European Polymer Journal 49 (2013) 167–176

Contents lists available at SciVerse ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

# Partially crystalline polyols lead to morphology changes and improved mechanical properties of cationically polymerized epoxy resins

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ARTICLE INFO

*Article history:*
Received 8 May 2012
Received in revised form 6 September 2012
Accepted 23 October 2012
Available online 8 November 2012

*Keywords:*
Cycloaliphatic epoxy resin
Toughening
Poly(ε-caprolactone)
Polyol
Morphology

ABSTRACT

The influence of partially crystalline polymeric diols on the morphology and mechanical properties of a cationically polymerized cycloaliphatic epoxy resin is described and significantly enhanced material properties were observed. In particular, poly(ε-caprolactone) (PCL) could be integrated covalently into the epoxy network leading to a toughened material with higher tensile strength and elongation at break combined with less brittleness and enhanced flexibility in the completely transparent thermosetting epoxy polymer. The PCL containing polymers were compared with polycarbonate containing epoxy polymers as rigid polyol phase. Scanning electron microscopy of samples broken below and above the glass transition temperature of PCL as well as above the melting point of PCL showed different fracture behavior of the elastified samples and an ordered morphology of the PCL in the epoxy matrix was observed. A distinct morphology known well from thermoplastic block-copolymers is formed in the prepared thermosetting polymers.

## 1. Introduction

Epoxy resins are widely used as printing inks, adhesives, and coatings due to their high mechanical moduli, good chemical resistance, and good adhesive properties to various materials [1,2]. For most high performance applications their high glass transition temperature as well as their high temperature resistance are essential. However, cationically polymerized highly crosslinked epoxy networks are brittle polymers and toughening is often required to enhance the material properties and achieve a high tensile strength combined with a high elongation at break.

A possible approach to achieve this combination and maintain the good properties of pure epoxy polymer is the combination of an epoxy matrix resin with elastomer particles such as silicone or rubber, forming a separated phase in the polymer network [3–6]. This leads to an increase in impact strength, flexibility, and tensile strength without lowering the glass transition temperature due to the phase separated morphology.

Another approach is to toughen the polymer with inorganic fillers such as surface modified silica nanoparticles. The particles are dispersed in the epoxy matrix and form a hard separate phase that is in some cases surrounded by a flexible shell due to the particle surface modification. This leads to less brittle and rigid but fracture toughened polymers, in which the glass transition temperature is not significantly decreased due to the phase separated morphology [7–10].

A third common practice for cationically polymerized epoxy resins is to plasticize the polymer with diol components covalently integrated in the epoxy network during living polymerization of the epoxy groups due to the hydroxyl groups [11–14]. This is often called “activated monomer mechanism”. A major drawback of this method is that basically a softening of the polymer combined with reduction of $T_g$ occurs, besides the desired toughening of the material. Accordingly, the toughening effect could be

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http://dx.doi.org/10.1016/j.eurpolymj.2012.10.015

obtained by integrating partially crystalline poly(tetrahydrofuran) (PTHF) able to phase separation in the epoxy matrix leading to high elasticity of the polymer [15]. Unfortunately, the polymers have poor thermal stability and emit tetrahydrofuran caused by chain cleavage in the presence of superacid used as the polymerization catalyst.

The objective of this work is to enhance elasticity and toughness without lowering the outstanding thermal stability of the cationically polymerized cycloaliphatic epoxy resin, using partially crystalline polyol components which are not able to form volatile cleavage-products of low molecular weight. Hence hydroxyl terminated and partially crystalline diols, especially poly(ε-caprolactone) (PCL), were used to provide the required properties. High PCL contents were inserted into the epoxy polymers to study the changes in the network structure and morphology.

The mechanical properties of the resulting materials were examined and compared with those of the epoxy polymer containing a polycarbonate diol (PC) as a polymeric diol with more rigid backbone covalently integrated into the epoxy network, in order to get information about the influence of molecular flexibility in the polymer network on the mechanical properties.

## 2. Experimental

### 2.1. Materials

The cycloaliphatic diepoxy resin 3,4-epoxy-cyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate (Omnilane OC1005) was purchased from IGM resins (Krefeld, Germany). To initiate the thermal cationic polymerization benzyl tetrahydrothiophenium hexafluoroantimonate was used which was prepared according to the literature [16]. The structures of epoxide and thermoinitiator used in this work are shown in Fig. 1A and B. Poly(ε-caprolactone) (Fig. 1C) with molecular weights of 400, 2000, 4000, 8000, and 10,000 g/mol and poly[oxycarbonyloxy(2,2-dimethyl-1,3-propanediyl)] as an also partially crystalline polycarbonate diol (PC) with molecular weight of 1000 g/mol (Oxymer D112) were from Perstorp Polyols and are summarized in Table 1.

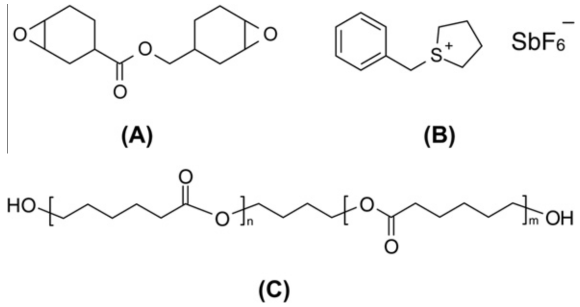

**Fig. 1.** Structures of the applied compounds: (A) epoxy resin 3,4-epoxycyclohexylmethyl 3′,4′-epoxycyclohexanecarboxylate, (B) thermoinitiator benzyl tetrahydrothiophenium hexafluoroantimonate, (C) butanediol initiated poly(ε-caprolactone).

All other chemicals were purchased from Sigma–Aldrich and were used as received without further purification.

### 2.2. Sample preparation

To initiate the polymerization 1 wt.% (0.6 mol.%) of the thermoinitiator was dissolved in the epoxy resin by stirring at room temperature. The obtained solution was mixed with the polymeric diol components poly(ε-caprolactone) (PCL) or polycarbonate diol (PC) and heated under stirring to 75 °C. At this temperature the partially crystalline diols melt and a clear liquid solution is obtained.

