PAPER

Epoxy vitrimers incorporating physical crosslinks produced by self-association of alkyl chains†

F. I. Altuna, [ID] U. Casado, [ID] I. E. dell'Erba, [ID] L. Luna, [ID] C. E. Hoppe [ID] and R. J. J. Williams [ID] *

Epoxy vitrimers were synthesized employing stoichiometric amounts of diglycidyl ether of bisphenol A (DGEBA), sebacic acid (20% eq.) and an *n*-alkylamine, either octylamine (OA), dodecylamine (DA) or hexadecylamine (HA) (80% eq.). Apart from the chemical crosslinks generated by diester groups formed in transesterification reactions, these vitrimers include physical crosslinks arising from self-association of alkyl chains. The relative fraction and strength of physical crosslinks was high for octylamine (OA), intermediate for dodecylamine (DA) and low for hexadecylamine (HA). This was reflected by rubbery moduli that increased significantly from HA to OA. The covalently bonded tertiary amine generated in the epoxy-amine addition reaction was an efficient catalyst of transesterification reactions. Relatively fast stress relaxation rates were observed driven by transesterification reactions coupled to the dynamic exchange of self-associated alkyl chains. The occurrence of this last mechanism was evidenced by the stress relaxation observed for the linear polymer synthesized with stoichiometric amounts of DGEBA and OA that forms a permanent network up to temperatures close to degradation due to the presence of a high fraction of self-associated *n*-octyl chains. These vitrimers might find applications in several fields such as soft robotics, electro and magnetorheological elastomers, soft tissues and in additive manufacturing.

Introduction

Epoxy vitrimers, first described by Leibler and co-workers,[1] are polymer networks based on epoxy-carboxylic acid or epoxy-anhydride reactions that can exchange covalent bonds in an associative path, at appropriate temperatures located above their glass transitions. This exchange of covalent bonds enables flow of the polymer network keeping its crosslinked structure. The viscosity associated with this flow decreases very slowly by increasing temperature above the glass transition, in a similar way than inorganic silica. This enables thermoforming of parts made of epoxy vitrimers paralleling the manufacture of objects made of inorganic glass. Moreover, the possibility of flowing by exchange of covalent bonds leads to a set of outstanding properties like recyclability, welding, self-healing and stress relaxation that produced an increasing interest in these new materials. Following the pioneering paper of

Leibler's group[1] there was an exponential growth of publications in the field of epoxy vitrimers, particularly in those derived from epoxy-carboxylic acid reactions. They covered different areas such as formulations,[2–5] catalysts,[6–10] advanced functional products,[11–16] composites,[17–26] properties,[27–34] and the remote activation of the exchange of covalent bonds.[35–39] At the same time, vitrimers arising from a variety of different chemistries were reported, as described in recent reviews.[40–45]

Studies with model compounds showed that two consecutive reactions take place in stoichiometric blends of epoxides and carboxylic acids employing appropriate catalysts.[46] The first reaction (Scheme 1a) produces the (almost) complete conversion of epoxy groups and carboxylic acids into hydroxyester groups (monoester, ME). This reaction is followed by a slow transesterification reaction where two ME groups are converted into one glycol group (G) and one diester (DE), as shown in Scheme 1b. This second reaction attains an equilibrium state,[8,46–48] and is responsible for the presence of a sol fraction (capping of polymer segments by glycol groups) and the formation of a gel in the reaction of diepoxides (A2) with dicarboxylic acids (B2).[47,48] The experimental value of the equilibrium constant of the transesterification reaction at 110 °C was $K = 0.15$, leading to an equilibrium conversion of hydroxyester groups equal to 44%.[47,48] Therefore, once this condition is achieved, the polymer network contains 56% ME, 22% G and 22% DE groups, a composition that is not reflected

Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET), J. B. Justo 4302, 7600 Mar del Plata, Argentina. E-mail: williams@fi.mdp.edu.ar

†Electronic supplementary information (ESI) available: Fourier transform – infrared study of the epoxy-carboxylic acid reaction; stress relaxation curves at 130 °C; welding experiment of the epoxy vitrimer based on HA; concentration of crosslinks and elastic modulus predicted by the statistical model. See DOI: 10.1039/c9py01787a
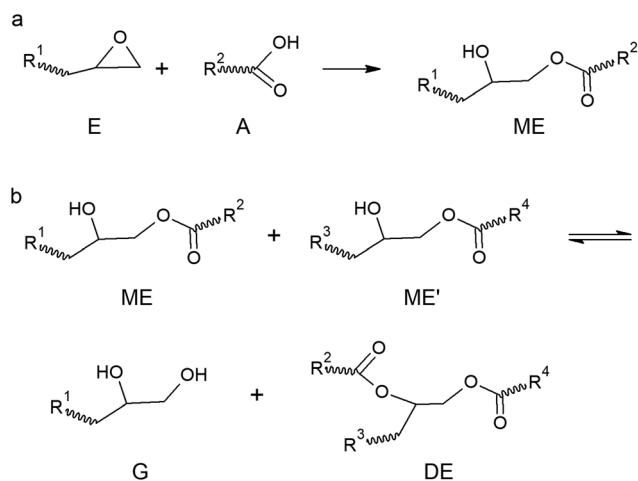
Scheme 1 (a) Reaction of epoxy (E) and carboxylic acid (A) groups leading to hydroxyester groups (ME); (b) equilibrium transesterification generating glycol (G) and diester groups (DE).

in schemes depicted in several papers showing the proposed chemical structure of epoxy vitrimers. Another important experimental evidence of this transesterification reaction was recently reported by Tournilhac's group.[8] They studied the reaction of model G and DE compounds catalyzed by Zn^{+2} salts, at 150 °C. The equilibrium conversion to ME compounds was close to 56%, indicating that the value of the equilibrium constant did not change significantly in the 110–150 °C temperature range.

The transesterification reaction shown in Scheme 1b occurs in both ways in an epoxy vitrimer and contributes to the observed flow of the polymer network at an appropriate temperature range. However, a different set of transesterification reactions might also take place:

$$ME + ME' = ME'' + ME''' \qquad (1)$$

$$ME + G = ME' + G' \qquad (2)$$

$$ME + DE = ME' + DE' \qquad (3)$$
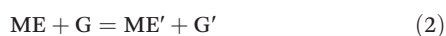
In these equilibrium reactions the chemical groups on both sides of the equation are identical, meaning that the equilibrium constants are equal to one and independent on temperature. Unfortunately, in several papers and reviews the only reaction identified as responsible of the network flow is the addition–elimination reaction expressed by eqn (1), forgetting reactions involving G and DE groups present in the polymer structure.

Properties of epoxy vitrimers may be modified by introducing changes in their chemical structures. For example, catalysts of transesterification reactions can be covalently bonded to the polymer network avoiding the possible degradation or leaching of non-bonded catalysts. In this sense, we recently showed that *n*-butylamine (BA) added in a small proportion (10 mol% with respect to epoxy groups) was converted to a tertiary amine present in the middle of polymer segments that

was effective in catalyzing transesterification reactions.[10] The aim of the present study was to investigate the action of other *n*-alkylamines with different chain lengths: octylamine (OA), dodecylamine (DA) and hexadecylamine (HA). In previous papers we analyzed the structure and properties of the linear polymers obtained by reaction of stoichiometric amounts of diglycidylether of bisphenol A (DGEBA) and an alkylamine.[49,50] Following the complete reaction of epoxy and amine groups, an annealing process at a convenient temperature promoted the formation of a physical gel by the self-assembly of the pendant alkyl chains. The gels produced by DA and HA showed a reversible behavior with temperature whereas the one arising from OA could not be turned into a liquid state by increasing temperature up to values close to degradation.

