

Epoxy vitrimers incorporating physical crosslinks produced by tail-to-tail associations of alkyl chains

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Epoxy-carboxylic acid addition reaction

The epoxy-aliphatic amine addition reaction is very fast at 100 °C and is certainly completed after 3 h. To assess that the epoxy-carboxylic acid addition reaction was also completed after a heating step of 3 h at 100 °C, we used a model system based on stoichiometric amounts of DGEBA and palmitic acid catalyzed by tributylamine (0.02 molar ratio with respect to epoxy groups). Fourier-transformed infrared (FT-IR) spectra of initial and final materials were obtained with a Nicolet 6700 FTIR Thermo Scientific device in the transmission mode. NIR spectra in the range 4000-7000 cm^{-1} were obtained for samples coated on glass slides. MIR spectra in the range 500-4000 cm^{-1} were obtained by ATR. For all spectra 64 scans were averaged.

Fig. 1S shows the complete disappearance of the characteristic absorption peak of epoxy groups at 4530 cm^{-1} in FT-NIR spectra after 3 h reaction at 100 °C. Besides, spectra in the MIR region (Fig. 2S) confirm the disappearance of the epoxy peak at 915 cm^{-1} after reaction and the replacement of the peak of carboxylic acid at 1699 cm^{-1} by an ester peak at 1734 cm^{-1} .

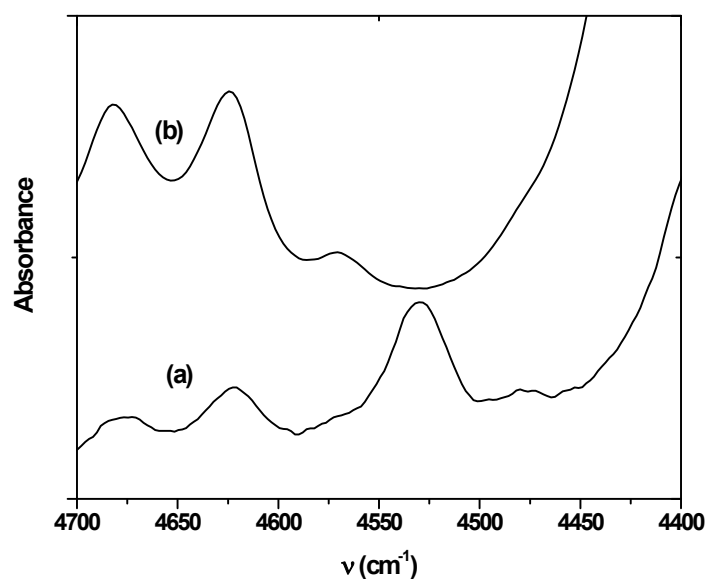


Fig. 1S. FT-NIR spectra of a stoichiometric mixture of DGEBA and palmitic acid with 2 % molar ratio of tributylamine with respect to epoxy groups; (a) $t = 0$ and (b) 3 h at 100°C .

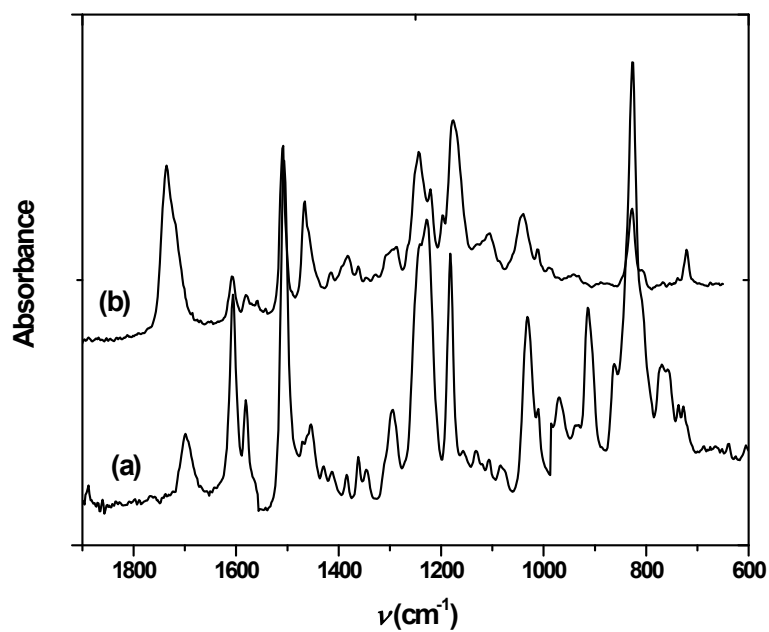


Fig. 2S. FT-IR spectra of a stoichiometric mixture of DGEBA and palmitic acid with 2 % molar ratio of tributylamine with respect to epoxy groups; (a) $t = 0$ and (b) 3 h at 100°C .