The curing cycle for all samples was chosen with respect to the high reaction enthalpy of the epoxy resin to cure under mild conditions and prevent thermal degradation or mechanical stresses. The temperature program included three consecutive heating steps: 1 h at 110 °C, 1 h at 125 °C and 30 min at 145 °C.

For dynamic mechanical analysis (DMA), Shore D hardness measurement and thermogravimetric analysis (TGA), the samples were cured in aluminum molds, precoated with the release agent Acmosan 82–6007 from Acmos Chemie KG (Bremen, Germany), of dimensions $4 \times 1 \times 0.3\ \text{cm}^3$. Specimens of the same size were used to test the swelling behavior in solvent atmosphere. For this examination the specimens were stored for 24 h in an acetone containing exsiccator under water jet vacuum at 21 ± 2 °C. After removing the samples from the exsiccator, the weight uptake was measured.

For determination of the gel content of the polymers by Soxhlet extraction, 0.8 g of PCL400 or PCL2000 were mixed at 75 °C with 2 g epoxy resin and were cured, along with the pure epoxy resin, as 150 μm thick films. 1.5 g of the polymer film was broken into small pieces, filled in an extraction thimble and extracted with acetone as solvent under reflux for 24 h. After solvent evaporation, the residue as well as the soluble content were determined.

For the tensile tests aluminum molds of dimensions $10 \times 8 \times 0.3\ \text{cm}^3$, also precoated with the release agent Acmosan 82-6007, were used to cure the polymer and the final specimen shape according to DIN EN ISO 527 part 1 and 2 shape 1BA [18,19] was cut via waterjet cutting.

### 2.3. Measurements

Infrared spectra were recorded with a Bruker Equinox 55 FTIR-spectrometer equipped with a Golden Gate cell for measurements in attenuated total reflexion (ATR) in a range between 4000 and 650 $\text{cm}^{-1}$ with a resolution of 2 $\text{cm}^{-1}$.

Differential scanning calorimetry (DSC) was carried out with a TA Instruments DSC 2920 at a heating rate of 10 K/min.

Shore D Hardness was measured according to DIN EN ISO 868 [20] with a portable Shore D measuring instrument with fivefold determination on specimens of dimensions $4 \times 1 \times 0.3\ \text{cm}^3$.

Scanning electron microscopy (SEM) was performed with a LEO438 VP SEM from Zeiss and a LEO1530 SEM also from Zeiss for examinations with higher resolution. SEM

**Table 1**
Chemical structure and physical properties of the used polyols.

| Name | Molecular weight $M_n$ g/mole | Starter diol | Melting enthalpy in J/g (DSC 10 K/min) | Crystallinity in% (DSC 10 K/min) [17] | Melting range (°C) |
|---|---|---|---|---|---|
| Poly(ε-caprolactone) | 400 | 1,4-Butanediol | 22.5 | – | −15–(+5) |
| Poly(ε-caprolactone) | 2000 | 1,4-Butanediol | 85.7 | 63.2 | 30–50 |
| Poly(ε-caprolactone) | 4000 | 1,4-Butanediol | 87.1 | 64.2 | 40–56 |
| Poly(ε-caprolactone) | 8000 | 1,4-Butanediol | 71.4 | 52.6 | 44–59 |
| Poly(ε-caprolactone) | 10,000 | 1,4-Butanediol | 70.8 | 52.2 | 45–63 |
| Polycarbonate diol | 1000 | – | 21.3 | – | 99–111 |

examination was carried out at fracture surfaces formed after annealing and breaking at −196 °C, room temperature and 125 °C respectively. The samples were sputtered with a thin film of platinum/palladium in a ratio of 80/20 to provide an electrically conductive surface.

Dynamic mechanical analysis (DMA) was performed with a 2980 Dynamic Mechanical Analyzer from TA Instruments in the temperature range from −150 to 200 °C at a heating rate of 2 K/min.

Stress–strain measurements were carried out according to the standard DIN EN ISO 527 part 1 and 2 shape 1BA [18,19] at a test temperature of 21 ± 2 °C. A Zwick-Z050 with testing speed of 1 mm/min and a maximum gage load of 10 kN was used as testing machine.

Thermogravimetric analysis (TGA) was performed with a TGA Q5000 from TA Instruments at a heating rate of 10 K/min from room temperature to 800 °C in air.

## 3. Results and discussion

### 3.1. Epoxy/polyol polymerization

The influence of partially crystalline polyols on the structure and the mechanical properties of cationically polymerized thermosetting epoxy polymer was examined. The cycloaliphatic epoxy resin 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (Fig. 1A) with two epoxy groups per molecule was selected in order to obtain a highly crosslinked polymer structure with ether linkages. The epoxy groups were polymerized by cationic initiation with the latent thermoinitiator benzyl tetrahydrothiophenium hexafluoroantimonate [16] due to the formation of the super-acid $HSbF_6$. The polymerization mechanism of epoxy resins in the presence of hydroxyl-functional polymers has been described in the literature [11,13] as the “activated monomer mechanism”. via this mechanism the polymer chains were built into the epoxy matrix during living polymerization via the hydroxyl groups to prepare flexible areas in the polymer network in order to toughen the otherwise brittle epoxy polymer. Poly(ε-caprolactone) (PCL) was used as the polymeric alcohol component with different morphologies and properties due to their different molecular weight. While the PCL with low molecular weight of 400 g/mol was received as clear liquid with no measurable melting behavior above room temperature, the polymers of higher molecular weight from 2000 up to 8000 g/mol were solids and showed a degree of crystallization between 50 and 65% (Table 1). The longest polymer chain with a molecular weight of 10,000 g/mol was received as thermoplastic polymer. All polymers were started with butandiol and the structure is shown in Fig. 1C.

In addition to PCL, neopentyl glycol polycarbonate with a molecular weight of 1000 g/mol (PC1000), which is also partially crystalline and hydroxyl terminated, was used to compare the effect of the flexible PCL with the more rigid polymer structure of a PC.

For both kinds of polymers, molecular ordering due to crystalline interactions between the polymer chains at the sub-micron level is suggested and discussed in this article as one reason for the obtained toughening.