The specific aim of the present study was to analyze the possibility of introducing pendant alkyl chains in epoxy vitrimers and discuss the effect on the properties of the resulting materials. The tail-to-tail association of alkyl chains and the formation of nanoscopic alkyl domains is employed as the basis of advanced materials for different technological applications.[51–53]

The paper is organized as follows. In a first section the effect of adding small amounts (10 mol% with respect to epoxy groups) of BA, OA, DA and HA in a formulation based on DGEBA, citric acid (CA) and sebacic acid (SA), is discussed. Variations of α-relaxation temperatures and rubbery moduli of the resulting vitrimers are analyzed and the catalytic effect of the covalently bonded tertiary amines (resulting from the reaction of the alkylamines with epoxy groups) is reported employing stress relaxation tests. In following sections, formulations containing larger amounts of OA, DA or HA (40 mol% with respect to epoxy groups) and a stoichiometric amount of sebacic acid (10 mol% with respect to epoxy groups), are employed to promote the association of alkyl chains. An appropriate annealing process that proved to be useful in inducing gelation in linear DGEBA-alkylamine polymers is selected for this purpose. Then, the epoxy vitrimer based on DA is discussed in detail by analyzing the effect of the association of alkyl chains on dynamic mechanical properties and on the stress relaxation at different temperatures. In a following section, a comparative analysis of vitrimers based on OA, DA and HA is presented. Finally, a statistical model of the network structure is developed to estimate the fraction of associated alkyl chains in the annealed vitrimers and its influence on the observed increase of the rubbery modulus. The main findings of this study are briefly pointed out in the conclusions section.

Experimental

Materials

Diglycidylether of bisphenol A (DGEBA, DER 332 Dow Chemicals, epoxy equivalent weight, 174 g per eq.), citric acid monohydrate (CA, 99%), butylamine (BA, 98%), octylamine (OA, 99%), dodecylamine (DA, 98%) and hexadecylamine (HA, 98%), were purchased from Sigma-Aldrich. Sebacic acid (SA,

98%) was kindly provided by Castor Oil (Buenos Aires, Argentina).

Synthesis of epoxy vitrimers containing 10 mol% alkylamine with respect to epoxy groups

The procedure was similar than the one previously reported for BA.[10] Briefly, the alkylamine (BA, OA, DA or HA; 4 mmol = 8 meq) was mixed with DGEBA (20 mmol = 40 meq) in a glass vial that was closed and placed in a convection oven at 100 °C for 1 h, followed by 25 min at 130 °C. Additionally, CA·H$_2$O (16 meq) and SA (16 meq) were mixed in another glass vial and heated in a convection oven at 140 °C. The vial was periodically stirred during 20 min leading to a clear solution. After cooling to 125 °C, the solution was poured into the vial containing the DGEBA-alkylamine product preheated to the same temperature, stirring with a glass rod to obtain a homogeneous solution. It was then casted into a glass mold coated with an anti-adherent film and polymerized at 120 °C for 3 h. Then, materials were heated to 160 °C for 6 h to drive the transesterification reactions towards the equilibrium composition.

Synthesis of epoxy vitrimers containing 40 mol% alkylamine with respect to epoxy groups

In a first step, DGEBA (25 mmol, 50 meq) and SA (5 mmol, 10 meq) were heated to 140 °C in a convection oven. When the SA melted the two components were mixed by manual stirring until a clear solution was obtained. Then, temperature was lowered to 120 °C and a small amount of alkylamine (OA, DA or HA, 1 mmol, 2 meq) was added to generate the tertiary amine catalyst for the subsequent epoxy-carboxylic acid addition reaction (Caution: when this step was performed adding the stoichiometric amount of alkylamine at 120 °C, a fast uncontrollable reaction was observed; it was not possible to decrease temperature in this step due to the crystallization of SA). The solution was kept for 20 min at 120 °C to complete the rapid epoxy-amine addition and advance the epoxy-carboxylic acid addition reaction preventing SA crystallization when cooling to room temperature. After cooling, the remaining 38 meq (19 mmol) of alkylamine were added and temperature was increased to 100 °C. Solutions were manually stirred to assure homogeneity and casted into an open mold made of glass with anti-adhesive coating. The polymerization was carried out for 3 h at 100 °C, leading to the complete conversion of epoxy groups by reaction with both carboxylic acids and amine groups (see ESI†). Then, materials were heated to 160 °C for 6 h to drive the transesterification reactions towards the equilibrium composition.

Synthesis of linear epoxy-alkylamine polymers

Stoichiometric amounts of DGEBA and the alkylamine (OA, DA or HA) were mixed by stirring at 100 °C and polymerized during 24 h at this temperature. During this prolonged period the polymerization was completed and physical gels were obtained by the association of alkyl chains. The influence of temperature on the fraction of physical associations was investigated by performing the synthesis in two steps. The first step was carried out at 100 °C during 3 h and then temperature was varied to a value located in the range 50 °C–130 °C and polymers were annealed during 21 h.

Gel fraction

The gel fraction of linear epoxy-alkylamine polymers annealed at different temperatures was determined gravimetrically for samples cut in pieces of approximately $1 \times 1 \times 0.2$ cm^3. The gel fraction was determined by weighing the insoluble fraction obtained after extraction with tetrahydrofuran (THF) for 24 h at room temperature. These conditions were derived from the analysis of the gel fraction and swelling degree of these amphiphilic polymers in different solvents.[54]

Dynamic-mechanical thermal analysis

Dynamic-mechanical thermal analysis (DMTA) was performed employing an Anton Paar Physica MCR 301 rheometer provided with a CTD 600 thermo chamber, with a parallel plate geometry, at a frequency of 1 Hz (oscillatory mode) and an amplitude of 0.1%, using specimens of 25 mm diameter and a gap of 2 mm between plates. Tests were carried out at a heating rate of 1 °C min^{-1}, from −5 °C to 160 °C or 200 °C, using normal force control to compensate thermal expansion and following the evolution of the storage modulus (G') and loss modulus (G''). α-Relaxation temperatures (T_α) were defined as the maxima of the damping factor (tan $\delta = G''/G'$) peaks.

Applied strains were located in the linear viscoelastic (LVE) region. Typical torque values measured during these tests were below 4×10^{-3} Nm whilst the rheometer is capable to work up to a limit value of 200×10^{-3} Nm. Regarding the normal force, the rheometer was set to maintain its value below 1 N, preventing any normal force value that could damage the equipment.

Stress relaxation tests

Shear stress relaxation was determined with an Anton Paar Physica MCR 301 rheometer provided with a CTD 600 thermo chamber, using specimens with a rectangular cross section (1.5 mm × 5 mm) and a distance of 15 mm between the clamps. Isothermal tests were carried out at different temperatures: 90 °C, 130 °C and 160 °C. When the sample reached the desired temperature, a torsion deformation $J = 5\%$, corresponding to a deflection angle (Θ) of about 30° was applied and the stress relaxation, expressed as a relaxation modulus, $G(t)$, was recorded as a function of time.

