

Covalent integration of differently structured polyester polyols improves the toughness and strength of cationically polymerized, amorphous epoxy networks

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ABSTRACT: The structure–property relationship of polyester polyols in cationically polymerized, amorphous epoxy-based copolymers is investigated. An epoxy resin is polymerized in the presence of structurally different polyesters. These resulting copolymers show improved tensile strength and toughness. The optimal epoxide/polyester ratio depends on the structure of the polyesters. Poly(δ -valerolactone) (PVL) reveals the highest ester group density of the investigated polyesters, which enhances physical interactions with the epoxide during polymerization as well as in the network. Furthermore, PVL leads to outstanding tensile strength, strain at break, and toughness. Among all polyester polyols examined, PVL leads to the highest gel fraction or, in other words, the most complete integration into the epoxy network. This work shows that polyesters that are present in the reactive system should be covalently integrated into the polymer network as completely as possible to obtain good mechanical properties of the amorphous copolymer. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43986.

KEYWORDS: cationic polymerization; epoxy resin; poly(δ -valerolactone); toughness

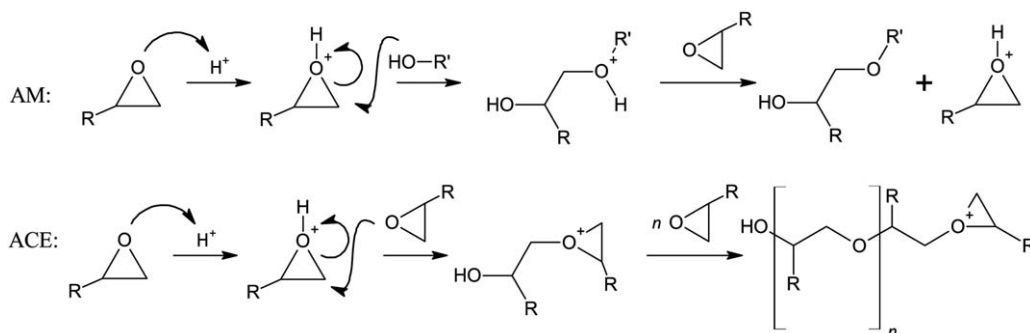
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INTRODUCTION

Epoxy resins are high performance materials with excellent thermal and chemical stability as well as good mechanical properties.¹ They are applied as adhesives, composites, and coatings. Furthermore, epoxy resins have been used in materials that can undergo self-healing,² moldability,³ and shape-memory behavior.^{4,5} Nevertheless, epoxy resins are usually brittle materials, and numerous studies are still dedicated to the improvement of their mechanical properties. Several toughening strategies have been investigated, including nanostructuring,^{6–8} the incorporation of rubber and inorganic fillers,^{9–11} twin copolymerization,¹² and recently the adjustment of crystallinity by partially crystalline polyesters.^{4,13–19} In the last case, polyester polyols are incorporated into the network during the cationic polymerization of an epoxy resin and partly segregate into small amorphous or crystalline domains by reaction-induced phase separation.¹³ In these systems, parts of the polyesters are covalently integrated into the epoxy network by the so-called activated monomer (AM) mechanism (Scheme 1).^{13,20–22} Compared to the neat epoxide propagation by reaction of only epoxide units to a polyether, known as the activated chain end (ACE) mechanism

(Scheme 1), the AM mechanism describes the reaction of a nucleophile, typically an alcohol or humidity, with an epoxide leading to an integration of the nucleophilic species into the network while the epoxide chain becomes terminated. Simultaneously, the terminated chain abstracts a proton which is able to activate a new epoxide.²³ By using alcohols of various size and functionality, the network of the resulting copolymer can be extended and flexibilized. In particular, polyols, such as polyester polyols, are said to be strongly involved in chain transfer reactions leading to a lower crosslink density for epoxy based systems. Flexibility depends on the chain length of the alcohol component as described by Dillman and Jessop,²² who also reported that acidic alcohols, steric challenging ones, or alcohols with long chains lower the chain transfer rate of the cationic epoxide polymerization. Thus, the combination of a certain network extension by partial integration of a polyester polyol of high chain length and the possibility to form nanoscopic domains might be a feasible concept for enhancing toughness. Partially crystalline polyesters are known for their segregation behavior when their concentration is appropriately high or when they are not able to react with the epoxy resin.^{13,15} This phase separation and crystal formation lead to enhanced



Scheme 1. Cationic polymerization of an epoxide through the AM mechanism and the ACE mechanism.

strength and toughness. How polyester polyols influence the epoxy network structure, and thus, what the properties are when crystallization is prevented, for example, when the concentration is appropriately low or a stimulus for crystallization is absent, remains unclear. The influence of structurally different polyesters, for example, differences in ester group density, on cationic epoxide polymerization and network formation has not yet been discussed. Recently, the influence of poly(ϵ -caprolactone) (PCL) integration into an epoxy resin was published.¹⁵ Therefore, this polyester will be used as reference.

In this work, we investigate the influence of the polyester polyol structure, such as ester group density and the effect of the polyesters' semicrystallinity, on the mechanical behavior of cationically polymerized, cycloaliphatic epoxy resins. For this, a noncrystalline polyester and three partially crystalline polyesters with the same molecular weight and hydroxyl end groups, but different molecular structures were compared regarding their structure–property relationships.

EXPERIMENTAL

Materials

All chemicals were used as received from commercial suppliers if not otherwise mentioned in the syntheses section. The cycloaliphatic epoxide 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate (Omnilane OC1005) was purchased from IGM resins (Krefeld, Germany). Poly(ϵ -caprolactone) with a molecular weight of 4000 g mol⁻¹ and hydroxyl end groups (PCL, Capa 2402; initiated with 1,4-butanediol) was donated by Perstorp (Warrington, UK). Dibutyltin(IV) oxide (DBTO), tin(II) chloride (98%), δ -valerolactone, 1,4-butanediol (99%), 3-methyl-1,5-pentanediol ($\geq 98.0\%$), 1,6-hexanediol (97%), toluene ($\geq 99.7\%$, p.a.), and adipic acid ($\geq 99.6\%$) were purchased from Sigma-Aldrich (Steinheim, Germany). Dichloromethane and diethyl ether (p.a.) were obtained from Merck (Darmstadt, Germany). The thermolent initiator benzyl tetrahydrothiophenium hexafluoroantimonate (activation temperature around 110–130 °C) was prepared according to Endo and Uno.²⁴ The release agent ACMOScoat 82-6007 was obtained from ACMOS Chemie KG (Bremen, Germany).