To verify the covalent linkage of the PCL to the epoxy polymer, Soxhlet extractions of thermally polymerized films were performed using PCL400 and PCL2000 as examples of amorphous and partially crystalline PCL. The extractions showed only 4.2 and 4.5 wt.% respectively of soluble compound for the 28.6 wt.% PCL400 and PCL2000 containing samples and 6.1 wt.% for the pure, cured epoxy polymer. On the one hand, these results show that a covalent linkage between PCL and the epoxy resin was obtained during the polymerization reaction and no low molecular weight components were formed due to ester cleavage in the PCL by the formed superacid. On the other hand, they show that reaction conversion for epoxy containing PCL is at least the same or higher than that of pure epoxy, as described in literature for polyol components [11].

IR-spectra, recorded from the PCL containing epoxides as well as the pure epoxy polymer showing no residual epoxy groups under the given measurement accuracy. Additionally DSC experiments were performed and showed neither a residual reaction enthalpy nor measurable melting enthalpy of the partially crystalline polyol in the transparent polymers. Only in the case of opaque samples at high polyol content were low melting enthalpies of a few J/g observed. If small ordered domains on a scale below macroscopic demixing were formed in the polymer, we would expect only a lowering in the baseline of the DSC-thermogram due to broadening of the melting peak of various small domains without a clearly observable melting peak.

### 3.2. Polymer appearance and hardness

Depending on the PCL and PC content respectively, the polymers showed different hardness characteristics which were characterized by Shore D measurement. Fig. 2 shows the results for PC1000 and PCL of different molecular weights and contents of 0–60 wt.%.

Supporting information available: Photos of the epoxy polymers containing different amounts of PCL4000.

All samples shown in Fig. 2 contain less than 0.4 equivalents of alcohol compared to the epoxy content. For example, the epoxy sample with the highest amount of PCL400 of 48.8 wt.% in the polymer contains 0.375 mol OH-groups compared to the epoxy groups. This excess of epoxy groups was chosen to ensure that all added polymeric alcohol was covalently integrated into the polymer network.

As shown in Fig. 2, the low molecular weight and amorphous PCL400 showed no noteworthy softening with increasing PCL content from 0 up to nearly 30 wt.%. Further increase of the PCL400 content leads to nearly spontaneous softening and formation of a sticky material with a low crosslinking density with amounts above 45 wt.% (30.4 mol.%). This indicates that $T_g$ is above room temperature if the polyol amount is below 30 wt.%.

The samples with partially crystalline PCL2000, PCL4000 and PCL8000 showed a more continuous softening with rising PCL content. A minimum in Shore D hardness was observed for the PCL4000 samples. By comparison, the PCL10000 with the highest molecular weight and almost thermoplastic behavior as pure polymer showed lower softening in high concentrations in the epoxy matrix compared to the lower molecular weight PCLs. Hence the softening effect depends strongly on the molecular weight of the PCL reacted with the epoxy matrix.

With amounts of 55 wt.% and above of partially crystalline PCL4000 (7.2 mol.%), PCL8000 (3.7 mol.%) and PCL10000 (3 mol.%), phase separation occurs in the crosslinked polymer which appears opaque instead of clear and transparent. This separation leads to a significant increase in Shore D hardness (arrow in Fig. 2). With the amorphous PCL400, no turbidity of the cured polymer occurred even with concentrations up to 60 wt.%.

Due to the fact that only partially crystalline PCL4000, PCL8000 and PCL10000 leads to opaque epoxy polymers, the crystalline interactions of the higher molecular weight PCL were proposed as the driving force for the heterogeneous morphology in the formed epoxy network polymer. The crystallization seems to be a dynamic process in the already formed thermoset epoxy network unexpected for crosslinked polymers so it occurs gradually after cooling at room temperature. In other words, crystalline domains are formed in the thermosetting polymer on a time scale between hours and days.

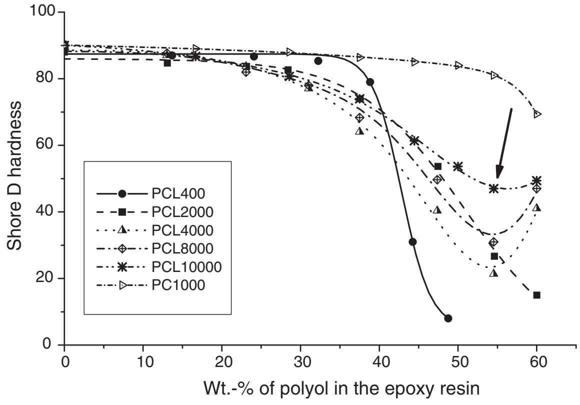

**Fig. 2.** Dependence of Shore D hardness on the PCL content of epoxy samples with different PCL molecular weight. Arrow: higher amounts of PCL4000, PCL8000, and PCL10000 lead to turbid samples.

To investigate the influence of polymeric structure on the flexural properties of epoxy resin, PC1000 was applied as a diol with less flexible polymer chain together with the epoxy resin. This leads, in contrast to PCL containing samples, to more rigid and less flexible samples. They were received as completely transparent polymers up to 60 wt.% (27.5 mol.%) of PC1000. The Shore D hardness only decreases from 89 to 81 for PC contents up to 55 wt.%. Only between 55 and 60 wt.% PC1000 was a small decrease of hardness observed. Hence, as expected for rigid connecting polymers between the crosslinks of the also rigid epoxy matrix, with PC1000 only less softening could be observed for the epoxy polymer.

### *3.3. Fractography*

In order to examine the polymeric structure and the possibility of phase separation of PCL in different concentrations due to intermolecular interactions between PCL units, scanning electron microscopy (SEM) images of 31 and 55 wt.% PCL4000 containing samples as well as a reference of the pure epoxy polymer were recorded. The polymer samples were broken after cooling in liquid nitrogen to preserve the morphology in a condition below $T_g$ of PCL (−60 °C). The concentrations of PCL4000 were chosen with respect to the possibility of observable phase formation. While the 31 wt.% PCL4000 containing sample appeared as homogeneous and transparent polymer, the 55 wt.% PCL4000 containing sample is an opaque polymer due to the suggested phase separated morphology. The images of the fracture surface are shown in Fig. 3.