Results and discussion

The catalytic effect of covalently bonded alkylamines on transesterification reactions

It was previously shown that butylamine (BA, 10 mol% with respect to epoxy groups) covalently bonded to an epoxy vitrimer was able to catalyze transesterification reactions as assessed from stress relaxation tests.[10] We now report the effect of three other alkylamines (OA, DA and HA) as covalently bonded catalysts in the same molar ratios.
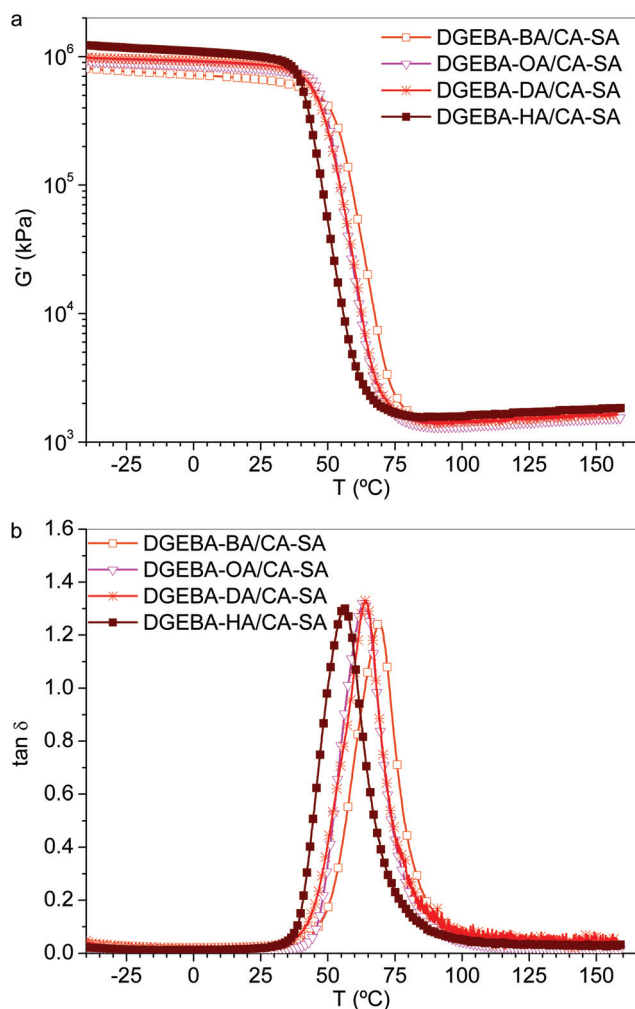
Fig. 1 (a) Storage modulus *vs.* temperature and (b) damping factor *vs.* temperature for epoxy vitrimers containing 10 mol% of different alkyl-amines (BA, OA, DA and HA) with respect to epoxy groups.
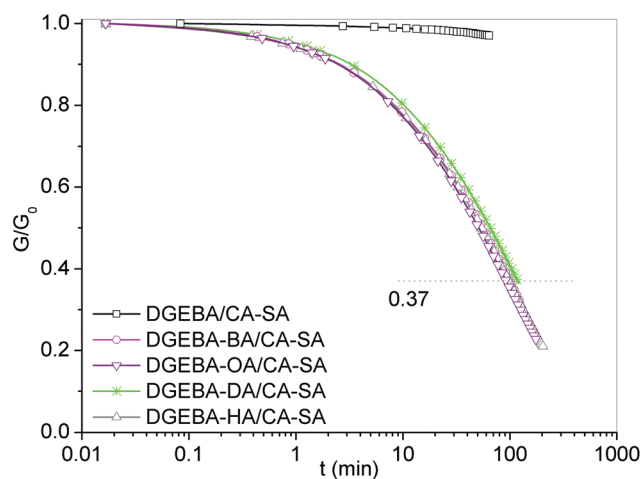

Fig. 2 Stress relaxation at 160 °C for epoxy vitrimers containing 10 mol% of different covalently bonded alkylamines (BA, OA, DA and HA) with respect to epoxy groups, and for a reference sample synthesized with a stoichiometric amount of the same hardeners and without alkylamines.

Fig. 1 shows the storage modulus and tan δ as a function of temperature for epoxy vitrimers synthesized with the four different alkylamines. Increasing the length of the alkylamine chain led to a slight decrease of the α-relaxation temperature (associated with the glass transition) without a significant change of the rubbery modulus (values lie in the range of 1–2 MPa for every formulation).

Fig. 2 shows the stress relaxation at 160 °C for the epoxy vitrimers containing 10 mol% of the four different alkylamines as well as for an epoxy vitrimer synthesized with a stoichiometric amount of the same hardeners and without alkyl-amines. The stress relaxation of this reference sample is negligible supporting the fact that the presence of alkylamines in the initial formulation is necessary to catalyze transesterification reactions. Curves for samples containing the different alkylamines are practically superimposed meaning that their catalytic effect is similar. The characteristic time that brings the relaxation to $1/e$ of the initial value is $\tau \sim 100$ min, a value that lies in the same range reported for other epoxy vitrimers

when using external catalysts at the same temperature.[7] In summary, covalently bonded alkylamines catalyze both the epoxy-carboxylic acid addition reaction as well as transesterification reactions, with rates located in the same range as those obtained using external catalysts.

Generation of alkyl associations in epoxy vitrimers containing covalently bonded alkylamines

In order to generate associations of alkyl chains in an epoxy vitrimer, the amount of alkylamine (OA, DA and HA) was increased to 40 mol% with respect to epoxy groups (80% in equivalents) and a relatively long dicarboxylic acid (SA) was employed as a source of COOH groups (20% in equivalents). This led to epoxy networks with a small concentration of covalent crosslinks generated by a fraction of the diester groups produced by transesterification reactions. The dilution of crosslinks generated polymer networks with rubbery moduli in the range of $10–10^3$ kPa. Materials with this range of rubbery moduli find potential appli-cations in the fabrication of soft robots,[55] electro and magne-torheological elastomers,[56,57] soft tissues,[58] and in additive manufacturing.[59]

We have previously reported the formation of physical gels by thermal annealing of linear polymers formed by the reac-tion of DGEBA and alkylamines (OA, DA and HA).[49,50] We pos-tulated that this physical gelation process occurred by the tail-to-tail association of alkyl chains following a time and temp-erature-dependent process. The presence of these associations was clearly confirmed by small angle X-ray scattering (SAXS) and rheological experiments.

In order to select an efficient annealing process for the epoxy vitrimers we analyzed the gel fraction produced by annealing the linear DGEBA-alkylamine polymers at different temperatures. The linear polymers were synthesized at
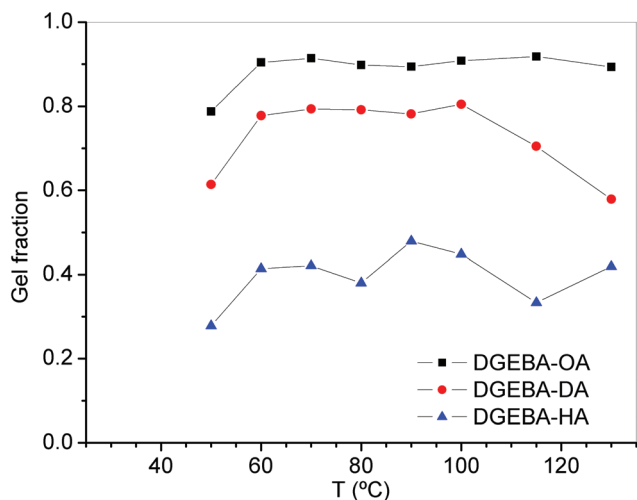
Fig. 3 Gel fractions produced by tail-to-tail associations of alkyl chains after annealing the linear polymers synthesized by reaction of DGEBA with OA, DA or HA (3 h at 100 °C), for 21 h at several temperatures.

100 °C for 3 h and then annealed at different temperatures for 21 h. Fig. 3 shows the resulting gel fractions. It seems evident that the fraction of associated alkyl chains for a fixed time of 21 h decreases in the order OA > DA > HA. We have previously reported that physical gels obtained with DA and HA exhibit a reversible behavior (turned to a liquid state by increasing temperature and gel again during cooling), while those based on OA keep their gel state up to degradation temperatures.[50]

We can infer that the relatively large distance between pendant alkyl chains in the main polymer backbone together with the steric hindrance produced by presence of rigid DGEBA segments acts against the formation of nanodomains containing several associated alkyl chains. Even assuming the possibility that pairs of associated chains can be at relatively close distances, their interactions would be much less significant that those involved in an individual tail-to-tail association. The thermodynamic driving force for this association is the decrease in enthalpy produced by the van der Waals interaction among associated methylene units of both chains. This effect must overcome the simultaneous decrease in entropy produced by the reduction of the number of possible conformations of the individual chains. Increasing temperature enhances the influence of entropy leading to an increase in the fraction of dissociated alkyl chains. The observed increase in the fraction and thermal stability of alkyl associations when decreasing the length of the alkyl chain might respond to the decrease in the entropic penalty for short alkyl chains. Other factors like the increase in the interactions between the main polymer backbones when decreasing the size of the alkyl chains might also play a role.