Methods

Spectroscopic Methods. ¹H NMR spectra were measured with a Bruker DPX-200 spectrometer (200 MHz). The spectra were recorded in CDCl₃ at ambient conditions, and tetramethylsilane

was used as external standard. In the case of polyester synthesis via ring-opening polymerization, the shift of the —CH₂—O— group from the ring-closed to the ring-opened structure was followed. Furthermore, the appearance of the —CH₂—OH end group was detected until the signal did not increase any further. The molecular weights M_n were determined by the relationship of the integrals of the —CH₂—O— (approximately 4.0 ppm) signal and the —CH₂—OH (approximately 3.6 ppm) end group signal under consideration of the molecular weights of the educts and the functionality of the initiator used in the case of ring-opening polymerization or the molar ratio of the educts in the case of condensation reaction, respectively. A high scan number of 128 was carried out to obtain a good signal to noise ratio, enabling the reproducible determination of the molecular weights of the polyester polyols. NMR investigations of the sol of Soxhlet extraction experiments were carried out to control the completeness of the polymerization reaction and to determine the identity of the extracted components. Infrared (IR) spectroscopy was carried out with a Bruker Equinox 55 FTIR spectrometer in attenuated total reflection (single-reflection ATR, diamond crystal) equipped with a Golden Gate cell. The resolution was 4 cm⁻¹ (32 scans).

Size Exclusion Chromatography. Size exclusion chromatography (SEC) was performed with a 1260 Infinity Refractive Index Detector from Agilent Technologies (Waldbronn, Germany) to determine the molecular weights and the polydispersities of the polyester polyols. The columns were a PLgel 5 μ m Guard (50 mm \times 7.5 mm; Agilent Technologies), a PLgel 5 μ m MIXED-C (7.5 mm \times 300 mm; Agilent Technologies), and a PLgel 10⁴ Å (7.5 mm \times 300 mm; Agilent Technologies). The measurements were carried out in tetrahydrofuran as solvent with a flow rate of 1 mL min⁻¹ and PMMA as calibration standard at a temperature of 23 \pm 1 °C.

Characterization of Thermal and Mechanical Behavior. Differential scanning calorimetry (DSC) was performed in a sealed pan with a Discovery DSC from TA Instruments in a temperature range of 0–250 °C with a heating rate of 10 °C min⁻¹ for the determination of the polymerization temperature and reaction enthalpies of uncured epoxy/polyester mixtures. The reaction enthalpy was determined from the integral of the occurring exothermic signals and the polymerization temperature from the maximum of the signal. For the investigation into the melting behavior of the pure polyesters and the

epoxy/polyester copolymers, a cyclic DSC was performed with the following thermal profile ($10^{\circ}\text{C min}^{-1}$): (1) cooling to -90°C , (2) holding at -90°C for 10 min, (3) heating to 100°C , (4) holding at 100°C for 5 min, (5) cooling to -20°C , (6) holding at -20°C for 5 min, and (7) heating again to 100°C . The melting enthalpy was determined from the integral of the occurring endothermic signal, whereas the melting and crystallization temperatures (T_m and T_c) were observed from the maximum of this signal. The glass transition temperature T_g of the pure polyesters was determined by the turning point of the decline in the baseline. Shore D hardness was carried out according to standard DIN EN ISO 868 at $22 \pm 2^{\circ}\text{C}$.²⁵ For this, each sample of the copolymers was tested five times. Dynamic mechanical analysis (DMA) was carried out with a DMA 2980 instrument from TA Instruments in a temperature range from -150 to 250°C (heating rate: $2^{\circ}\text{C min}^{-1}$, one heating ramp, measurement frequency 1 Hz, sample was measured as single cantilever) to determine the storage modulus and the glass transition temperature of the copolymer samples. The storage modulus was evaluated at 0 and 250°C . The glass transition temperature T_g (alpha-relaxation temperature T_{α}) was determined from the maximum of loss factor. Stress-strain measurements of the epoxy/polyester copolymers were performed with a Zwick-Z050 at $22 \pm 2^{\circ}\text{C}$. The measurements were carried out according to standard DIN EN ISO 527-2 shape 1BA²⁶ with a testing rate of 1 mm min^{-1} and a maximum gage load of 10 kN. Five specimens were tested for each sample type.

Determination of the Gel Fraction. The gel fraction, that is, the nonsoluble part of the crosslinked network, was determined by Soxhlet extraction experiments. For this, crushed epoxy/polyester copolymer specimens were extracted in a cellulose thimble with 250 mL dichloromethane under reflux for 24 h. Furthermore, no additional weight change was observed after extending the extraction time to 72 h. Thereafter, the sol (extract) and the gel (extracted polymer) were dried in a vacuum oven (10^{-2} mbar) at 65°C until weight constancy. The gel fraction was determined by the weight loss of the gel and was cross-checked by the obtained weight of the sol.

Syntheses

Synthesis of Poly(δ -valerolactone). Poly(δ -valerolactone) (PVL) was synthesized according to the literature with some modifications.²⁷ First, 1,4-butanediol and δ -valerolactone were dried over a molecular sieve (4 Å) and DBTO under vacuum (10^{-2} mbar) for 24 h. A three-necked flask containing a reflux condenser and a septum was flooded with nitrogen. Then 177 mL (1.91 mol) δ -valerolactone, 4.32 mL (0.049 mol) 1,4-butanediol, and 0.190 g (0.8 mmol) DBTO were placed in the flask under magnetic stirring. The solution was stirred at a 75°C bath temperature for 16 days. Later, the resulting polymer was further heated to 130°C for 2 days to obtain complete polymerization. The raw product was dissolved in 250 mL dichloromethane and precipitated in 2000 mL cold diethyl ether. The polymer was filtered and washed three times with 150 mL cold diethyl ether. Finally, the PVL was dried under vacuum (10^{-2} mbar). A white powder was obtained with a yield of 75%.

$^1\text{H NMR}$ (200 MHz, CDCl_3 , δ): 4.08 (t, 2H, $\text{CH}_2\text{—O—}$); 3.65 (t, 2H, $\text{CH}_2\text{—OH}$ end group); 2.34 (t, 2H, $\text{CH}_2\text{—COO—}$); 1.66–1.69 (m, 4H, CH_2).