The SEM image of the 31 wt.% PCL4000 containing sample showed fiber like structures on the surface, broken out of the polymer (image 3C and D). The surface did not appear smooth and has a layer like structure which branches out at the end, and at its rounded edge the fibers jut out. Most likely these “fibers” are the edges of the terraces (image 3D) formed during breakage. The terraces have a height of about 2–5 micrometers. The pure epoxy resin showed a more smooth surface which is only structured towards the sharp edge where branches are also observable (image 3A and B). The fracture surface shows a “conchoidal fracture” typical for brittle polymers. However, fewer fiber-like structures on the surface and not such a regular layer like structure than that of the 31 wt.% PCL4000 containing sample are observable.

In contrast, spherically shaped domains of PCL4000 as result of phase separation in the polymer were observed in the 55 wt.% PCL4000 containing sample (image 3E and F). The surface of this polymer sample does not appear smooth but has a rough morphology which can dissipate the fracture propagation and can lead to a high fracture energy of the polymer. The size of the present structure can be estimated to be in the low micrometer range.

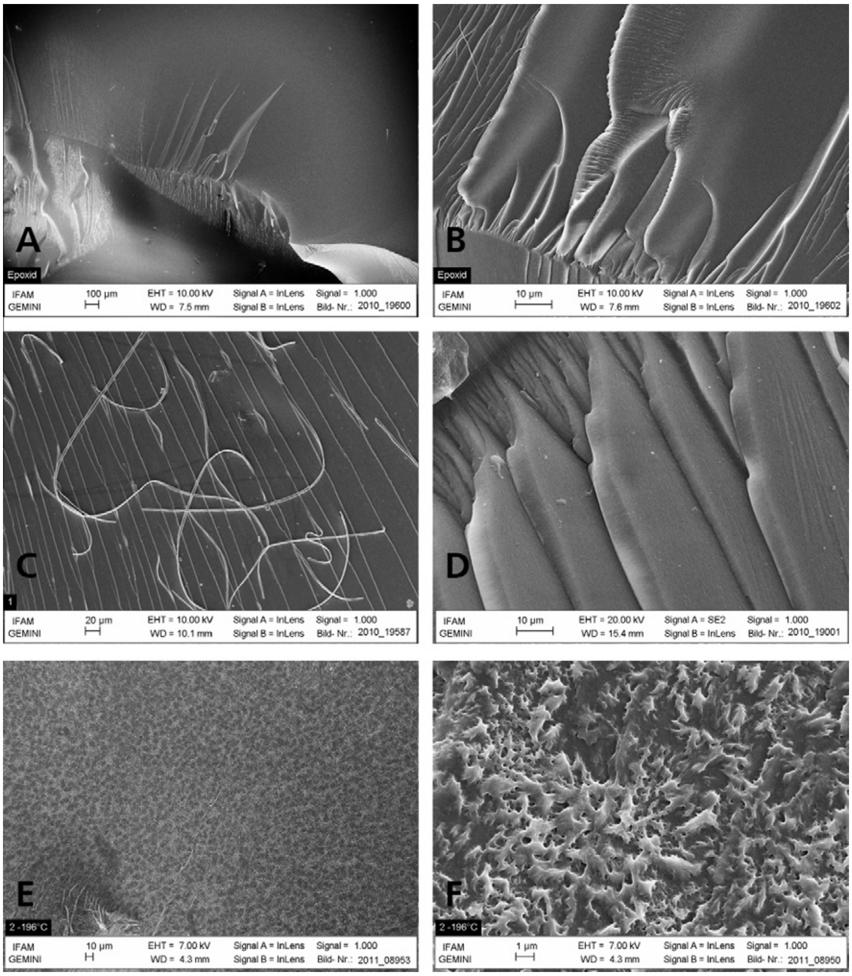

**Fig. 3.** SEM images of the fracture surfaces of pure epoxy polymer (top, A and B), 31 wt.% (middle, C and D), and 55 wt.% PCL4000 containing epoxy polymer (bottom, E and F), broken after cooling in liquid nitrogen.

Polymer samples of the same PCL4000 compositions fractured at room temperature and 125 °C showed only slightly structured surfaces without spherical shaped formations. Supporting information available: SEM micrographs of the PCL4000 containing polymers, fractured at room temperature and 125 °C respectively.

At room temperature the PCL4000 is in a state above $T_g$ but below the melting point (55–60 °C). At this temperature we observed less structured surfaces than at the fracture temperature of −196 °C for both PCL4000 concentrations. This could be expected for the increase in flexibility of PCL4000 chains above $T_g$ but they do not show a complete softening because the temperature is still below the melting point, leading to elastic areas by partially preserving the observed heterogeneous morphology.

Even at 125 °C, above $T_g$ and the melting point of the PCL, a layer like structure could be observed on the fracture surface of the 31 wt.% PCL containing sample. In contrast, the spherically shaped domains for the 55 wt.% PCL4000 containing sample disappeared and the fracture surface becomes smooth. This means that due to the flexibility of PCL4000 above the melting point no crack scattering at the spherical domains occurs and lower fracture energy could be expected.

As shown in the SEM images, the determination of separated phases is not possible if the samples are broken at temperatures above the glass or melting temperature of the compounds being the expected main compound of the different phases. Alternatively, methods using a spectroscopic contrast could be applied but this is not possible in our case as all compounds contain the same elements and chemical groups.

### 3.4. Network structure

Dynamic mechanical analysis was used to characterize the effect of PCL on the temperature dependence of the mechanical moduli as well as on the glass transition temperature. The storage modulus curves of the pure epoxy polymer as well as the curves for the samples containing 13, 23, and 31 wt.% PCL4000, PCL400, and PC1000 are shown in Fig. 4.