Based on results shown in Fig. 3, any temperature between 60 and 100 °C could be suitable for the annealing of the epoxy vitrimers described in next sections. We selected the annealing for 21 h at 100 °C.

Characterization and properties of the epoxy vitrimer synthesized with 40 mol% DA with respect to epoxy groups

A detailed analysis of the epoxy vitrimer synthesized with DA is reported in this section while a comparison of main properties of materials synthesized with OA, DA and HA is discussed in the next section.

Epoxy-amine and epoxy-carboxylic acid addition reactions were carried out to completion after the heating step at 100 °C for 3 h (see ESI†). The material was a liquid ($G'' > G'$), meaning that transesterification reactions (Scheme 1b) did not advance to a significant extent (a small conversion in transesterification reactions would produce a gel).[48] In order to drive transesterification reactions towards equilibrium, a heating step at 160 °C during 6 h was performed. Fig. 4 shows the evolution of the storage and loss modulus during this heating step. The crossover of both moduli indicates the formation of a gel by the crosslinks arising from diester fragments. The storage modulus increases towards an equilibrium value (not yet attained after 6 h heating).

At 160 °C, the extent of tail-to-tail association of dodecyl chains is not expected to be significant, as inferred from the fact that the DGEBA-DA linear polymer gelation was not observed at this temperature.[49,50] Hence, in order to generate these physical crosslinks in the vitrimer, the sample was annealed at 100 °C for 21 h. Fig. 5 shows a three times increase of the elastic modulus after annealing produced by the physical crosslinks generated by tail-to tail associations between dodecyl chains. These crosslinks add to those formed by diester groups produced by the previous transesterification process. See also that the initial value of the experiment of Fig. 5 was slightly higher than the one attained after 6 h of heating at 160 °C (final point of G' in Fig. 4). This is explained by the fast build-up of some associations during cooling from this temperature and further conditioning of the sample at 100 °C.

Fig. 6a and b show, respectively, the influence of annealing on the variation of the storage modulus and loss factor with
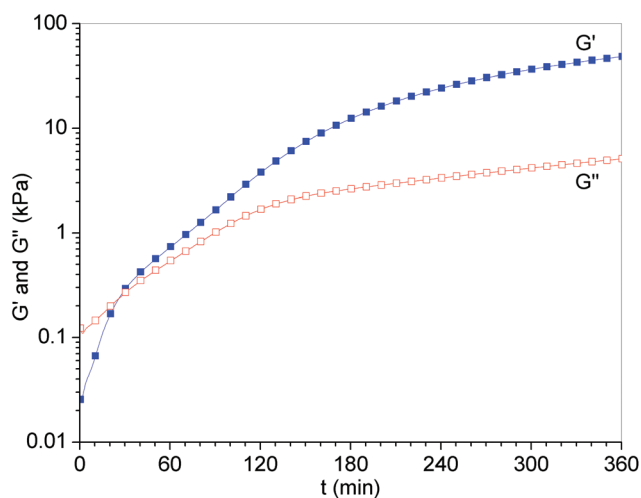

Fig. 4 Evolution of the storage (G') and loss modulus (G'') of the epoxy vitrimer synthesized with DA during the final heating step at 160 °C.
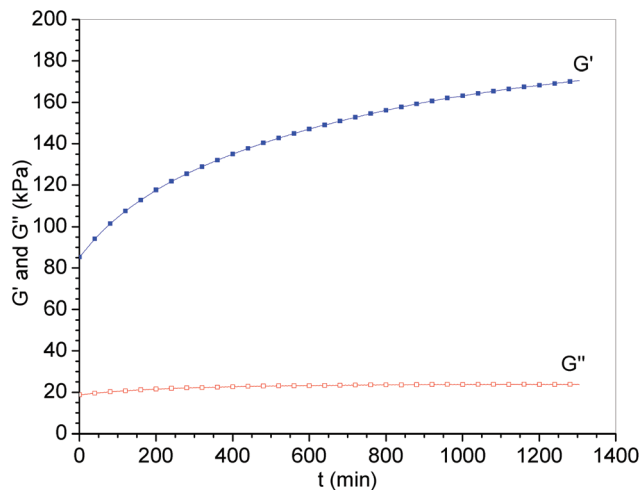
Fig. 5 Evolution of the storage (G') and loss modulus (G'') of the epoxy vitrimer synthesized with DA during the annealing at 100 °C.
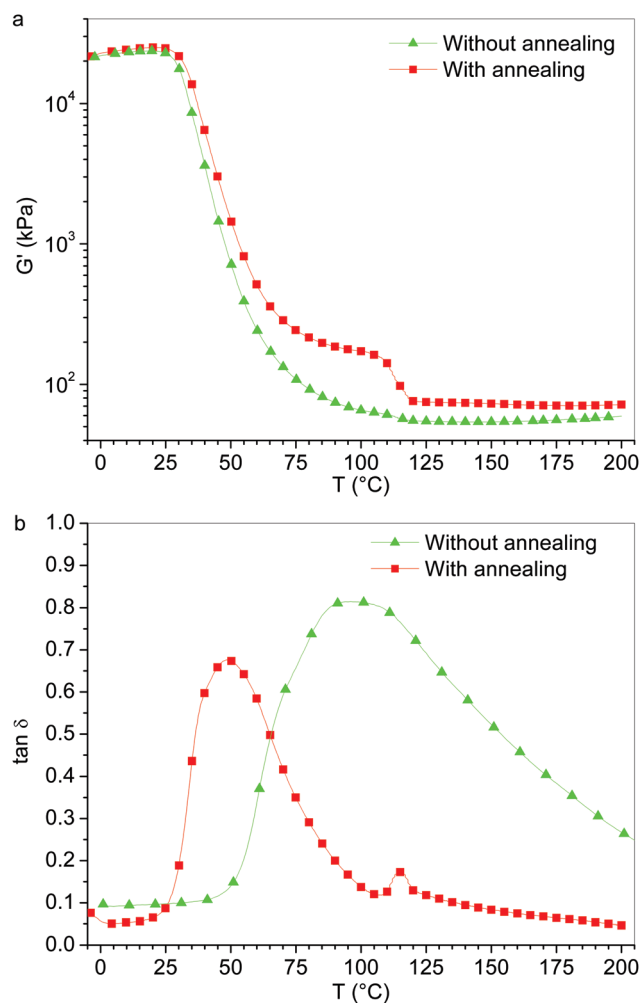

Fig. 6 (a) Storage modulus *vs.* temperature and (b) damping factor *vs.* temperature for the epoxy vitrimer synthesized with 40 mol% DA, with or without a previous annealing process at 100 °C.

temperature. Besides the main drop in G' associated with the α relaxation of the network (with a beginning at about 25 °C) the annealed sample shows a relatively sharp decrease of the rubbery modulus (Fig. 6a) associated with a small relaxation peak (Fig. 6b) in the 110–120 °C temperature range. The sample without annealing displays a continuous decrease in G' and a slight shoulder in the tan δ curve at 110–120 °C.

A possible explanation of the relaxation observed at 110–120 °C may be related to the increase in the concentration and strength of the associations of dodecyl chains (physical crosslinks), produced by the annealing process. The annealed sample exhibits a rubbery plateau at about 100 °C significantly higher than the plateau attained by the sample without annealing. The higher plateau value reflects the contribution of physical crosslinks to the storage modulus. At about 110–120 °C, the presence of transesterification reactions is evidenced at the rate of temperature increase used in the test. The exchange of covalent bonds produced by these reactions facilitates the dissociation of physical crosslinks and leads to the sharp decrease of the storage modulus to a new plateau value.

