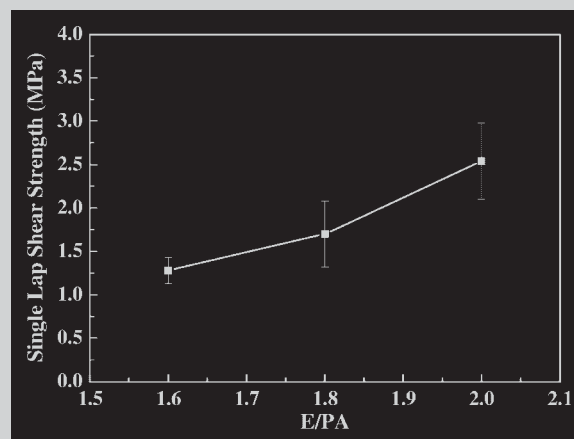


Summary: Reactions taking place in a homogeneous solution of an epoxy monomer based on the diglycidyl ether of bisphenol A (DGEBA) and palmitic acid (PA), in the presence of benzyldimethylamine (BDMA), were investigated using Fourier-transformed infrared spectroscopy (FTIR) and size exclusion chromatography (SEC). In the stoichiometric formulations prepared with equal molar ratios of epoxy (E) to carboxyl groups, $E/PA = 1$, the main reaction was the carboxyl addition to the epoxy giving a β -hydroxy ester. This reaction was followed by transesterification that occurred to a very small extent. In the formulations prepared with an epoxy excess, $E/PA > 1$, the transesterification reactions were very significant as well as the homopolymerization of the epoxy excess that took place to an almost complete conversion. Reaction products synthesized in the range of $1 < E/PA < 2$ were solids at room temperature due to the crystallization of a fraction of fatty acid chains. Above the melting temperature, reaction products recovered the liquid state. The formulation synthesized with $E/PA = 2$ exhibited a good behavior as a hot-melt adhesive of steel sheets with a single lap-shear strength of 2.5 MPa and an interfacial-cohesive failure. For $E/PA > 3$, the gelation took place leading to the networks exhibiting a single glass transition temperature (T_g) without any evidence of crystallization or phase separation. T_g varied

from 90 °C for the neat epoxy to 0 °C for the formulation with $E/PA = 3$.



Single lap-shear strength values of hot-melt adhesives corresponding to reaction products synthesized with $E/PA = 1.6, 1.8,$ and 2 .

Epoxies Modified by Palmitic Acid: From Hot-Melt Adhesives to Plasticized Networks

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Introduction

One of the earliest successful commercial applications of epoxy resins, in the late 40s, was a clear varnish formulated with an ester derived from a solid epoxy resin based on bisphenol A and linseed fatty acid plus a small amount of rosin.^[1] Since then, coatings based on the epoxy resin-fatty acids formulations are used in a broad variety of applications including maintenance paints, aluminum paints, varnishes, baking enamels, and in general, any uses where alkyds are employed.^[1] Epoxy resin esters with fatty acids are noted for excellent adhesion, flexibility, brushing and grinding ease, and resistance to water and alkalis. Un-

saturated fatty acids are used for air-dried coatings while saturated fatty acids are used in a sub-stoichiometric ratio and the cure is performed adding polyamines or other suitable hardeners.

The epoxy-acid chemistry is complex involving different possible reactions. In the presence of tertiary amines and in the formulations containing an epoxy excess, main reactions are those shown in Figure 1.^[2–6] The epoxy-acid addition (1) and the transesterification (2), are the most important reactions taking place in the stoichiometric formulations.^[2–4] In these formulations the epoxy-acid addition takes place first, followed by transesterification of the resulting β -hydroxy ester. However, the transesteri-

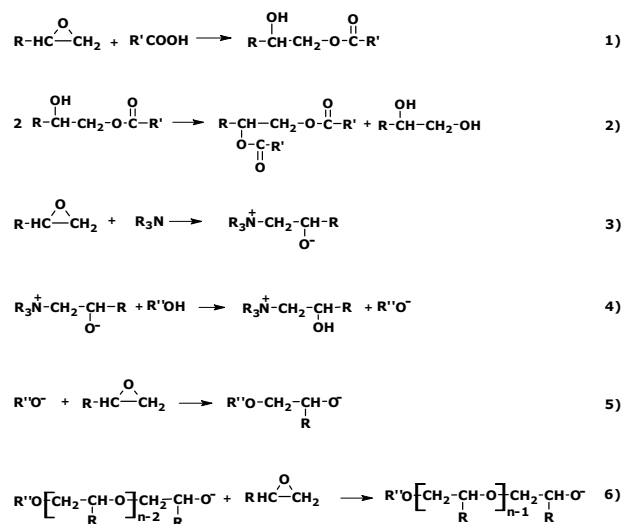


Figure 1. Main reactions taking place in an epoxy-acid formulation with an epoxy excess, in the presence of a tertiary amine.