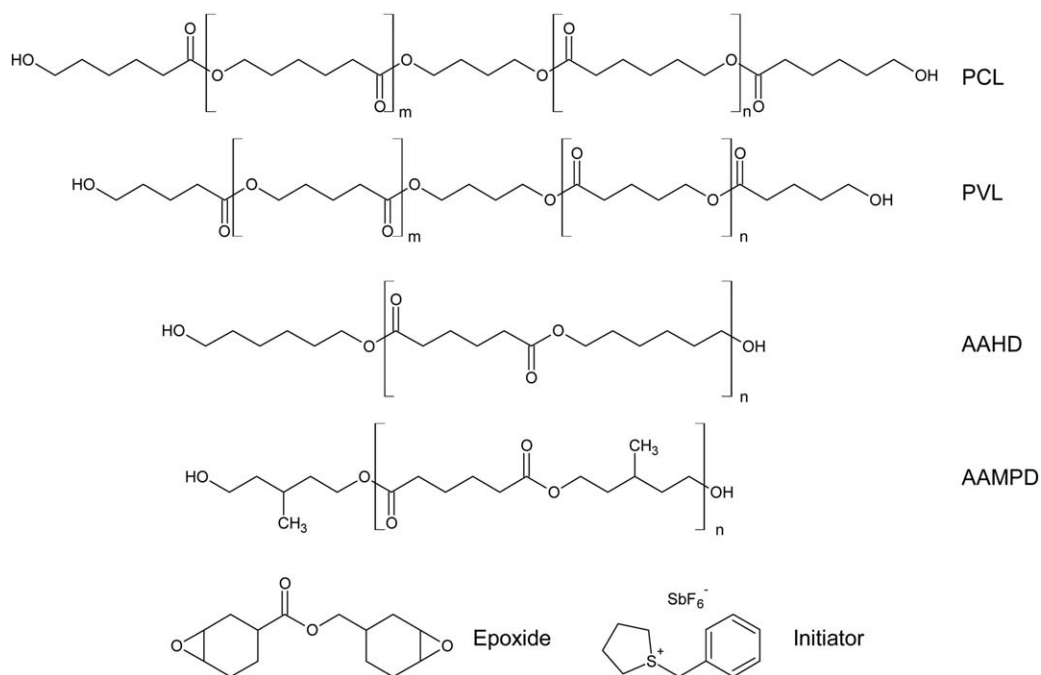
Synthesis of Poly(1,6-hexanediol adipate). A total of 116.71 g (0.799 mol) adipic acid, 100.00 g (0.846 mol) 1,6-hexanediol, and 0.217 g (1.1 mmol) tin(II) chloride were placed in a two-necked flask with a water separator and a reflux condenser. After this, the system was flooded with nitrogen. A total of 250 mL toluene was added to the educts. The mixture was heated at a 130°C bath temperature under magnetic stirring to obtain a complete dissolution of the educts. Then, the solution was stirred at 130°C for 2 days. The water resulting from the condensation reaction was removed by azeotropic distillation. Thereafter, the toluene was removed. Finally, the reaction was completed by heating to 180°C under vacuum (10^{-2} mbar) for 3 h. Poly(1,6-hexanediol adipate) (AAHD) was obtained as a white solid with a yield of 70%.

$^1\text{H NMR}$ (200 MHz, CDCl_3 , δ): 4.04 (t, 4H, $\text{CH}_2\text{—O—}$); 3.63 (t, 2H, $\text{CH}_2\text{—OH}$ end group); 2.33 (t, 4H, $\text{CH}_2\text{—COO—}$); 1.34–1.67 (m, 12H, CH_2).

Synthesis of Poly(3-methyl-1,5-pentanediol adipate). A total of 81.81 g (0.560 mol) adipic acid, 70.00 g (0.592 mol) 3-methyl-1,5-pentanediol, and 0.152 g (0.8 mmol) tin(II) chloride were placed in a two-necked flask with a water separator and a reflux condenser. After this, the system was flooded with nitrogen. A total of 250 mL toluene was added to the educts. The mixture was heated at a 130°C bath temperature under magnetic stirring to obtain a complete dissolution of the educts. Then, the solution was stirred at 130°C for 2 days, and the water formed was removed by azeotropic distillation. After that, the toluene was removed. At last, the reaction was completed by heating to 180°C under vacuum (10^{-2} mbar) for 6 h. Poly(3-methyl-1,5-pentanediol adipate) (AAMPD) was obtained as a viscous, transparent liquid with a yield of 77%.

$^1\text{H NMR}$ (200 MHz, CDCl_3 , δ): 4.07 (t, 4H, $\text{CH}_2\text{—O—}$); 3.65 (t, 2H, $\text{CH}_2\text{—OH}$ end group); 2.28 (t, 4H, $\text{CH}_2\text{—COO—}$); 1.39–1.71 (m, 9H, CH_2); 0.89–0.92 (d, 3H, CH_3).

Preparation of Epoxide/Polyester Copolymers. The epoxy-based copolymers were each prepared with PCL, PVL, AAHD, and AAMPD in concentrations of 10, 20, 30, 40, and 50 wt % polyester. The neat epoxy resin was also polymerized. First, 1 wt % of the cationic initiator benzyl tetrahydrothiophenium hexafluoroantimonate was dissolved in the epoxy resin. Then, the polyester was added and homogenized in an oil bath by heating to 85°C under magnetic stirring for 30 min. Subsequently, the homogenized mixture was transferred into aluminum molds (coated with a release agent) with the dimensions $4 \times 1 \times 0.3$ and $10 \times 10 \times 0.3 \text{ cm}^3$. After that, the samples were polymerized in a preheated oven under the following temperature profile: 30 min at 75°C , 1 h at 110°C , 1 h at 125°C , and 1 h at 145°C . This profile was chosen to ensure a complete cure, but also to avoid an uncontrolled temperature increase due to reaction enthalpy. The samples were cooled to $22 \pm 1^{\circ}\text{C}$ and removed from the molds. The specimens for tensile tests were cut to size by water jet.



Scheme 2. Chemical structures of PCL, PVL, AAHD, AAMPD, 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate (epoxy resin), and benzyl tetrahydrothiophenium hexafluoroantimonate (cationic initiator).

RESULTS AND DISCUSSION

Cationic Copolymerization of an Epoxy Resin with Differently Structured Polyester Polyols

Toughening cationically polymerized epoxy resins with unreactive and reactive additives has been previously investigated.¹³ PCL has been shown to be an effective toughening agent. To obtain information on the structure–property relationship of such polyester polyols polymerized cationically together with epoxy resins, the influence of structurally different polyesters was examined. PCL was used as a standard with known behavior,¹⁵ and in addition, PVL, AAHD, and AAMPD were investigated (Scheme 2). PCL and PVL have a similar structure with the exception of PVL having only five carbon atoms per unit whereas PCL has six. This also leads to a higher ester group density for PVL of the same molecular weight and, therefore, to a higher polarity. In addition to the structural difference, the polymers have different crystallization abilities. AAHD is a polycondensation product of 1,6-hexanediol and adipic acid; thus, the carbonyl groups are arranged alternating but separated by alternating four and six carbon atoms. These three polyester polyols, such as PCL, PVL and AAHD, are partially crystalline and, therefore, potentially more suitable to segregate into nanodomains within an epoxy resin, as previously shown for high amounts of PCL.^{13,15} This is said to be driven by crystallization. On the other hand, crystallization and phase separation are inhibited at low polyester concentrations.¹³ This means that even partially crystalline polyesters are, to a distinct extent, well-miscible in the cycloaliphatic epoxy network used. The question arises whether the semicrystalline character and ester group density of the polyesters have an influence on the thermal polymerization of the epoxy resin when their concentrations are so low that they do not segregate into crystalline domains.

AAMPD is an amorphous telechelic because of its alternating methyl group within the polymer structure, leading to the inhibition of crystallization. PCL was obtained commercially, PVL was synthesized by ring-opening polymerization, and both AAHD and AAMPD were prepared by polycondensation. The molecular weights M_n of the polyesters, measured by ^1H NMR and SEC, are presented in Table I. The molecular weight M_w and the polydispersity P_D , measured with SEC, are also given. The discrepancy between these two measurements results from the PMMA (external) standard used in the case of SEC measurements. PMMA and the polyesters exhibit different solvation, which leads to differences, compared to molecular weight determination by ^1H NMR, which is a method to measure the molecular weight directly by determining functional groups within the polymer structure and is only suitable for telechelic polymers (internal standard). ^1H NMR, with a good signal to noise ratio, is therefore a more reliable method for the molecular weight determination of the polyester polyols used. The calculated molecular weights of approximately 4000 g mol^{-1} are in good agreement with the ones obtained by synthesis. It has been shown that molecular weights M_n of around 4000 g mol^{-1}

Table I. Molecular Weights M_n and M_w as Well as Polydispersity P_D of the Pure Polyester Polyols Determined by Both ^1H NMR and SEC.