The influence of annealing on the behavior as a vitrimer was analyzed by stress relaxation tests carried out at temperatures located below and well above the relaxation peak shown in Fig. 6b. Fig. 7 shows stress relaxations tests at 90 °C and 160 °C (stress relaxations tests at 130 °C are shown in ESI†).

At 90 °C, the stress relaxation of the vitrimer without annealing shows a rapid decrease of the modulus from 80 kPa to 50 kPa in about 1 min (Fig. 7a). This last value is close to the one obtained in the final step of the synthesis at 160 °C and is assigned to the vitrimer without physical crosslinks. The initial value of 80 kPa reflects the presence of extra physical crosslinks that were produced during the cooling step and the heating to the test temperature. A similar finding was discussed in connection with Fig. 5. It is also interesting to observe that these extra crosslinks, produced outside the annealing process, are labile and are destroyed during the first minute of the relaxation test. After removing these physical crosslinks, stress relaxation is produced by transesterification reactions following the typical behavior of a vitrimer. The modulus of 50 kPa is reduced to $(1/e)$ at about 300 min, a remarkable fact taking into account the low temperature of the test and the absence of an external catalyst.

The annealed vitrimer also shows a fast decrease of the fraction of labile physical crosslinks in the stress relaxation test at 90 °C (Fig. 7a). The storage modulus decreases from about 170 kPa to 130 kPa in less than 1 min. At this temperature, the fraction of physical associations generated during annealing at 100 °C should not be reduced. The occurrence of stress relaxation is explained by the coupling of transesterification reactions that produce the spatial rearrangements of covalent crosslinks, with a dynamic process involving continuous association and dissociation of physical crosslinks.

At 160 °C no signs of labile physical crosslinks remain in both materials (Fig. 7b). Initial values of modulus are 50 kPa for the material without annealing and about 125 kPa for the
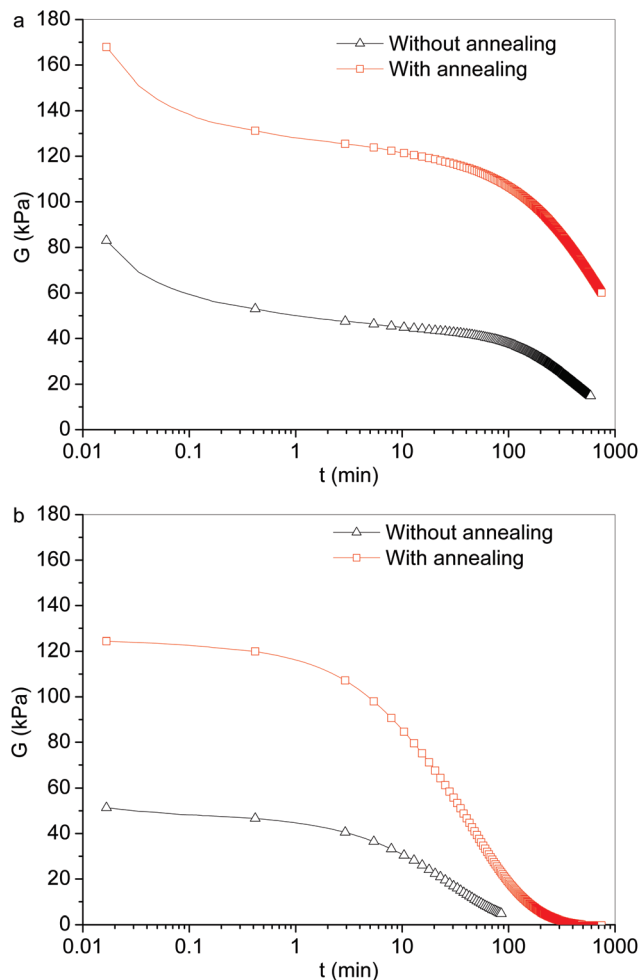
Fig. 8 Stress relaxation tests at 160 °C for the annealed epoxy vitrimers based on OA, DA and HA.

Fig. 7 Stress relaxation at 90 °C (a) and 160 °C (b) for the epoxy vitrimer synthesized with 40 mol% DA, with or without a previous annealing process at 100 °C.

annealed vitrimer. The remaining physical crosslinks were not instantaneously destroyed by fast heating of the sample to this high temperature. As previously mentioned, formation and dissociation of these physical crosslinks is a slow process that depends on temperature and time. Hence, stress relaxation was activated by the spatial rearrangements of covalent crosslinks coupled with the dissociation of physical crosslinks. For both samples, relaxation occurred at relatively fast rates. Characteristic times to reduce the initial modulus to $(1/e)$ are 26.4 min for the vitrimer without annealing and 41.4 min for the annealed material. These fast rates are in part explained by the low crosslink density of the polymer networks.

Comparison of properties of epoxy vitrimers synthesized with 40 mol% OA, DA or HA with respect to epoxy groups

Stress relaxation tests of annealed epoxy vitrimers synthesized using OA, DA and HA are compared in this section. Fig. 8 shows stress relaxation tests at 160 °C of the three families of annealed vitrimers (stress relaxation tests at 130 °C are shown in ESI†).
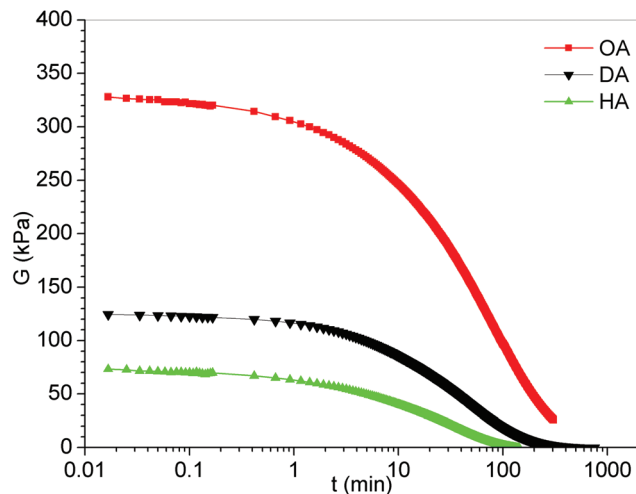
Initial values of storage moduli decrease with the length of the amine alkyl chain: OA > DA > HA, evidencing the increase of physical associations resulting from the decrease in the length of the alkyl chain. The increase with respect to the modulus of vitrimers without physical associations is about 1.5 times for HA, 2.5 times for DA and 6 times for OA. Vitrimers with lower values of the initial modulus relaxed at a faster rate as expected. Characteristic relaxation times to $(1/e)$ of the initial values, were 22.9 min for HA, 41.4 min for DA and 74.9 for OA. In particular, the epoxy vitrimer based on HA shows very fast stress relaxations at low temperatures (at 130 °C, characteristic times were 104 min for the annealed sample and 35 min for the sample without annealing). The possibility of a rapid welding of the epoxy vitrimer based on HA is shown in ESI.†