Stress relaxation tests at 130 °C

Fig. 3S shows the influence of the previous annealing process on the stress relaxation at 130 °C for the epoxy vitrimer synthesized with 40 mol % DA with respect to epoxy groups. Even if heated at a temperature where a partial dissociation of physical crosslinks is expected, the annealed sample does not show a sudden decrease of the initial storage modulus. Stress relaxation of the annealed vitrimer requires the activation of transesterification reactions in order to produce the spatial rearrangements of crosslinks making it possible the partial dissociation of physical crosslinks.

Stress relaxation tests at 130 °C of the annealed epoxy vitrimers synthesized with 40 mol % OA, DA and HA, are compared in Fig. 4S.

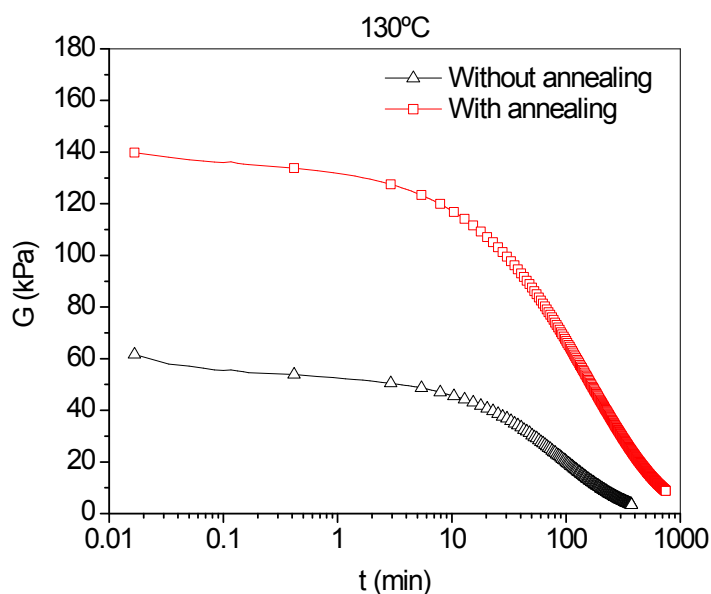


Fig. 3S. Stress relaxation at 130 °C for the epoxy vitrimer synthesized with 40 mol % DA, with or without a previous annealing process at 100 °C.

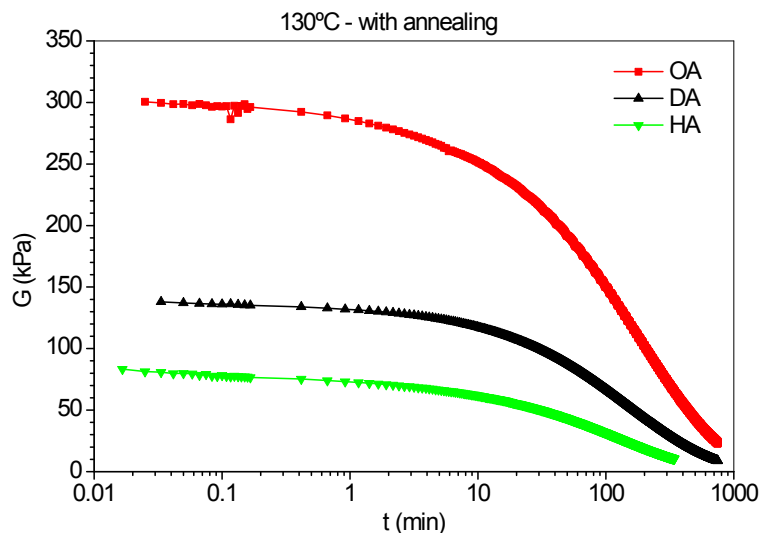


Fig. 4S. Stress relaxation tests at 130 °C for the annealed epoxy vitrimers based on OA, DA and HA.