The storage modulus of the pure epoxy resin is above 1000 MPa up to a temperature of 160 °C as expected for highly crosslinked thermosetting structures. On increasing the PCL4000 concentration (Fig. 4A), the modulus at high temperature decreases significantly and continuously as a result of lowering the crosslinking density. An increasingly significant sharp kink in the curves was observed with increasing PCL4000 concentration at about −50 °C at the beginning of the modulus decrease. A possible explanation for this could be an increase of flexibility of PCL4000 in the polymer above its glass transition temperature (−60 °C for pure PCL [21]) that leads to formation of a step in the modulus curves with increasing PCL-content. As a separate transition could be determined which can be assigned to one of the components, this indicates also that different phases are present and become more pronounced with increasing PCL content.

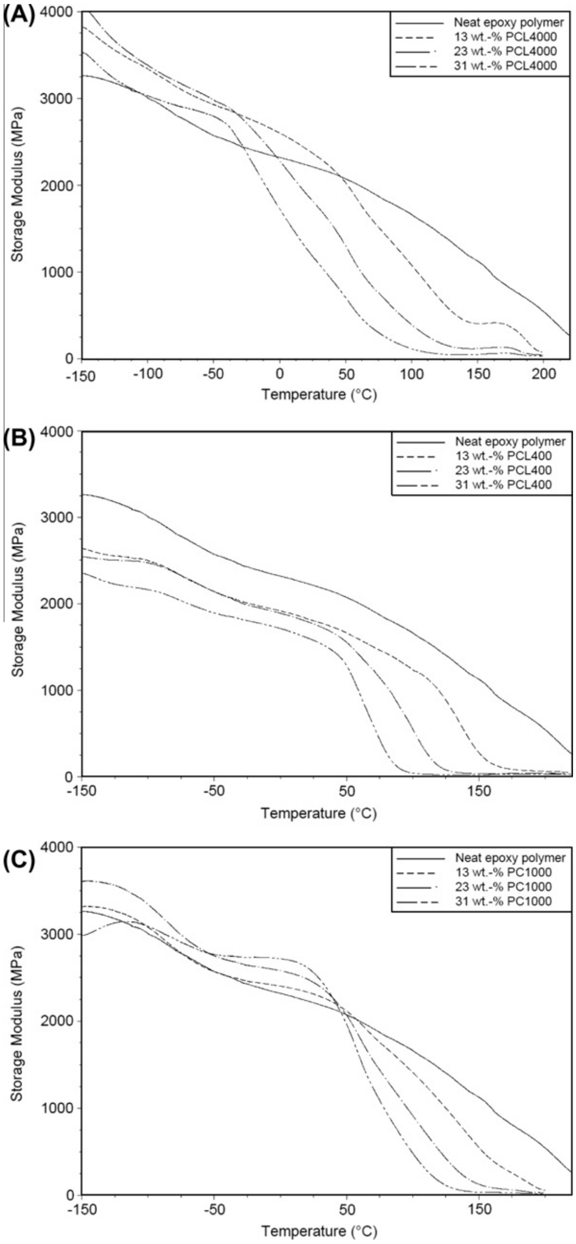

**Fig. 4.** Storage modulus curves of the neat epoxy polymer and the samples containing 13, 23, and 31 wt.% PCL4000 (A), PCL400 (B), and PC1000 (C).

With PCL400 and PC1000 as polyol component (Fig. 4B and C), the same decrease in the modulus was found at a higher temperature of about +50 °C in a sharper step due to lowering the crosslinking density in the epoxy polymer network. The high modulus of the polymer could be preserved up to this temperature.

The absence of a separated transition step in the storage modulus at the melting point of the partially crystalline polyols indicates that no macroscopic demixing of the polyol component from the epoxy matrix occurs. Thus, if phase separation occurs, the scale of the ordered phase seemed to be considerably smaller than a completely demixed PCL, confirmed by the transparent appearance of the polymers.

An important indicator for the changes in the polymer network after copolymerization with polymeric diols is the glass transition temperature ($T_g$). It was determined by DMA as the maximum of tangent delta. Fig. 5 shows example tangent delta curves of the epoxy resin with different amounts of PCL4000 (Fig. 5A) and the $T_g$ of polymer samples containing different amounts of PCL400, PCL4000, and PC1000 (Fig. 5B).

The pure epoxy polymer showed a glass transition temperature as high as 217 °C, as expected for a highly crosslinked thermosetting polymer.

On copolymerization of PCL4000 with the epoxy resin, the $T_g$ decreases with increasing amount of PCL4000 (Fig. 5A). Only one glass transition temperature could be detected which decreases with increasing PCL4000 content from 144 to 126 °C and down to 103 °C for the samples with 13, 23, and 31 wt.% PCL4000 respectively.

With regards to the course of the curves, a kink at about −50 °C, already observed in the storage modulus curves, appears more and more with increasing PCL4000 content as the beginning of tangent delta increase. This could be an indicator of separation of the partially crystalline PCL4000 polymer chains in the epoxy matrix polymer. In contrast, the tangent delta curves of the epoxy polymer with the amorphous PCL400 showed no kink at −50 °C. A second kink at about +40 °C was also observed in the PCL400 containing samples as the beginning of tangent delta peak and the decrease in the storage modulus of the samples. Supporting information available: Tangent delta curves of the PCL400 and PC1000 containing epoxy polymers.

For PCL400 this indicates a polymer in which the PCL is distributed homogeneously because no second glass or other phase transition of separated PCL-phase was observed. The glass transition temperature decreases from 159 to 121 °C and down to 90 °C for the samples with 13, 23, and 31 wt.% PCL400 respectively and showed a stronger decrease for 31 wt.% than with PCL4000.

Hence, due to PCL penetrating the epoxy network the crosslinking density decreases and hence the glass transition temperature also decreases.