Fig. 9 shows the evolution of the damping factor with temperature for the annealed epoxy vitrimers based on OA, DA and HA. For the material synthesized with HA, the sharp α-relaxation with a maximum at 32 °C is followed by a broad relaxation extending to high temperatures, assigned to the dissociation of physical crosslinks. The vitrimer synthesized with OA exhibits a similar behavior with a sharp α-relaxation at 45 °C, followed by a broad relaxation of lower intensity than that of the material with HA. This reflects the small fraction of physical crosslinks that dissociate when increasing temperature in this vitrimer. The material synthesized with DA shows a much complex behavior that can be understood by comparison with those of vitrimers based on OA and HA. The initiation of the α-relaxation follows the sequence OA > DA > HA. However, the sharp maximum is absent because of the superposition of this relaxation with the strong relaxation produced by the dissociation of physical crosslinks. For the material with HA, the fraction of physical crosslinks was small so that the broad relaxation produced by their dissociation did not mask the α-relaxation. In turn, the vitrimer with OA has a high amount of physical crosslinks but only a small fraction
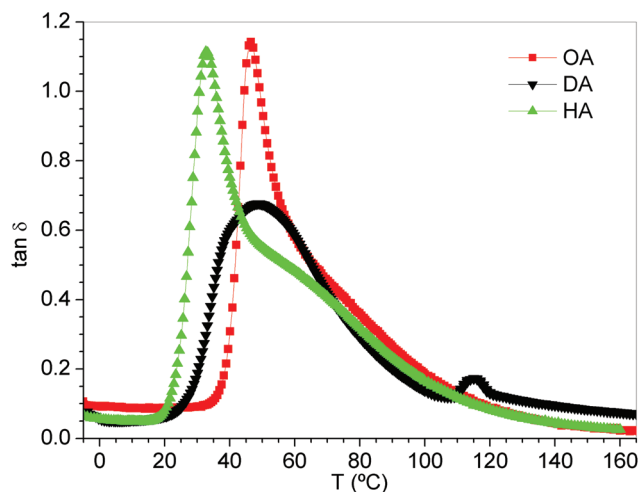
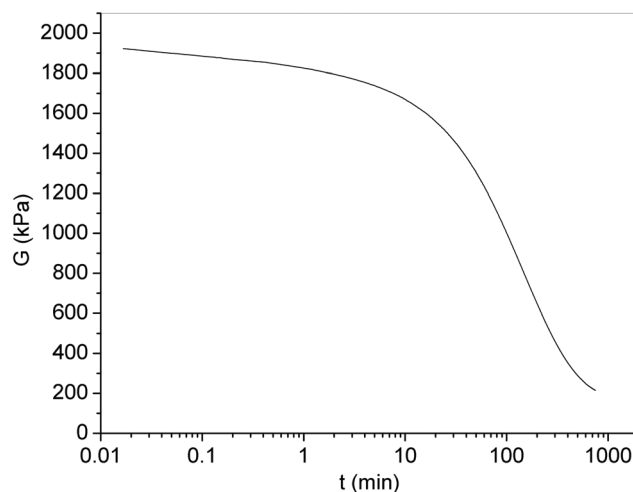Fig. 9 Damping factor *vs.* temperature for the annealed epoxy vitrimers synthesized with OA, DA and HA.

Fig. 10 Stress relaxation test at 160 °C for the linear polymer synthesized with stoichiometric amounts of DGEBA and OA.

dissociates by increasing temperature. The material containing DA forms a relatively high concentration of physical crosslinks that begin to dissociate as soon as the α-relaxation makes it possible. We speculate that more labile crosslinks are first dissociated as soon as the α-relaxation takes place. Dissociation of the strongest physical crosslinks occurs at the small relaxation peak present at the 110–120 °C range, as previously explained.

The storage modulus of these epoxy vitrimers at 20 °C is 12 MPa for the one with HA, 24 MPa for the material synthesized with DA and 30 MPa for the network with OA. They can be classified as soft materials with a broad range of possible applications.

The complete stress relaxation observed for the epoxy vitrimer based on OA requires transesterification reactions occurring together with dynamic association and dissociation processes of the large fraction of physical crosslinks. It is interesting to verify if the dynamic character of these physical crosslinks can be observed in the linear polymer synthesized with stoichiometric amounts of DGEBA and OA (in this case there are no transesterification reactions). The corresponding stress relaxation test is shown in Fig. 10.

The first interesting observation related to Fig. 10 is the significantly higher value of the initial rubbery modulus (1.9 MPa) compared to the value of the epoxy vitrimer (0.3 MPa), obtained by replacing 20% equivalents of OA by sebacic acid (SA). The second important result is the fact that these associations must be dynamic enabling the observed stress relaxation. The process is much slower (characteristic relaxation time equal to 176 min) than the one observed for the epoxy vitrimer obtained with OA (80% in eq.) − SA (20% in eq.) (74.9 min). This is probably due to the much higher elastic modulus of the DGEBA-OA linear polymer and to the absence of transesterification reactions as an additional mechanism to promote stress relaxation.

The DGEBA-OA linear polymer forms a permanent gel up to degradation temperatures due to the high concentration and strength of physical crosslinks.[50] Its stress-relaxation capacity derives from the dynamic exchange of the strong physical crosslinks. These materials cannot be classified as vitrimers because their behavior does not arise from the exchange of covalent segments but from the exchange of physical bonds. They can be classified as vitrimer-like materials because they share with vitrimers the fact of keeping the network integrity during stress relaxation as well as the possibility of self-healing, welding and recycling.

Statistical analysis of network structure considering tail-to-tail associations of alkyl chains

A statistical analysis of the network structure was performed to estimate the fraction of associated alkyl chains that accounts for the observed increase in the rubbery modulus with respect to a reference value obtained at conditions where physical associations are negligible. The fragment approach was used for this purpose.[48,60]

Scheme 2 shows the 5 fragments that may be identified in the epoxy vitrimer after the annealing step. This representation has several implicit assumptions: (a) individual tail-to-tail associations are considered as possible crosslinks without interactions among these physical crosslinks, (b) complete conversion of the epoxy-amine and epoxy-carboxylic acid reactions, (c) attainment of equilibrium in the transesterification reactions involving the generated hydroxyester groups (see the Introduction), (d) no participation of OH groups generated by the epoxy-amine addition on transesterification reactions (see ESI†).

Fragment u-A represents a primary amine that is covalently bonded to two epoxy groups and has an unassociated alkyl tail. Half of both diepoxy monomers are included in this fragment; bonds (a) must be joined to similar bonds present in this and other fragments to complete the struc-
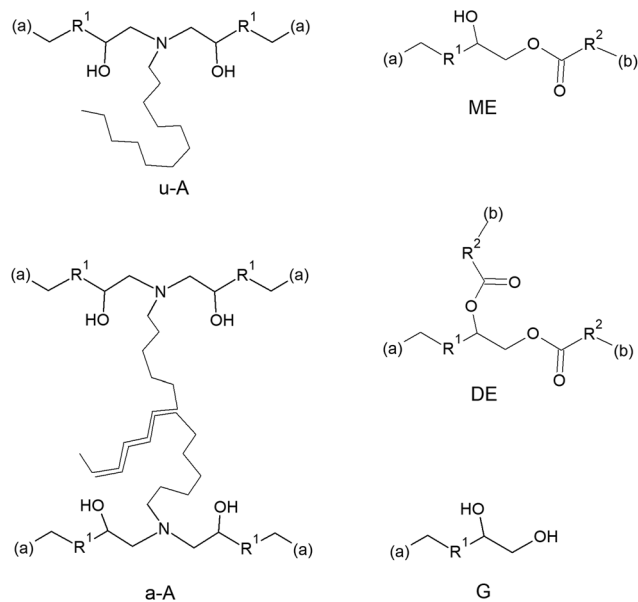
Scheme 2 Fragments present in the epoxy vitrimer.

ture. The initial molar ratio of the amine with respect to epoxy groups was 0.4 (or 0.8 in NH equivalents). Then, the concentration of this fragment in the polymer structure is given by:

$$(\text{u-A})/(E_0) = 0.4\ (1 - f)$$

where f indicates the (unknown) fraction of associated alkyl chains.