Polyester	^1H NMR M_n (g mol^{-1})	SEC M_n (g mol^{-1})	SEC M_w (g mol^{-1})	SEC P_D
PCL	4316	9017	11,378	1.26
PVL	4100	6912	9082	1.70
AAHD	4500	14,388	25,368	1.76
AAMPD	4683	13,033	19,633	1.51

Table II. Melting Temperature (T_m), Crystallization Temperature (T_c), and Glass Transition Temperature (T_g) of the Pure Polyesters Determined with Cyclic DSC.

Polyester	T_m (1) heating (°C)	T_c cooling (°C)	T_m (2) heating (°C)	T_g (°C)
PCL	61	33	51	-63
PVL	53	28	49	-74
AAHD	59	38	54	-59
AAMPD	—	—	—	-67

The T_g was determined from the first heating run.

already lead to a high degree of crystallinity and, therefore, to a strong driving force for phase separation within epoxy resins.^{13,14} The polydispersities range from 1.26 for PCL to 1.76 for AAHD. In order to observe only the partial integration of the polyester polyols used into the epoxy resin, the results by Dillman and Jessop, showing that long chained alcohols result in a reduced chain transfer reaction, need to be considered.²² Therefore, molecular weights of 4000 g mol⁻¹ seem to be suitable to obtain a partial integration of the polyesters into the network leading to flexibility on one hand and segregation on the other hand.

Cyclic DSC was used to determine the melting and crystallization temperatures (T_m and T_c) as well as the glass transition temperature (T_g) of the pure polyesters (Table II). Due to the thermoplastic character of the polymers, this is difficult with other methods such as DMA. AAMPD shows no melting and crystallization as would be expected for an amorphous polymer (Figure 1). Its T_g value is very low at -67°C. PCL, AAHD, and PVL are partially crystalline, as shown by endothermic signals in the DSC heating runs (Figure 1). The presence of crystallinity is known to be beneficial for the mechanical properties of thermoplastics, as reported for other systems.²⁸ The first heating deletes the thermal history so that the cooling run and the second heating step are used for comparisons. The melting and crystallization temperatures (endothermic peaks are taken as T_m

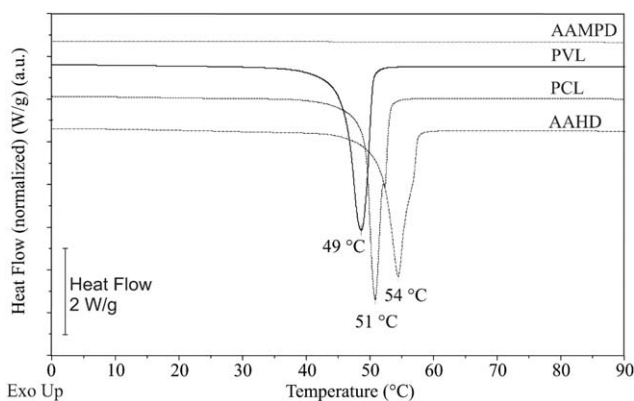


Figure 1. Presentation of the second heating run of cyclic DSC measurements (10°C min⁻¹) of the pure polyester polyols AAMPD, PVL, PCL, and AAHD. The peak temperatures assigned in the thermogram are taken as melting temperatures T_m . For a better illustration, the curves are shifted along the y-axis.

and T_c) of the polyesters decrease in the following order: AAHD > PCL > PVL (54–49°C). Nevertheless, their melting points are similar with a difference of only 5°C. The T_g values of these polyester polyols decrease in the same order as the melting and crystallization temperatures (Table II), which is in agreement with the literature.²⁹

The epoxy-based copolymers were prepared in 10 wt % intervals from pure cycloaliphatic epoxy resin to a content of 50 wt % polyester polyol and polymerized cationically by thermal initiation. The structures of the epoxy resin and the initiator are shown in Scheme 2 in addition to those of the polyesters. IR spectroscopy reveals a complete conversion of the epoxy groups (within the accuracy of the method) as shown by the disappearance of the typical signals at 898 and 789 cm⁻¹ for the cycloaliphatic epoxy resins, which are clearly visible in the spectra of the uncured systems. The reaction behavior was investigated with DSC. For all compositions the reaction enthalpy decreases almost linearly with increasing polyester content, evidencing that the AM mechanism shows a similar effect on heat release compared to pure epoxy propagation (ACE mechanism) (Figure 2). Furthermore, slightly higher values were observed for the epoxide/polyester mixtures compared to the extrapolated epoxy equivalent (theoretical pure epoxide polymerization through the ACE mechanism under consideration of the epoxide content in the mixtures), which indicates a reaction between the epoxide and the polyester polyol. In addition, the DSC measurements reveal two partly overlapping exothermic signals for each polymerization, which are, respectively, assigned to the AM mechanism proceeding in the presence of an alcohol function and the epoxide propagation, known as ACE mechanism. For illustration, both the DSC thermogram of the pure epoxide

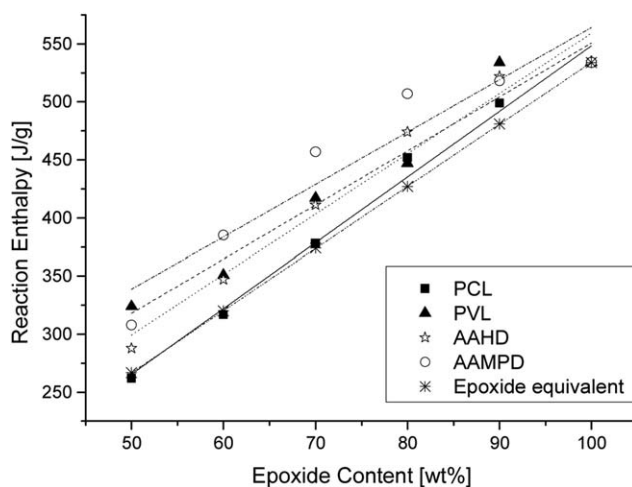


Figure 2. Reaction enthalpies in dependence on the epoxide content for the formation of epoxide/polyester copolymers. Additionally, the reaction enthalpy is given for the epoxy equivalent which means the reaction only through the ACE mechanism. For this, the measured value of the pure epoxide polymerization is extrapolated to a content of 50 wt % (-----). The reaction enthalpy was determined by the exothermic signals in DSC (10°C min⁻¹). The best-fit lines with values of the variance R^2 are given for PCL (—) ($R^2 = 0.99$), PVL (---) ($R^2 = 0.95$), AAHD (···) ($R^2 = 0.96$), and AAMPD (-·-·-) ($R^2 = 0.88$).