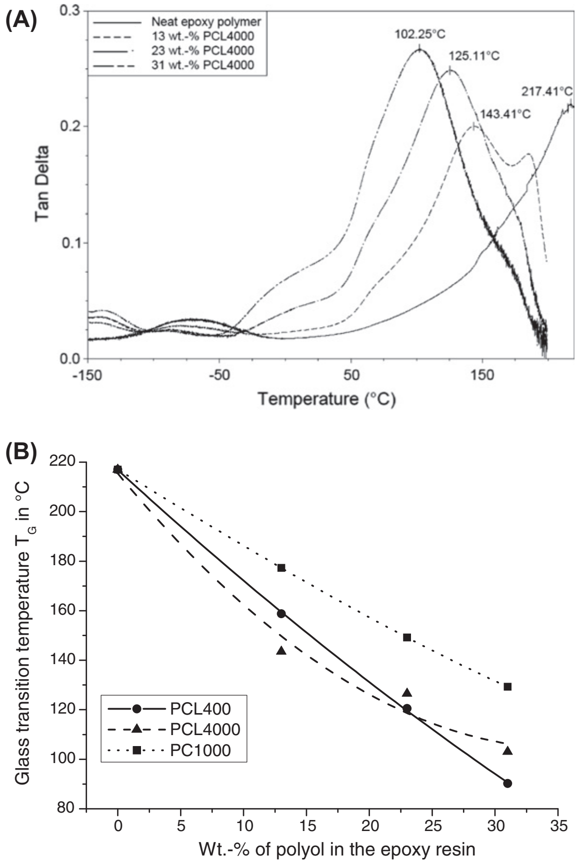

**Fig. 5.** Tangent delta curves of the neat epoxy polymer as well as the curves for 13, 23, and 31 wt.% PCL4000 containing samples (A) and dependence of glass transition temperature on the PCL400, PCL4000, and PC1000 content of epoxy polymers determined by DMA (B).

Fig. 5B shows also the comparison with partially crystalline PC1000 that has a more rigid polymer backbone and a higher melting point (99–111 °C) as pure component than the PCL4000 (40–56 °C). With increasing amount of the PC1000 in the epoxy polymer the $T_g$ decreases in the same way as for PCL400 and PCL4000 from 177 °C to 149 °C and down to 129 °C for 13, 23, and 31 wt.%. However, in general, the $T_g$ for the PC containing samples was 25 K higher than with PCL4000 because of the more rigid polymer backbone leading also to a higher $T_g$ of pure polycarbonate diol. A second glass transition temperature, suggesting a heterogeneous morphology, could not be observed and no melting enthalpy could be measured by DSC for PCL and PC containing samples respectively.

### 3.5. Swelling behavior in acetone atmosphere

A second method for the examination of changes in the polymer network structures is the swelling behavior of polymer samples in solvent. A highly crosslinked thermosetting structure such as the pure epoxy polymer shows no significant swelling in organic solvent atmosphere. By decreasing the crosslink density, solvent molecules can be dissolved in the polymer and swelling occurs. In the case of homogeneous distribution of PCL in the polymer network the crosslinking density decreases with increasing PCL content but in the case of phase separation the epoxy network inhibits the solvent diffusion to the PCL domains and less swelling should be observed. Fig. 6 shows the swelling behavior of polymerized epoxy samples with different amounts of PCL and PC1000 after storage in acetone vapor for 24 h at 21 °C.

As expected the pure epoxy polymer with its highly crosslinked network structure showed nearly no swelling in acetone atmosphere. PCL400 and PC1000 containing epoxides showed a continuous increase of swelling with increasing polyol content caused by the decreasing crosslinking density. If the concentration of the PCL4000, PCL8000, and PCL10000 was below approximately 45 wt.%, the swelling of the samples also increases. At higher concentrations, however, if turbidity occurs due to phase separation of PCL, the swelling decreases.

Assuming that the phase separation occurs by encapsulation of PCL-domains, the swelling behavior can be explained by the hindered diffusion of solvent molecules through the highly crosslinked epoxy barrier and crystalline PCL phases. As soon as the PCL concentration is high enough for phase formation, crosslinking of the epoxide increase as the PCL is deposited in separate domains leading to a decreasing amount of PCL in the epoxide phase with increasing total PCL amount.

Additionally, at PCL concentrations above approximately 45 wt.%, a dependence of swelling on the molecular weight of the PCL4000, PCL8000, and PCL10000 was observed, leading to a minimum of swelling in the case of PCL8000 polymers. This dependence could be explained by the degree of phase separation of the pure PCL domains. In the case of PCL8000, the depletion from the epoxy matrix most likely occurs more effectively than in the case of the other molecular weights used in this study. The resulting degree of phase separation largely determines the final decrease in swelling at 60 wt.% polyol. Nevertheless, the PCL is strongly fixed – most likely by covalent

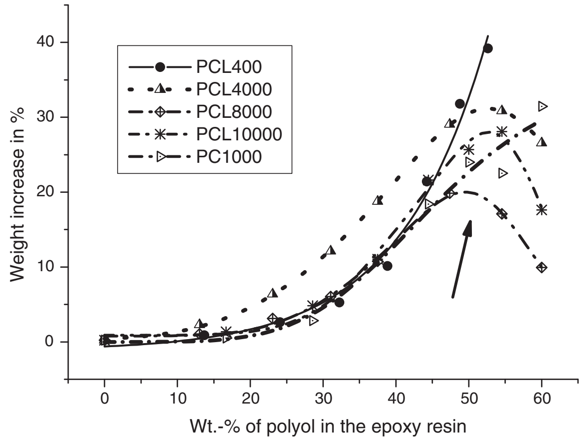

**Fig. 6.** Dependence of the swelling behavior of epoxy polymers in acetone atmosphere (21 ± 2 °C, 24 h) on the amount of different polymeric diols. Arrow: up to higher amounts of PCL4000, PCL8000, and PCL10000 turbidity occurs and swelling decreases.

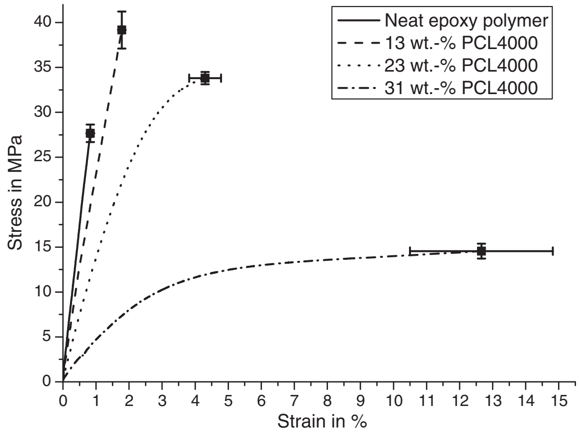

**Fig. 7.** Stress–strain behavior of epoxy resin containing different amounts of PCL4000.

bonds – in the polymer network as PCL cannot be dissolved by Soxleth extraction.