fication reactions take place at a fast rate and compete with the epoxy-acid addition in the presence of an epoxy excess. This is due to the catalytic effect of the alkoxide anions generated by reactions (3) and (4).^[5,6] These alkoxide anions initiate the epoxy homopolymerization indicated by reactions (5) and (6) as shown in Figure 1. Chain transfer and the chain termination reactions, not indicated in Figure 1, do also take place leading to relatively short polyether chains produced by the epoxy homopolymerization.^[7,8]

A stoichiometric formulation based on a diepoxy monomer and a monofunctional fatty acid will first lead to the epoxy-acid adduct, a di(β -hydroxy ester), and then to a family of compounds containing 0–4 fatty acid moieties and 4–0 free OH groups, respectively, joined to the epoxy monomer skeleton, through the transesterification reactions. In the formulations containing an excess of epoxy groups, homopolymerization leads to branched structures. At a critical epoxy excess, gelation will take place at a complete conversion of epoxy groups. Increasing further the epoxy amount will lead to crosslinked epoxy networks plasticized by the monofunctional fatty acid.

In this study we are interested in properties of the products synthesized in the range of epoxy excesses that are not enough to produce a gel at a full conversion. For these products the crystallization and the melting of a fraction of the fatty ester chains may be expected to occur in appropriate temperature ranges. Above the melting temperature the product will behave like a liquid; below the melting temperature a physical gel should be formed with crosslinks introduced by the fatty ester crystals. These characteristics are typical of the hot-melt adhesives that have become very popular because they satisfy environmental requirements due to the absence of solvents in their formulations.^[9,10] These adhesives are liquids at the appli-

cation temperature and solidify at room temperature. Typical formulations are based on the blends of ethylene vinyl acetate copolymers (EVA) with the aromatic hydrocarbon resins used as tackifiers.^[11–13] The single lap-shear strength values of this family of adhesives lies in the range of about 2–4 MPa.^[13–15]

The aim of this study is to analyze the performance of the epoxy-fatty acid formulations as the hot-melt adhesives, an application that, to our knowledge, has not been reported before. The idea is to join the outstanding adhesive-bonding properties of the epoxy resins with the possibility of crystallization and melting of the fatty ester chains covalently bonded to their structures. Palmitic acid (PA) was selected as the fatty acid because the melting temperature of methyl palmitate is 31 °C, which is convenient for the applications in the hot-melt adhesive formulations. The selected diepoxy monomer was a commercial product based on the diglycidyl ether of bisphenol A (DGEBA). The behavior of the neat epoxy-acid reaction product will be reported without adding tackifiers to improve its properties. The results will be presented and discussed in the following sequence. First the phase diagram of DGEBA-PA binary systems previous to the reaction will be analyzed to find the temperature range where the initial system is homogeneous. The chemistry of the reaction will be then investigated to find the time-temperature conditions to achieve a significant (almost complete) conversion of the epoxy groups and confirm the sequence of reactions shown in Figure 1. Then the epoxy-acid ratio where the hot-melt adhesives may be obtained will be analyzed. This range corresponds to products that are not gelled at a complete conversion and exhibit crystallization and melting of fatty ester chains. The single lap-shear strength values of the resulting hot-melt adhesives will be reported and discussed. In a final section, glass transition temperatures of the formulations synthesized with an epoxy excess beyond the critical value, and cured to complete conversion, will be reported to show that the fatty acid modification can also be used to plasticize the epoxy networks.

Experimental Part

Materials

The selected fatty acid was PA (Aldrich, 99% purity). The epoxy monomer was based on DGEBA (Der 332, Dow), with a mass per mole of epoxy groups equal to 174.3 g·mol⁻¹. Benzylidimethylamine (BDMA, Sigma), was used both as a catalyst of the epoxy-acid reaction and as an initiator of the epoxy homopolymerization. Chemical structures of the different compounds are shown in Figure 2. The molar ratio of BDMA to epoxy groups was equal to 0.06 for all formulations. This amount of initiator was the same as used in the previous studies to obtain an acceptable rate of epoxy homopolymerization and an almost full conversion of epoxy groups at reasonable reaction times.^[16]

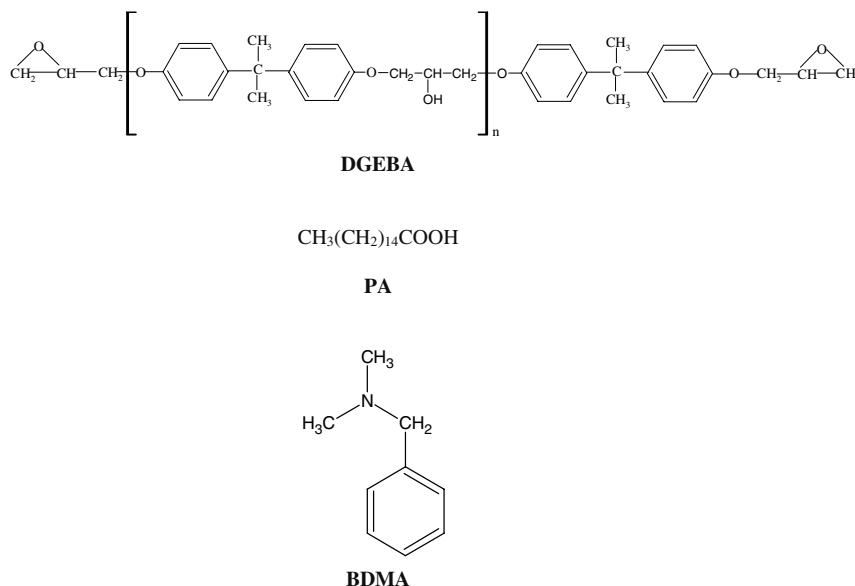


Figure 2. Chemical structures of the epoxy monomer diglycidyl ether of bisphenol A (DGEBA), palmitic acid (PA), and benzyldimethylamine (BDMA).