Welding of the epoxy vitrimer based on HA

A welding test was performed on a sample of the epoxy vitrimer based on HA without annealing. Dimensions of the sample were 25 mm x 10 mm x 2 mm. The sample was transversally cut with a razor and divided in two pieces, as shown in Fig. 5S. Then, both pieces were put in contact and placed in an oven at 120°C for 1 h. After this time, only a thin scar line was barely visible. In order to test qualitatively the strength of the welded sample, two small holes were made with a pin near both extremes of it. Through these holes a nylon fishing line was used to hang the sample vertically supporting a 300 g weight, as shown in Figure 6S.

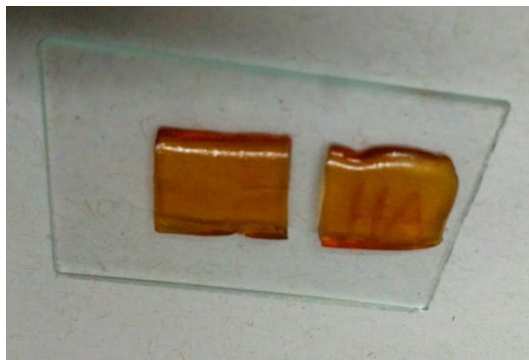


Fig. 5S. Epoxy vitrimer based on HA cut in two pieces with a razor.



Fig. 6S. Welded epoxy vitrimer based on HA after 1 h at 120 °C, supporting a 300 g weight.

Concentration of crosslinks and elastic modulus predicted by the statistical model

Fig. 7S shows the concentration of tri- and tetra-functional crosslinks predicted by the statistical model as a function of the fraction of tail-to-tail associations of alkyl chains. The experimental value of density equal to 1.02 g/cm³ was used to calculate molar concentrations per unit volume.

The predicted value of the shear modulus of vitrimers without physical crosslinks may be calculated from:

$$G = \phi [v(0)] (RT)$$

In this equation, R is the gas constant, T is absolute temperature and ϕ is the front factor that takes a value equal to 1 for an affine deformation and 1/3 for a phantom network with X₃ crosslinks. Besides, the front factor includes corrections of the assumptions incorporated to the statistical model (e.g., equilibrium in transesterification reactions,

absence of ineffective intramolecular loops). The predicted value at 433 K (160 °C) was $G \sim 300$ kPa leading to a front factor $\phi \sim 1/6$ to account for the value actually observed ($G \sim 50$ kPa). It is interesting to remark that due to the large concentration of tertiary amines in the polymer network, the participation of neighboring OH groups in transesterification reactions would lead to values of crosslink density and rubbery modulus much higher than those experimentally observed. Therefore, we can infer that these OH groups do not participate in transesterification reactions, at least to a significant extent.

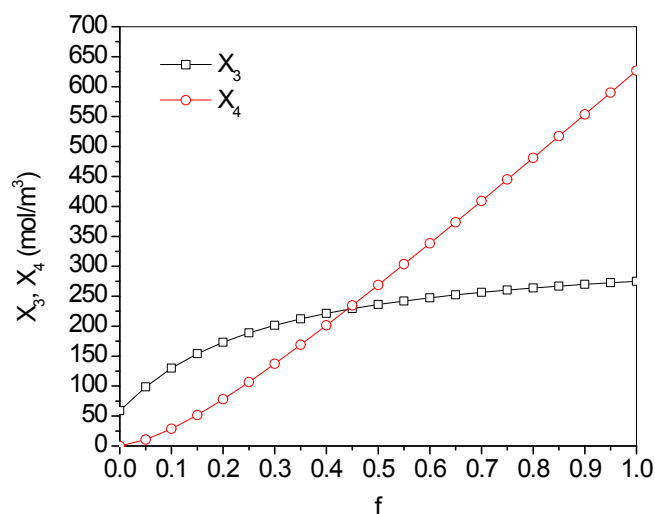


Fig. 7S. Concentration of tri- and tetra-functional crosslinks predicted by the statistical model as a function of the fraction of tail-to-tail associations of alkyl chains.