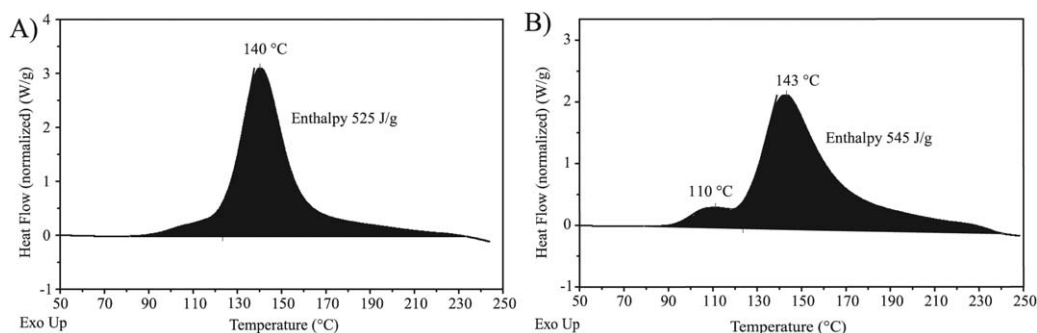


Figure 3. DSC thermogram of the cationic polymerization of (A) the pure cycloaliphatic epoxy resin and (B) the epoxide in presence of 10 wt % PVL measured with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. The temperatures of maximum heat flow and the reaction enthalpy are assigned in the thermogram.

polymerization and the polymerization of the epoxide in the presence of 10 wt % PVL are depicted in Figure 3. The thermogram in Figure 3(B) shows the coexistence of both mechanisms exhibiting two signals, whereas the thermogram for the pure epoxide polymerization [Figure 3(A)] gives only one signal. This behavior of different polymerization temperatures for both mechanisms, which proceed to some extent concomitantly, was identified in previous work on a reactive and a nonreactive polyester.¹³ The temperature of the peak maximum, or shoulder dependent on the epoxy content, is depicted in Figure 4. The signals at a lower polymerization temperature T_{c1} [Figure 4(A)] are assigned to the AM mechanism between the polyester polyol and the epoxy resin generating new protons, which are then able to start a new polymerization. Higher polyester polyol contents lead to an increase in the signal caused by the AM mechanism relative to that originating due to the ACE mechanism. This demonstrates an increasing portion of the AM mechanism proceeding in addition to the ACE mechanism. On the other hand, the signals at a higher temperature T_{c2} [Figure 4(B)] are representative of the epoxide polymerization via the ACE mechanism. Thus, the AM mechanism (T_{c1}) takes place at a temperature 20–30 °C lower than the ACE mechanism (T_{c2}) for low polyester polyol contents and a slightly less reduced temperature (by 10–20 °C) for high polyester contents, as evidenced by the DSC data (Figure 4). This means that initially low concentra-

tions of a polyester polyol lead to a significant reduction in the initiation temperature of the polymerization compared to the ACE mechanism. Within the concentration series, a slight increase in the polymerization temperature T_{c1} , assigned to the AM mechanism, is observed with increasing polyester amount due to increasing dilution of the epoxy functions. On the other hand, the ACE mechanism is shifted to a higher polymerization temperature in the case of increasing polyester content as observed by T_{c2} (second peak maximum in DSC) [Figure 4(B)]. This could be caused by simple dilution effects or by a negative catalytic effect of the ester functions in the polyester polyol, as described by Crivello and Varlemann.³⁰ PVL and AAMPD exhibit the lowest peak maxima for the AM mechanism [Figure 4(A)]. It seems that the hydroxyl end groups of PVL and AAMPD are better accessible for a reaction with the epoxide compared to PCL and AAHD. Furthermore, there is no distinct trend for the influence of the polyesters on the ACE mechanism regarding their structure, as seen by the curing temperature of the pure epoxide propagation under consideration of dilution and negative catalytic effects [Figure 4(B)]. The AAMPD shows the lowest polymerization temperature enhancement of the epoxide propagation followed by AAHD, whereas the other polyesters, PVL and PCL, gave similar effects. In conclusion, the polyester polyols of the same molecular weight and different molecular structure exhibit no clear trend regarding reaction

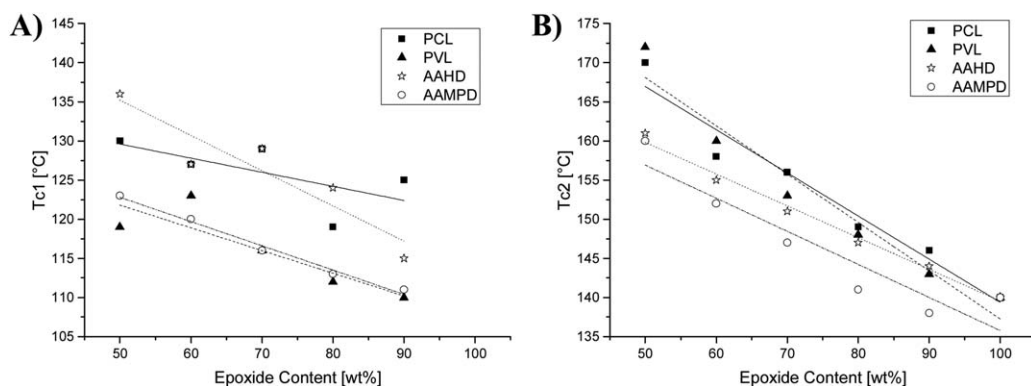


Figure 4. Polymerization temperatures T_{c1} (A) and T_{c2} (B) of the reaction between the epoxy resin and the different polyesters measured by DSC with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. T_{c1} is assigned to the low temperature maximum and T_{c2} to the high temperature maximum, as seen in Figure 3(B). The polymerization temperatures are determined by the peak maxima of the exothermics in DSC measurements. The best-fit lines with values of the variance R^2 are given for PCL (—) [$R^2(T_{c1}) = 0.24$; $R^2(T_{c2}) = 0.95$], PVL (—) [$R^2(T_{c1}) = 0.69$; $R^2(T_{c2}) = 0.95$], AAHD (···) [$R^2(T_{c1}) = 0.82$; $R^2(T_{c2}) = 0.99$], and AAMPD (---) [$R^2(T_{c1}) = 0.99$; $R^2(T_{c2}) = 0.85$].

