epoxy resins segregate by reaction-induced phase separation when cured in the presence of a polyester polyol [3]. Furthermore, it has been shown that the AM mechanism occurs at significantly lower temperatures than the activated chain end mechanism (ACE), which describes the propagation of the pure epoxide. For example, this has been demonstrated by the cationic epoxide polymerization in presence of a reactive PCL (hydroxyl end groups) and a non-reactive one (ester end groups). The respective DSC thermogram shows the typical signal for the epoxide propagation and additionally in the presence of PCL bearing hydroxyl end groups also a second one at lower temperature, which has not been observed for PCL with ester end groups [3]. This means that the integration of polyester polyols takes place during the early stages of the polymerization process. Under consideration of a faster proceeding AM mechanism, flexibilization of epoxy resins with polyester polyols should be carried out under mild conditions in order to reach a high portion of integration into the crosslinked network by kinetic selection. This kinetic selection means that a higher temperature makes (alternative) reactions less selective and leads to an acceleration of the ACE mechanism so that the relation of ACE to AM mechanism increases. Hence, the proportion of polyester polyol that integrates into the epoxy network decreases in the case of increased temperatures.

In this work we highlight controlled crystallization as a concept for enhancing toughness in a cycloaliphatic epoxide model system. For this, partially crystalline poly(ϵ -caprolactone) (PCL) is integrated into a cationically polymerized three dimensional epoxide network by both the activated monomer mechanism and the transesterification reaction under different curing conditions in order to adjust the degree of crystallinity. Furthermore, this crosslinked system is investigated regarding its formability and

stress relaxation potential at high temperatures in order to compensate for factors like curing shrinkage and mechanical load.

2. Experimental

2.1. Materials

All chemicals were used as received from commercial suppliers. The cycloaliphatic epoxide 3,4-epoxycyclohexyl-3',4'-epoxycyclohexane carboxylate (Omnilane OC1005) was purchased from IGM resins (Krefeld, Germany). Poly(ϵ -caprolactone) with a molecular weight of 4000 g/mol and hydroxyl end groups (PCL, Capa[™] 2402; initiated with 1,4-butanediol) was donated by Perstorp (Warrington, UK). Acetic anhydride ($\geq 98.0\%$), and 1,2,4-trichlorobenzene (anhydrous, $\geq 99\%$) were purchased from Sigma-Aldrich (Steinheim, Germany). Dichloromethane and 4-methoxybenzyl alcohol (p.a.) were purchased from Merck (Darmstadt, Germany). The latent initiator benzyl tetrahydrothiophenium hexafluoroantimonate was prepared according to the literature [44]. The release agent ACMOScoat 82–6007 was obtained from ACMOS Chemie KG (Bremen, Germany).

2.2. Physico-chemical characterization

¹H NMR spectroscopy. ¹H NMR spectra were recorded with a Bruker DPX-200 spectrometer (200 MHz). The spectra were measured in CDCl₃ at ambient temperature and tetramethylsilane was used as external standard.

Infrared spectroscopy. Infrared (IR) spectra were obtained in attenuated total reflection (ATR) with a Bruker Equinox 55 FTIR spectrometer equipped with a Golden Gate cell with a resolution of 4 cm⁻¹ (32 scans).

Differential scanning calorimetry. Differential scanning calorimetry (DSC) was performed in a sealed pan with a DSC 2920 Modulated from TA Instruments over a temperature range of 20 °C–120 °C for the determination of crystallinity and from 20 °C to 250 °C for investigations into the post-curing processes. In both cases the heating rate was 10 °C/min.

Dynamic mechanical analysis. Dynamic mechanical analysis (DMA) was carried out on a DMA 2980 instrument from TA Instruments with a heating rate of 2 °C/min over a temperature range of –150 °C to 100 °C with 1 Hz. The samples were measured as a single cantilever. The sample sizes are A) 17.94 × 9.75 × 4.02 mm³, B) 17.38 × 9.85 × 4.02 mm³, C) 18.53 × 9.83 × 4.11 mm³, and D) 17.85 × 9.67 × 4.10 mm³ (assignment of the samples A, B, C, and D is shown in Table 1).

Size exclusion chromatography. Size exclusion chromatography (SEC) was carried out with a 1260 Infinity Refractive Index Detector from Agilent Technologies. The columns used were a PLgel 5 μ m Guard (50 × 7.5 mm, Agilent Technologies), PLgel 5 μ m MIXED-C (7.5 × 300 mm, Agilent Technologies), and PLgel 10⁴ Å (7.5 × 300 mm; Agilent Technologies). The measurements were performed at a temperature of 23 ± 1 °C in tetrahydrofuran with a flow rate of 1 mL/min and PMMA as calibration standard.

Scanning electron microscopy. Scanning electron microscopy (SEM) was performed with a LEO1530 Gemini microscope from Zeiss. Fracture surfaces were prepared by cryofracture in liquid nitrogen.

Tensile tests. Stress–strain measurements were performed with a Zwick-Z050 according to standard DIN EN ISO 527-2 shape 1BA [45]. The testing rate was 1 mm/min, the maximum gage load was 10 kN, and the testing temperature was 24 ± 2 °C.

Shore D hardness. Shore D hardness was measured according to standard DIN EN ISO 868 at 22 ± 2 °C [46].

Determination of gel content. The gel yield was determined by

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