Fragment a-A represents fragments produced by associations of alkyl chains. Its concentration is given by:

$$(\text{a-A})/(E_0) = 0.2f$$

Fragment ME represents the hydroxyester groups that remain in equilibrium with glycol and diester groups. Half of the dicarboxylic acid is included in this fragment; bonds (b) must be joined to similar bonds present in this and other fragments to complete the structure. The initial molar ratio of carboxylic acid groups with respect to epoxy groups is 0.2. After attaining equilibrium in transesterification reactions 56% of hydroxyester groups remain in the structure (see the Introduction). Then, the concentration of fragment ME at equilibrium is:

$$(\text{ME})/(E_0) = 0.112$$

Fragments DE and G represent, respectively, diester and glycol fragments. Their concentrations are given by:

$$(\text{DE})/(E_0) = (G)/(E_0) = 0.044$$

From these concentrations it results that $\Sigma(a) = 1$ and $\Sigma(b) = 0.2$, as expected. In order to calculate the concentration of crosslinks in the epoxy vitrimer, the probability of having finite continuations when looking out from bonds (a) and (b)

must be determined. Let us call $F(a)$ and $F(b)$ these probabilities that are given by:

$$F(a) = \sum [\text{probability of joining fragment } i \text{ by a bond (a)}]$$
$$[\text{probability to have a finite continuation from fragment } i]$$

$$F(b) = \sum [\text{probability of joining fragment } i \text{ by a bond (b)}]$$
$$[\text{probability to have a finite continuation from fragment } i]$$

In our case, these probabilities are given by:

$$F(a) = 2 \times 0.4(1 - f)F(a) + 4 \times 0.2f\,[F(a)]^3$$
$$+ 0.112F(b) + 0.044[F(b)]^2 + 0.044$$

$$F(b) = (1/0.2)[0.112F(a) + 2 \times 0.044F(a)F(b)]$$

Crosslinks are derived from both a-A and DE fragments. The concentration of crosslinks with four infinite arms derived from fragment a-A, is given by:

$$X_4 = 0.2f\,[1 - F(a)]^4$$

Crosslinks with three infinite arms can be derived from both fragments a-A and DE. Their concentration is given by:

$$X_3 = 4 \times 0.2f\,F(a)[1 - F(a)]^3 + 0.044[1 - F(a)][1 - F(b)]^2$$

The concentration of elastic chains in the epoxy vitrimer is finally calculated as:

$$\nu = 1.5X_3 + 2X_4$$

By numerically solving the two equations in two unknowns, $F(a)$ and $F(b)$ could be obtained as a function of the fraction of alkyl associations. With these values, concentrations of X_3 and X_4 per unit volume were calculated as shown in ESI.†

Fig. 11 shows the relative increase in the concentration of elastic chains generated by alkyl associations, $\nu(f)/\nu(0)$. The observed increase of the rubbery moduli after the annealing
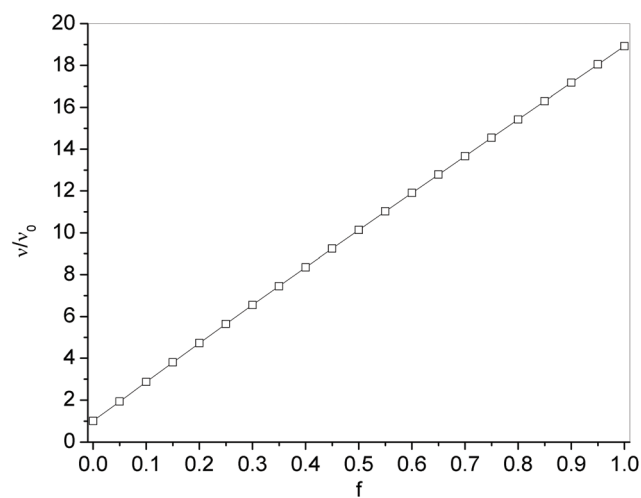

Fig. 11 Relative increase in the concentration of elastic chains as a function of the fraction of tail-to-tail associations, $\nu(f)/\nu(0)$.

process was 1.5 times for HA, 2.5–3 times for DA and 6 times for OA. Using Fig. 11, this leads to a fraction of alkyl associations, $f \sim 0.03$ for HA, 0.08–0.11 for DA and 0.28 for OA. In the case of epoxy vitrimers synthesized with DA and HA most of the crosslinks are trifunctional (X_3) while for vitrimers synthesized with OA, tetrafunctional crosslinks make a significant contribution to the elastic modulus.

Conclusions

Primary aliphatic amines can be employed in small amounts (*e.g.*, 10 mol% with respect to epoxy groups) in formulations of epoxy vitrimers as covalently bonded catalysts for both epoxy-carboxylic acid addition and transesterification reactions. In the series of *n*-alkylamines, varying the length of the alkyl chain from butylamine to hexadecylamine led to vitrimers with similar dynamic-mechanical properties and transesterification rates.

Epoxy vitrimers synthesized with much higher amounts of *n*-alkylamines (40 mol% with respect to epoxy groups) have a small concentration of covalent crosslinks leading to elastic moduli that are characteristic of soft materials. Apart from the catalytic effect of the generated tertiary amines on transesterification reactions, these materials added the possibility of introducing physical crosslinks by promoting associations of alkyl chains with an appropriate annealing process. The relative fraction and strength of these associations was high for octylamine (OA), intermediate for dodecylamine (DA) and low for hexadecylamine (HA). Therefore, the rubbery moduli of the epoxy vitrimers could be tuned in a significant range by the nature of the selected *n*-alkylamine. The increase in the concentration of physical crosslinks produced a corresponding increase in the rubbery modulus at the expense of a decrease in the stress relaxation rate. Stress relaxation was produced by usual transesterification reactions coupled to a dynamic exchange of associations of alkyl chains. The occurrence of this last mechanism was evidenced by the stress relaxation observed for the linear polymer synthesized with stoichiometric amounts of DGEBA and OA.

In summary, epoxy vitrimers containing a large fraction of OA, DA or HA covalently bonded to the polymer structure, exhibit relatively fast stress relaxations without the use of external catalysts. Their properties may be modulated in a broad range by the *n*-alkylamine selected and an annealing process. These vitrimers might find applications in several fields such as soft robotics, electro and magnetorheological elastomers, soft tissues and in additive manufacturing.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