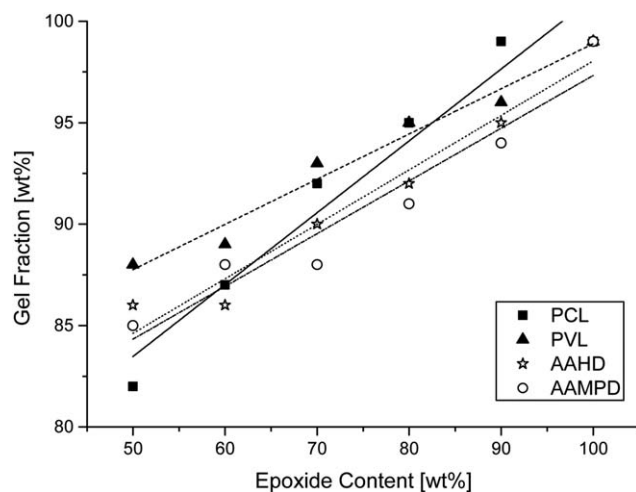


Figure 5. Gel fractions of the epoxy networks containing different amounts of polyester polyols. The gel fractions of the thermally polymerized samples were determined by Soxhlet extractions with dichloromethane for 24 h. The best-fit lines with values of the variance R^2 are given for PCL (—) ($R^2 = 0.94$), PVL (---) ($R^2 = 0.97$), AAHD (···) ($R^2 = 0.95$), and AAMPD (-·-·) ($R^2 = 0.92$).

behavior with the epoxy resin. Influences on polymerization temperatures by polyester polyols seem to be more complex than only being determined by the ester group density. Also, phase formation and molecular aspects of morphology by the polyesters themselves during the reaction could play an important role in cationic epoxide polymerization. For example, it is conceivable that parts of the hydroxyl groups of the polyester polyols are entrapped in the polyester phase during polymerization so that they are not accessible for reaction. In other words, they are more or less exhibited towards the epoxy resin and thus are available for reaction.

Gel fraction measurements point out that increasing polyester polyol contents result in lower gel fractions of the copolymers (Figure 5). For this reason, parts of the polyester polyols are not covalently integrated into the network structure of the epoxy resin. Nevertheless, even at high polyester polyol contents, the degree of integration into the epoxy network is high with more than 80% gel fraction. This observation evidences a high degree of reaction via the AM mechanism, confirming the results obtained by DSC. Thus, polyester polyols are suitable as chain transfer agents leading to a reaction in the early stage of polymerization and, therefore, to higher gel fractions due to a more favored reaction via the AM instead of the ACE mechanism. This observation is in good agreement with previous work showing that the AM mechanism is able to proceed under milder conditions than the ACE mechanism.¹³ Furthermore, it has been shown that higher curing temperatures favor the ACE mechanism in the cationic polymerization of cycloaliphatic epoxides, leading to just a low degree of polyester polyols' integration into the epoxy network.¹⁸ The sol fraction was analyzed by ¹H NMR spectroscopy and consists only of the polyester polyol, as expected for a complete conversion of the epoxy resin. In addition to the AM mechanism, a small amount of polyesters is also integrated into the epoxy network via transesterification,

as was shown recently.³¹ PVL reveals the highest gel fraction of the examined polyester polyols, which leads to the conclusion that it reacts well via the AM mechanism and, compared to the other polyesters, to a higher extent. It seems that the hydroxyl groups of PVL are more accessible during the reaction with the epoxy resin compared to PCL, AAMPD, and AAHD, which could be caused by a better miscibility of PVL with the epoxy resin during polymerization due to a higher ester group density. All copolymers are amorphous, as determined by cyclic DSC measurements (absence of endothermic signals), as a result of high gel fractions, and thus, they show a strong inhibition of crystallization in the concentration range examined.

Mechanical Properties

The copolymer formation was achieved under mild curing conditions and parts of the polyester polyols were covalently integrated into the epoxy network, as shown by the gel fraction and DSC measurements. The question is how this covalent integration of polyester polyols into the epoxy network, forming amorphous copolymers, influences the thermo-mechanical properties, namely glass transition temperature T_g , dynamic mechanical (DMA), Shore D hardness, and tensile properties.

The glass transition temperature T_g was determined by the maximum of loss factor ($\tan \delta$) measured with DMA (Figure 6). It corresponds to the alpha-relaxation process at the highest temperature, which is also termed the alpha-relaxation temperature (T_α). In the following, the term glass transition temperature is used. The T_g values decrease almost linearly with decreasing epoxy content due to both (1) the network extension (decreasing crosslink density, see below) due to the covalent integration of polyester polyols into the epoxy matrix and (2) a plastizing effect due to the presence of the non-bound but well-miscible polyesters within the copolymer. The ester groups adjust the polarity of the polyesters to that of the epoxy resin and it seems that all polyester polyols used have an ester group density which is high enough to

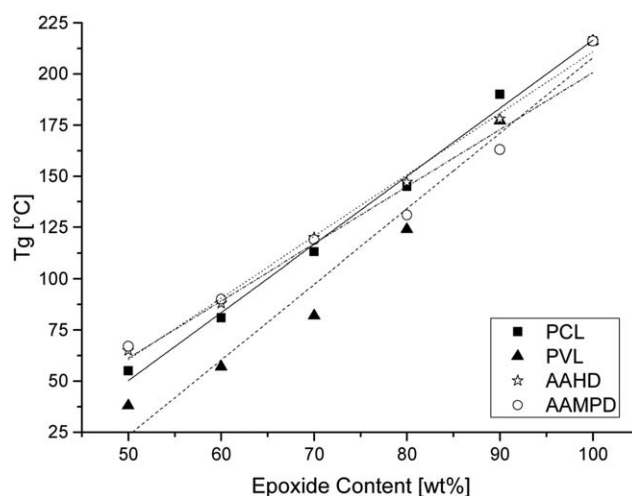


Figure 6. Glass transition temperatures T_g for epoxide/polyester copolymers of different composition determined by the maximum of loss factor (DMA, heating rate 2°C min^{-1}). The best-fit lines with values of the variance R^2 are given for PCL (—) ($R^2 = 0.95$), PVL (---) ($R^2 = 0.97$), AAHD (···) ($R^2 = 0.99$), and AAMPD (-·-·) ($R^2 = 0.95$).

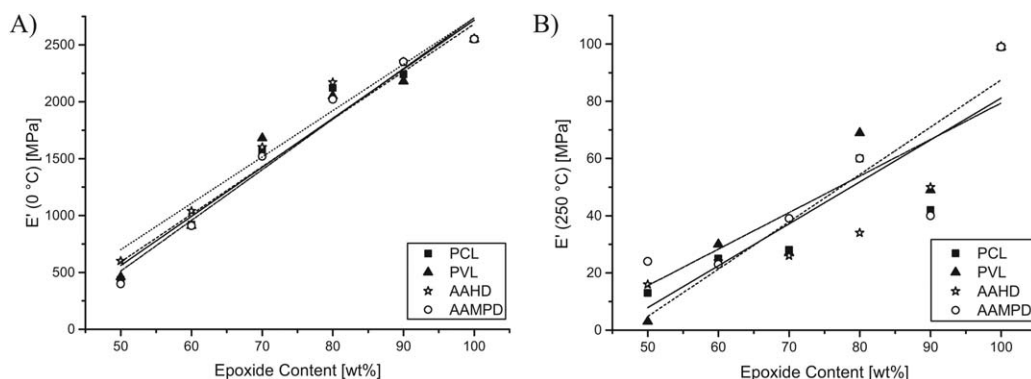


Figure 7. Storage moduli E' in dependence on the epoxide content of epoxy/polyester copolymers at 0 °C (A) and 250 °C (B) determined with DMA (heating rate 2 °C min⁻¹). Best-fit lines are given with their variance R^2 for PCL (—) [R^2 (A) = 0.97; R^2 (B) = 0.72], PVL (—) [R^2 (A) = 0.94; R^2 (B) = 0.78], AAHD (···) [R^2 (A) = 0.95; R^2 (B) = 0.62], and AAMPD (---) [R^2 (A) = 0.97; R^2 (B) = 0.62].

show good miscibility with the epoxy network. PCL, AAHD, and AAMPD result in very similar T_g values whereas PVL reveals distinctly lower ones (for concentrations of more than 10 wt %), which is in agreement with the relatively higher gel fraction and ester group density. Compared to the polyesters used here, poly(ω -pentadecalactone), which has a very low ester group density, is just slightly miscible in the polymerized epoxy network so that even at low concentrations segregation and crystal formation occurred.¹⁸ Furthermore, a mixed T_g according to the Fox equation must be taken into account. The T_g of the polyester is significantly lower than the T_g of the pure epoxy network and even if they were to just form a homogeneous mixture without reacting with each other, the T_g of the mixture should be reduced compared to the respective crosslinked copolymer. Unfortunately, quantification and differentiation of these two effects is not possible with the Fox equation.