### 3.6. Mechanical characterization of PCL containing samples

To test the effect of PCL and PC on toughening the epoxy resin, stress–strain measurements were performed according to the standard DIN EN ISO 527 [18,19]. The average of the stress–strain curves of at least five samples and the standard deviations of the maximum are shown in Fig. 7 for the PCL4000 samples. All stress–strain-results are summarized in Table 2.

While the pure epoxy resin showed the expected characteristics for a highly crosslinked thermosetting structure with relatively high tensile strength and low elongation at break, the 13 wt.% PCL4000 containing sample showed a simultaneous increase in strength and strain. If the concentration is increased to 23 wt.%, the tensile strength decreases but still remains higher than the tensile strength of the pure epoxy polymer. The higher PCL4000 content leads to a significant increase in elongation at break. A stronger increase of the elongation can be achieved by increasing the PCL4000 concentration to 31 wt.% but the increase in elongation is accompanied by significant and unwanted decrease of the tensile strength at break. Compared to the pure epoxy resin a toughening of the polymerized material was achieved with PCL4000 concentrations of 13 and 23 wt.%, with simultaneous increase in the elongation at break and tensile strength at break. Roughly, the same dependence was found with PCL400 and PCL8000 as polyol component at the same concentrations. However, the PCL400 showed the highest strength at break of 58.1 ± 1.2 MPa at a strain of 3.7 ± 0.4%.

The properties of the epoxy polymer with partially crystalline PCL4000 and PCL8000 changes in a smooth transition from a brittle and rigid thermosetting network to a flexural and elastomeric-like material. With PCL400 only the brittleness changes to toughened but rigid material properties. To achieve high elongation at break in combination with high tensile strength we suggest the crystalline interactions as principle reason to support flexibility and toughness. While PCL400 only reduces the brittleness of the epoxy polymer and high PCL400 contents lead to spontaneous softening, the interactions between partially crystalline polyol chains are able to strengthen the material even during elongation. Thus, even under elongation PCL4000 supplies the required interactions to achieve high strength.

All samples with PC1000 showed a rigid appearance. Due to the rigid polycarbonate backbone in the also rigid epoxy matrix no elastomeric properties could be observed. While the maximum strain could be increased with increasing PC1000 content, the elongation at break stays at a low level, expected for a rigid thermosetting material.

The fracture energy corresponds to the area under the stress–strain curves, was determined as the integral of stress–strain function (Fig. 8).

For all samples an increase of fracture energy compared to the pure epoxy polymer could be observed and an increase in polyol content leads to an increase in fracture energy. Due to the fact that elongation at break increases with increasing polyol content the fracture energy also increases, even if the strength at break strongly decreases. The amount of increase of fracture energy depends on the molecular weight of the polyol as well as on the polymeric structure, as seen by comparing PCL to PC. At constant

**Table 2**
Yield stress and strain and standard deviation of stress–strain measurements of polyol containing epoxy polymers.

| Sample | Yield stress in MPa | Yield strain in % |
|---|---|---|
| Pure epoxy polymer | 27.7 ± 0.97 | 0.83 ± 0.1 |
| PCL400 13 wt.% | 51.9 ± 3.2 | 1.9 ± 0.2 |
| PCL400 23 wt.% | 58.1 ± 1.2 | 3.7 ± 0.4 |
| PCL400 31 wt.% | 37.7 ± 3.3 at maximum stress; 30.0 ± 2.4 at maximum strain (due to creep) | 3.9 ± 0.1 at maximum stress; 10.4 ± 1.6 at maximum strain (due to creep) |
| PCL4000 13 wt.% | 39.2 ± 2.1 | 1.8 ± 0.1 |
| PCL4000 23 wt.% | 33.8 ± 0.7 | 4.3 ± 0.5 |
| PCL4000 31 wt.% | 14.6 ± 0.8 | 12.7 ± 2.2 |
| PCL8000 13 wt.% | 32.1 ± 3.8 | 1.3 ± 0.2 |
| PCL8000 23 wt.% | 29.1 ± 1.2 | 3.1 ± 0.4 |
| PCL8000 31 wt.% | 18.0 ± 0.5 | 6.2 ± 0.7 |
| PC1000 13 wt.% | 32.8 ± 1.7 | 0.9 ± 0.1 |
| PC1000 23 wt.% | 36.5 ± 3.7 | 1.2 ± 0.1 |
| PC1000 31 wt.% | 42.1 ± 2.9 | 1.6 ± 0.1 |

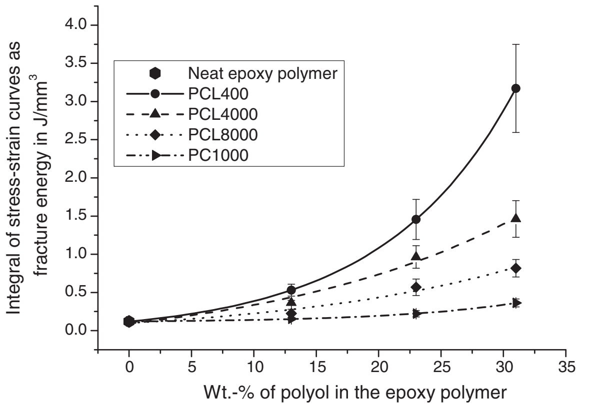

**Fig. 8.** Integral of stress–strain curves for the polymer compositions as fracture energy.

polyol content an increase in PCL molecular weight leads to a decrease in the fracture energy. A significantly lower increase could be observed by using the PC1000 where the low elongation at break leads to low fracture energy.

Regarding the SEM-images, the pure epoxy polymer showed a conchoidal fracture like surface whilst the PCL containing samples showed a more and more structured surface, leading to the enhanced fracture energy.