1 D. Montarnal, M. Capelot, F. Tournilhac and L. Leibler, *Science*, 2011, **334**, 965–968.
2 F. I. Altuna, V. Pettarin and R. J. J. Williams, *Green Chem.*, 2013, **15**, 3360–3366.
3 S. Ma and D. C. Webster, *Macromolecules*, 2015, **48**, 7127–7137.
4 S. Zhao and M. M. Abu-Omar, *Macromolecules*, 2019, **52**, 3646–3654.
5 Y. Liu, Z. Tang, S. Wu and B. Guo, *ACS Macro Lett.*, 2019, **8**, 193–199.
6 M. Capelot, D. Montarnal, F. Tournilhac and L. Leibler, *J. Am. Chem. Soc.*, 2012, **134**, 7664–7667.
7 M. Capelot, M. M. Unterlass, F. Tournilhac and L. Leibler, *ACS Macro Lett.*, 2012, 789–792.
8 A. Demongeot, S. J. Mougnier, S. Okada, C. Soulié-Ziakovic and F. Tournilhac, *Polym. Chem.*, 2016, **7**, 4486–4493.
9 X. Niu, F. Wang, X. Li, R. Zhang, Q. Wu and P. Sun, *Ind. Eng. Chem. Res.*, 2019, **58**, 5698–5706.
10 F. I. Altuna, C. E. Hoppe and R. J. J. Williams, *Eur. Polym. J.*, 2019, **113**, 297–304.
11 R. R. Vaidyula, P.-Y. Dugas, E. Rawstron, E. Bourgeat-Lami and D. Montarnal, *Polym. Chem.*, 2019, **10**, 3001–3005.
12 Z. Pei, Y. Yang, Q. Chen, E. M. Terentjev, Y. Wei and Y. Ji, *Nat. Mater.*, 2013, **13**, 36–41.
13 Q. Shi, K. Yu, X. Kuang, X. Mu, C. K. Dunn, M. L. Dunn, T. Wang and H. Jerry Qi, *Mater. Horiz.*, 2017, **4**, 598–607.
14 T. N. Tran, E. Rawstron, E. Bourgeat-Lami and D. Montarnal, *ACS Macro Lett.*, 2018, **7**, 376–380.
15 Y. Yang, E. M. Terentjev, Y. Wei and Y. Ji, *Nat. Commun.*, 2018, **9**, 1906.
16 M. Hayashi, R. Yano and A. Takasu, *Polym. Chem.*, 2019, **10**, 2047–2056.
17 A. Legrand and C. Soulié-Ziakovic, *Macromolecules*, 2016, **49**, 5893–5902.
18 K. Yu, Q. Shi, M. L. Dunn, T. Wang and H. J. Qi, *Adv. Funct. Mater.*, 2016, **26**, 6098–6106.
19 E. Chabert, J. Vial, J.-P. Cauchois, M. Mihaluta and F. Tournilhac, *Soft Matter*, 2016, **12**, 4838–4845.
20 K. Yu, P. Taynton, W. Zhang, M. L. Dunn and H. J. Qi, *RSC Adv.*, 2014, **4**, 10108.
21 Z. Yang, Q. Wang and T. Wang, *ACS Appl. Mater. Interfaces*, 2016, **8**, 21691–21699.
22 Z. Tang, Y. Liu, B. Guo and L. Zhang, *Macromolecules*, 2017, **50**, 7584–7592.
23 Y. Liu, Z. Tang, Y. Chen, C. Zhang and B. Guo, *ACS Appl. Mater. Interfaces*, 2018, **10**, 2992–3001.
24 M. Qiu, S. Wu, Z. Tang and B. Guo, *Compos. Sci. Technol.*, 2018, **165**, 24–30.
25 G. Chen, K. Wu, Q. Zhang, Y. Shi and M. Lu, *Macromol. Res.*, 2019, **27**, 526–533.

26 F. Lossada, J. Guo, D. Jiao, S. Groeer, E. Bourgeat-Lami, D. Montarnal and A. Walther, *Biomacromolecules*, 2019, **20**, 1045–1055.

27 Z. Pei, Y. Yang, Q. Chen, Y. Wei and Y. Ji, *Adv. Mater.*, 2016, **28**, 156–160.

28 L. Imbernon, S. Norvez and L. Leibler, *Macromolecules*, 2016, **49**, 2172–2178.

29 F. Snijkers, R. Pasquino and A. Maffezzoli, *Soft Matter*, 2017, **13**, 258–268.

30 F. I. Altuna, C. E. Hoppe and R. J. J. Williams, *RSC Adv.*, 2016, **6**, 88647–88655.

31 L. Lu, J. Fan and G. Li, *Polymer*, 2016, **105**, 10–18.

32 Q. Shi, K. Yu, M. L. Dunn, T. Wang and H. J. Qi, *Macromolecules*, 2016, **49**, 5527–5537.

33 M. Chen, L. Zhou, Y. Wu, X. Zhao and Y. Zhang, *ACS Macro Lett.*, 2019, **8**, 255–260.

34 Z. Feng, J. Hu, H. Zuo, N. Ning, L. Zhang, B. Yu and M. Tian, *ACS Appl. Mater. Interfaces*, 2019, **11**, 1469–1479.

35 Y. Yang, Z. Pei, X. Zhang, L. Tao, Y. Wei and Y. Ji, *Chem. Sci.*, 2014, **5**, 3486.

36 Y. Yang, Z. Pei, Z. Li, Y. Wei and Y. Ji, *J. Am. Chem. Soc.*, 2016, **138**, 2118–2121.

37 Q. Chen, X. Yu, Z. Pei, Y. Yang, Y. Wei and Y. Ji, *Chem. Sci.*, 2017, **8**, 724–733.

38 F. I. Altuna, J. Antonacci, G. F. Arenas, V. Pettarin, C. E. Hoppe and R. J. J. Williams, *Mater. Res. Express*, 2016, **3**, 045003.

39 Z. Wang, Z. Li, Y. Wei and Y. Ji, *Polymers*, 2018, **10**, 65.

40 C. J. Kloxin and C. N. Bowman, *Chem. Soc. Rev.*, 2013, **42**, 7161–7173.

41 W. Denissen, J. M. Winne and F. E. Du Prez, *Chem. Sci.*, 2016, **7**, 30–38.

42 W. Zou, J. Dong, Y. Luo, Q. Zhao and T. Xie, *Adv. Mater.*, 2017, **29**, 1606100.

43 Z. P. Zhang, M. Z. Rong and M. Q. Zhang, *Prog. Polym. Sci.*, 2018, **80**, 39–93.

44 G. M. Scheutz, J. J. Lessard, M. B. Sims and B. S. Sumerlin, *J. Am. Chem. Soc.*, 2019, **141**, 16181–16196.

45 J. M. Winne, L. Leibler and F. E. Du Prez, *Polym. Chem.*, 2019, **10**, 6091–6108.

46 L. Matějka, S. Pokorný and K. Dušek, *Polym. Bull.*, 1982, **7**, 123–128.

47 K. Dušek and L. Matějka, in *Rubber-Modified Thermoset Resins*, ed. C. K. Riew and J. K. Gillham, American Chemical Society, Washington, D.C., 1984, vol. 208, pp. 15–26.

48 F. Altuna, C. Hoppe and R. Williams, *Polymers*, 2018, **10**, 43.

49 I. A. Zucchi, C. E. Hoppe, M. J. Galante, R. J. J. Williams, M. A. López-Quintela, L. Matějka, M. Slouf and J. Pleštil, *Macromolecules*, 2008, **41**, 4895–4903.

50 J. Puig, I. A. Zucchi, C. E. Hoppe, C. J. Pérez, M. J. Galante, R. J. J. Williams and C. Rodríguez-Abreu, *Macromolecules*, 2009, **42**, 9344–9350.

51 C. E. Hoppe and R. J. J. Williams, *J. Colloid Interface Sci.*, 2018, **513**, 911–922.

52 H. Shi, Y. Zhao, X. Dong, Y. Zhou and D. Wang, *Chem. Soc. Rev.*, 2013, **42**, 2075–2099.

53 G. Gupta, V. Danke, T. Babur and M. Beiner, *J. Phys. Chem. B*, 2017, **121**, 4583–4591.

54 A. Ledo-Suárez, J. Puig, I. A. Zucchi, C. E. Hoppe, M. L. Gómez, R. Zysler, C. Ramos, M. C. Marchi, S. A. Bilmes, M. Lazzari, M. A. López-Quintela and R. J. J. Williams, *J. Mater. Chem.*, 2010, **20**, 10135.

55 D. Rus and M. T. Tolley, *Nature*, 2015, **521**, 467–475.

56 C. Niu, X. Dong and M. Qi, *Soft Matter*, 2017, **13**, 5409–5420.

57 A. K. Bastola, E. Ang, M. Paudel and L. Li, *Colloids Surf., A*, 2019, **583**, 123975.

58 K. M. Fischenich, J. T. Lewis, T. S. Bailey and T. L. Haut Donahue, *J. Mech. Behav. Biomed. Mater.*, 2018, **79**, 341–347.

59 S. Li, H. Bai, R. F. Shepherd and H. Zhao, *Angew. Chem., Int. Ed.*, 2019, **58**, 11182–11204.

60 J.-P. Pascault, H. Sautereau, J. Verdu and R. J. J. Williams, *Thermosetting Polymers*, Marcel Dekker, New York, 1st edn, 2002.