The storage modulus (E') was determined by DMA and is shown for two different temperatures (0 and 250 °C) to observe changes in different viscoelastic regions (Figure 7). At 0 °C, the storage modulus increases almost linearly with increasing epoxide content, showing no significant differences between the polyesters [Figure 7(A)]. This temperature is below the glass transition temperature T_g of the polymers. In this temperature region ($T < T_g$), the storage modulus is dependent on the free volume within the network rather than on the crosslink density, as is the case for higher temperatures ($T > T_g$), so that a linear behavior is observed for different polyester contents. A softening of the epoxy resin is observed due to polyester polyol integration into the network via the AM mechanism by an increase in the free volume³² and a simple plasticizing by the nonreacted polyesters in the copolymer network. Both also lead to a reduction in the glass transition temperature. The storage modulus in the rubbery region (250 °C) shows a decrease for higher polyester contents as a measure of a decrease in crosslink density [Figure 7(B)]. This means that the ratio of plasticizer (nonbound polyester) in the network increases with increasing polyester content, which is in agreement with the gel fractions detected. Obviously, there is no difference between partially crystalline and amorphous polyesters regarding the storage modulus of formed copolymers, evidencing similar morphologies of the amorphous copolymers. The crystallization is inhibited by the

network formation in the used concentration range from 0 to 50 wt % polyester. Furthermore, the loss factor exhibits no significant signal which could be assigned to a separated polyester phase (temperature region between -60 and -80 °C). Otherwise, the temperature region of around -80 °C is overlaid by a relaxation step of the epoxy network which just decreases when the epoxy content decreases. Thus, a relaxation step of a separated polyester phase cannot be completely excluded. Additionally, the signal for the T_g of the network in the loss factor curves becomes broader with increasing polyester content. Thus, the properties of the network depend on the compositions. These observations indicate a copolymer network formed by polyester and epoxide as well as additionally dissolved polyester within the network structure without significant phase formation. The results of Shore D hardness are in agreement with DMA data, which means that the hardness also increases with enhanced epoxide content without any differences between the types of polyesters used, as illustrated in Figure 8. In the case of different phase structures, both the hardness and the storage modulus would be different for each polymer system. This means that more strongly segregated epoxide/polyester polymers should result in higher hardness and storage modulus due to the higher crosslink density of the epoxy matrix.

Tensile tests were carried out to determine tensile strength, strain at break, and the deformation energy (area under the stress-strain curve) as a measure of toughness. Figure 9 depicts the tensile strength of the epoxy based copolymers. The pure epoxy resin exhibits a tensile strength of 28 ± 2 N mm⁻², which is the same as or lower than its copolymers containing 10–30 wt % polyester. 20 and 30 wt % of AAMPD and 30 wt % of PVL are exceptions to this behavior, showing lower tensile strengths. This means that the presence of polyester does not generally reduce the strength of the matrix, rather that PCL, PVL, and AAHD are able to improve the tensile strength of the copolymers. Probable explanations for this toughening are physical interactions between the network and the soluble parts by hydrogen bonds between hydroxyl groups and ester carbonyls or the formation of a morphology containing elastomeric domains in a hard matrix polymer. Particularly PVL containing polymers with a tensile strength up to 44 ± 2 N mm⁻² for 20 wt % PVL must be emphasized. PVL exhibits the highest

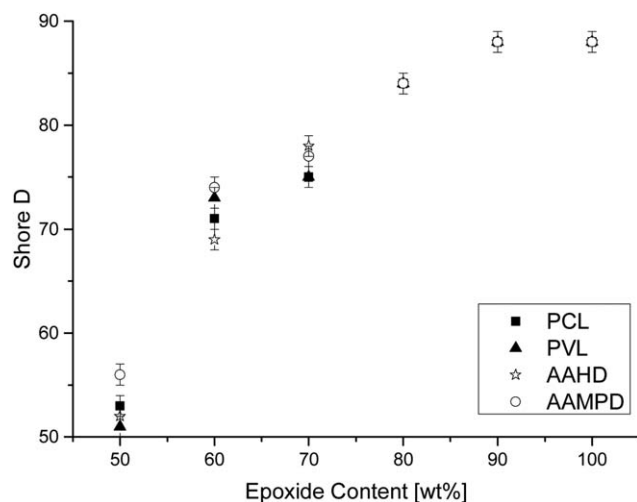


Figure 8. Shore D hardness of the cycloaliphatic epoxy resin copolymerized with varying amounts of different polyester polyols in dependence on the epoxide content.

ester group density of the examined polyester polyols, which would be in agreement with stronger physical interactions by hydrogen bonds. Furthermore, in the case of higher PVL concentrations, the tensile strength decreases strongly as it does for the other polyesters. Furthermore, a polyester content of around 20 wt % results in the highest tensile strength for copolymers, except the one containing AAMPD. Thus, high polyester contents lead to decreased strength due to a strong extension of the network structure and softening, as also shown by storage moduli and the decreasing gel fractions. As discussed before, the cross-link density decreases with increasing polyester content [Figure 7(B)]. The interplay between physical interactions, which are dependent on the molecular structure of the polyester polyols, and softening by decreasing cross-link density might explain the phenomenon of a maximum strength within the concentration series. The strain at break shows a strong nonlin-

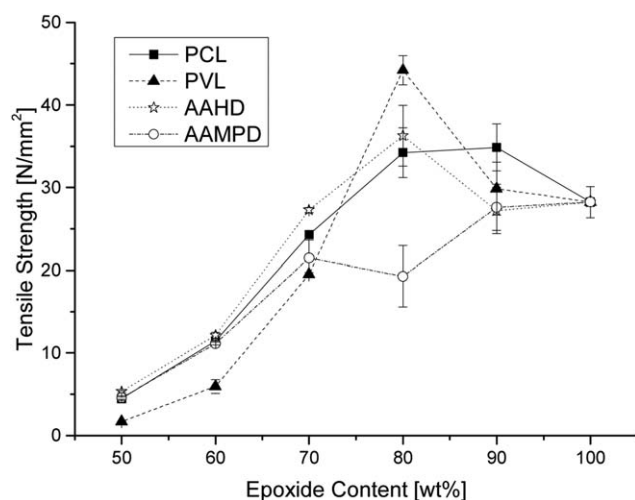


Figure 9. Tensile strength of epoxy/polyester copolymers depending on the content of epoxy resin determined by tensile tests with a testing rate of 1 mm min^{-1} . The connecting lines serve as a guide for the eyes.