These results show that toughening of the epoxy polymer, indicated by fracture energy, could be achieved on the one hand with PCL, depending on the molecular weight, and on the other hand with PC but to a lower degree.

Supporting information available: Adhesion characterization of the polymers.

### 3.7. Thermal properties

To examine the thermal properties of the epoxy resin, the thermal degradation of the sample with the highest PCL4000 content of 31 wt.% was compared to the degradation of neat epoxy polymer using thermogravimetric analysis (TGA) (Fig. 9).

Between 200 and 400 °C the weight decrease shows only minor differences between the PCL containing sample and the reference. The initiation of the thermal decomposition was determined at 95% and was 295 °C for PCL4000 containing polymer and 317 °C for the neat epoxy polymer, namely 31 wt.% of PCL4000 leads to an only 22 °C lower start of the decomposition. Similar behavior with a first degradation step for the caprolactone, slightly visible in Fig. 9, has been described in the literature for ε-caprolactone containing bisphenol A diglycidyl ether as well as for pure PCL [22,23]. Additionally, the initial degradation temperature depends strongly on the molecular weight of the PCL. Above 400 °C both curves show nearly the same characteristics with a plateau between 440 and 500 °C as a second degradation step. The derivation of weight decrease gave a maximum thermal degradation at 409 °C for the neat epoxy polymer and 407 °C for the PCL4000 containing sample. This shows that the excellent thermal stability of the neat epoxy polymer was essentially maintained on adding PCL. This is in contrast to previous examinations with poly(tetrahydrofuran) as ether based partially crystalline polyol [15] This confirms that high thermal stability of the PCL containing materials is observed as no volatile decomposition products are formed such as THF in the case of PTHF flexibilization. At higher temperature the smaller second degradation step occurs at 507 and 509 °C respectively, namely at about the same temperature for both

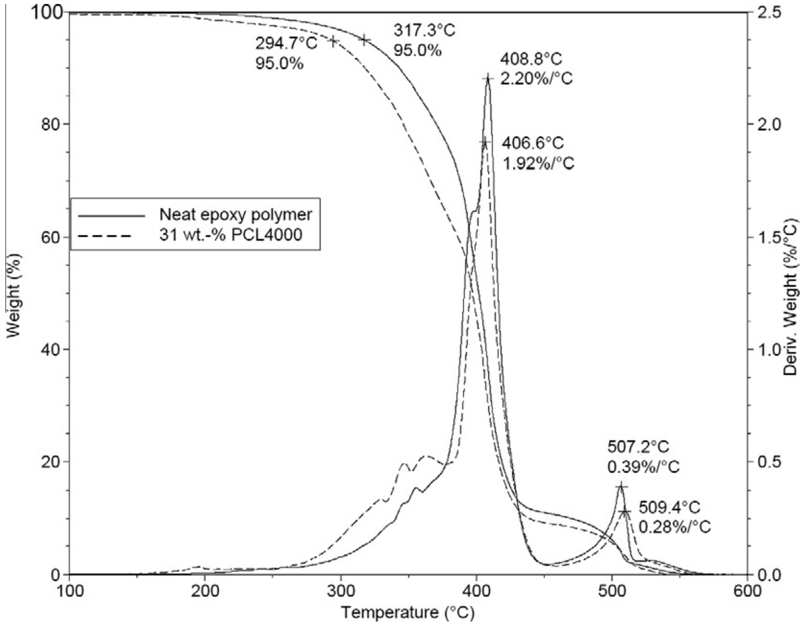

**Fig. 9.** TGA of neat epoxy polymer and 31 wt.% PCL4000 containing epoxy polymer in air with 10 K/min heating rate.

samples. This is most likely the oxidative decomposition of the formed char.

## 4. Conclusions

The use of poly(ε-caprolactone) as polymeric diol integrated in the cycloaliphatic epoxy resin changes the rigid thermosetting polymer to tough materials with low brittleness depending on the PCL content in the polymer and the PCL molecular weight. Toughening with increased tensile strength at break and increased elongation at break occurs even at low PCL concentrations and completely transparent polymers were obtained. The addition of a small concentration of PCL to the epoxy matrix changes the polymer structure from a highly crosslinked rigid epoxy network to a material with slightly reduced crosslinking density. This is shown by the glass transition temperature and swelling behavior and the polymers have a higher strength and are less brittle. This makes the use of PCL interesting for many applications, because stress cracking can largely be prevented and good thermal properties can be obtained.

Less flexible structures, and with it not such high elongation at break, were observed by using the rigid PC1000 as polyol component, indicating that the behavior of the modified epoxy resin does not only depend on the crosslinking density but also on the flexibility of the polymer chains between the crosslinks.

Structural characterization regarding the phase morphology in the polymers with partially crystalline PCL is difficult due to the fact that only small chemical differences exist between the potentially existing separated polyester phase of PCL and a polyester/polyether phase of the epoxy matrix polymer. If the samples are broken at a temperature clearly below the transition temperatures of all phases present in the material, SEM shows the presence of more than one phase, even in the samples with macroscopically homogeneous appearance as the fracture surfaces have a different appearance. The presence of a second phase is confirmed by a kink in the DMA curves and both findings suggest a heterogeneity in the presence of PCL as a result of crystalline interaction.

While the SEM images and the turbidity of the polymers only visualize phase separations at the sub-micron level, the DMA results suggested a kind of ordering of the partially crystalline polyols in dimensions below this scale and below the crystalline order. While these polymers showed a macroscopically homogeneous morphology, the possibility of interactions between the polymer chains of the polyol exist but these are difficult to detect and will be a focus of further studies. Generally, the observed layered structure of the fracture surface obtained by break at low temperatures shows that a morphology in the thermosetting polymer is present which is up until now only known for thermoplastic block-copolymers, but on a length scale which is 1–2 orders of magnitude larger than known for thermoplastic block copolymers.

## Acknowledgments

Funding by the German Research Foundation (project Geklebte Keramikschichtwerkstoffe höchster Zuverlässigkeit), support code HA 2420/11-1 and KO 1635/9-1, is gratefully acknowledged.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.eurpolymj.2012.10.015.

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