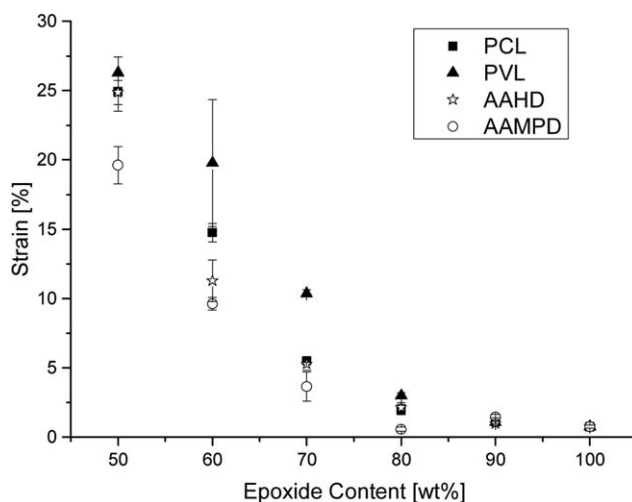


Figure 10. Strain at break of epoxy/polyester copolymers in dependence on the epoxide content determined from stress–strain curves measured with a testing rate of 1 mm min^{-1} .

ear decrease caused by a decreasing ductility when the epoxide content is raised (Figure 10). PVL exhibits the greatest increase in strain which fits well with the observed high gel fractions and low α -relaxation temperatures. On the other hand, AAMPD resulted in the lowest enhancement of strain, which is in agreement with the higher T_g and lower gel fractions. The observation that PCL and AAHD reveal comparable T_g and gel fractions, but a strain at break with values between that of PVL and AAMPD, leads to the conclusion that in addition to the degree of integrated polyester polyol the physical interactions, such as the ability to form hydrogen bonds, might play an important role in the structure–property relationship of amorphous epoxy/polyester copolymers. Additionally, deformation energies are given in Figure 11. As expected, the deformation energies increase in the case of polyester polyols present in the

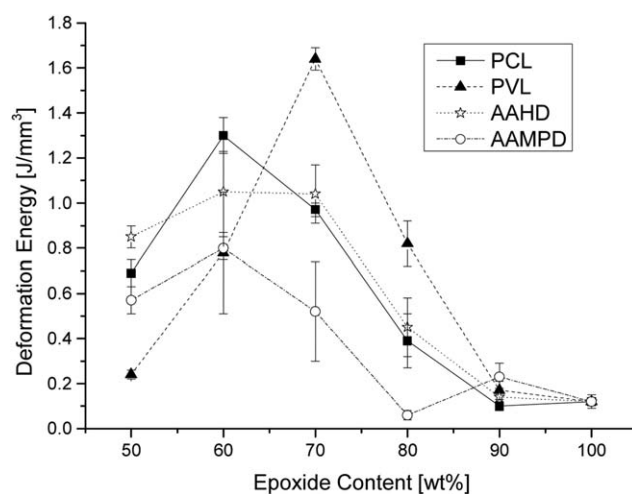


Figure 11. Deformation energy of epoxy networks containing different amounts of polyester. The deformation energy was determined by integration of the area below the stress–strain curves measured with a testing rate of 1 mm min^{-1} . The connecting lines serve as a guide for the eyes.

polymer. PVL, as a toughening agent, results in the highest energy value ($1.6 \pm 0.1 \text{ N mm}^{-3}$) with a content of 30 wt %. The copolymers based on the other polyesters have their maximum at 40 wt % content. The observation of a maximum in deformation energy may be the result of a trade-off between a network softening due to a certain degree of integration of polyester polyols and the physical interactions of the polyester polyols with the epoxy network structure. In summary, examinations of the mechanical properties of the amorphous copolymers show that polyester polyols (in the concentration range used) are able to toughen epoxy resins independently if they are amorphous or partially crystalline when crystal formation is inhibited.

CONCLUSIONS

The structure–property relationship of polyester polyols in cationically polymerized epoxy-based copolymers is examined. For this approach, differently structured polyester polyols, amorphous, and partially crystalline ones are integrated into a three dimensional epoxide matrix by the AM mechanism, as shown by DSC measurements and gel fraction determinations. The presence of the hydroxyl end groups of the polyester polyols leads to a reduced initiation temperature of the polymerization reaction (AM mechanism), whereas the pure epoxide propagation (ACE mechanism) is shifted to higher temperatures in the presence of such telechelics. PVL-based copolymers exhibit the highest gel fractions, which could be explained by a good solubility of PVL in the epoxide during polymerization because of a relatively high ester group density compared to the other polyesters used so that the reactive hydroxyl end groups have good access for reaction. Generally, the presence of polyester polyols leads to a decrease in gel fraction, storage modulus, alpha-relaxation temperature, as well as Shore D hardness and, furthermore, to enhanced toughness and strain at break compared to pure epoxide. In addition, cyclic DSC measurements reveal no crystallinity, which is evidence for an inhibition of crystallite formation in the case of the crystallizable polyesters used. Obviously, the polyester polyols behave similarly, which means that different structures do not have a strong effect on the mechanical properties of the formed amorphous copolymers in the examined concentration range, regardless of whether they are a partially crystalline polyester or not, because crystallization is inhibited by the network. PVL is an exception to this observation, as shown by the very high tensile strength of $44 \pm 2 \text{ MPa}$ for 20 wt % PVL content in the epoxy resin. Additionally, PVL exhibits the highest gel fraction for contents of more than 20 wt % polyester, which is also in good agreement with the lowest alpha-relaxation of the copolymers based on this polyester for the same concentration range due to fewer defects in the epoxy network by non-reacted, amorphous polyesters. Furthermore, PVL also reveals the highest strain at break for all examined polyester polyols because of the high degree of covalently integrated polymer chains and, therefore, pronounced network extension. The relatively high ester group density of PVL might lead to enhanced physical interactions with hydroxyl groups of the epoxy network. Finally, PVL also features the highest meas-

ured toughness, as shown by the deformation energy of $1.6 \pm 0.1 \text{ N mm}^{-3}$. In general, the structure–property relationship of amorphous epoxide/polyester copolymers is very complex, and thus, several aspects need to be considered, in particular the ester group density but also the phase formation and accessibility of reactive end groups during the polymerization as well as the molecular aspects of morphology by the polyesters themselves, and thus, the gel fractions and the crosslink density. This work shows that if a homogeneous network is desired, all components should be integrated into the polymer network as completely as possible to obtain the best mechanical properties. If a heterogeneous morphology is desired, further enhancements of mechanical properties of epoxide/polyester polymers might be possible through the concept of deactivating the AM mechanism.¹³ In this case, AAHD, PCL, and PVL, as partially crystalline soft segments, possibly lead to more distinct mechanical differences within the matrix compared to the amorphous AAMPD.

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