The selected amounts of PA and DGEBA were mixed at 100 °C until a homogeneous solution was obtained. After cooling to room temperature, the adequate amount of BDMA was added. Temperature was increased to 90 °C while stirring until a homogeneous solution was obtained. The reaction was performed at 90 °C for 6 h leading to the final material.

Techniques

Transmission optical microscopy (TOM) was employed to determine cloud-point temperatures of solutions of DGEBA and PA, as well as to obtain optical micrographs of final materials. A Leica DMLB microscope, provided with a video camera (Leica DC 100) and a hot stage (Linkam THMS 600), was used for these purposes. Cloud-point temperatures were determined by cooling solutions placed in a cell consisting of two glass slides and a 0.5 mm stainless steel spacer, at 1 °C · min⁻¹. Optical micrographs of coatings on glass substrates were obtained at room temperature.

Differential scanning calorimetry (DSC, Perkin-Elmer Pyris 1) was used to determine the glass transition (T_g) and the melting temperatures (T_m), during the heating scans at 10 °C · min⁻¹ under a nitrogen flow. T_g was defined at the onset of the transition while T_m was taken at the end of the melting peak.

Fourier-transformed infrared spectroscopy (FTIR, Genesis II, Mattson) was used to follow the decrease of the epoxy peak at 915 cm⁻¹ and of the carbonyl group of PA at 1710 cm⁻¹, during the reaction at 90 °C. The device was provided with a heated transmission cell (HT-32, Spectra Tech, KBr windows of 32 mm diameter and a 0.025 mm copper spacer) and a temperature controller (Omega, Spectra Tech).

Size exclusion chromatography (SEC, Knauer K-501, RI detector K-2301, Phenogel columns 50 Å, 100 Å, and M2 Phenomenex) was used to determine the molar mass distribution of ungelled products. Tetrahydrofuran (THF) was used as a

carrier at a rate of 1 ml · min⁻¹. The concentration of solutions of different samples in THF was close to 5 mg · ml⁻¹.

The possibility of attaining a liquid state when heating the reaction product was used to define gelation. The critical molar ratio of the epoxy groups to PA, leading to gelation, was defined as the highest of the epoxy-acid ratios leading to a liquid when heating the reaction product.

Single lap-shear strength tests were performed at 20 °C with a universal testing machine (Instron 4467), at a load rate of 3 kN · min⁻¹. These tests were carried out for materials that exhibited the typical behavior of the hot-melt adhesives. The adhesives were applied in the liquid state at about 40 °C, over 304 L steel sheets (25 × 100 × 1.45 mm), using an overlapping area of 25 × 12.5 mm and an adhesive thickness layer controlled in the 0.15–0.35 mm range. Setting of the adhesive layer was produced after cooling to room temperature. The samples were tested after a storage period of 72 h at room temperature.

Results and Discussion

Initial Phase Diagram

The phase diagram of the blend of DGEBA and PA is shown in Figure 3. Apart from the liquid (L) + crystal (K) co-existence regions the diagram shows the presence of an L + L equilibrium region. This demonstrates a significant lack of compatibility between the fatty acid and the epoxy monomer. At the selected reaction temperature of 90 °C the initial solutions were homogeneous.

Sequence of Reactions at 90 °C

The reactions taking place in the formulations prepared with different molar ratios of epoxy to carboxyl groups,

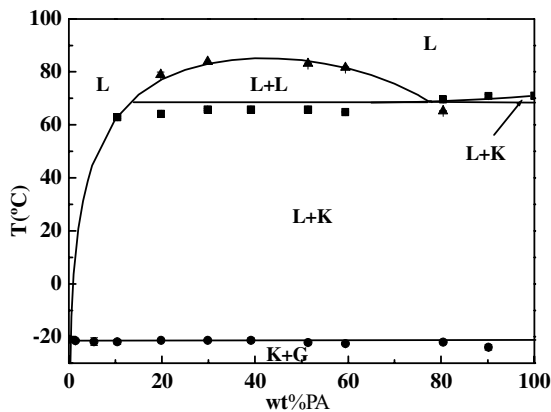


Figure 3. Phase diagram of a blend of DGEBA and PA.

E/PA, were analyzed. Figure 4 shows the evolution of the absorbance of the epoxy and the carbonyl groups in the FTIR spectra during reaction at 90 °C for a formulation with E/PA = 1. After 330 min no trace of the epoxy peak at 915 cm⁻¹ remained in the FTIR spectra shown in Figure 4(a). The evolution of the C=O stretching frequency

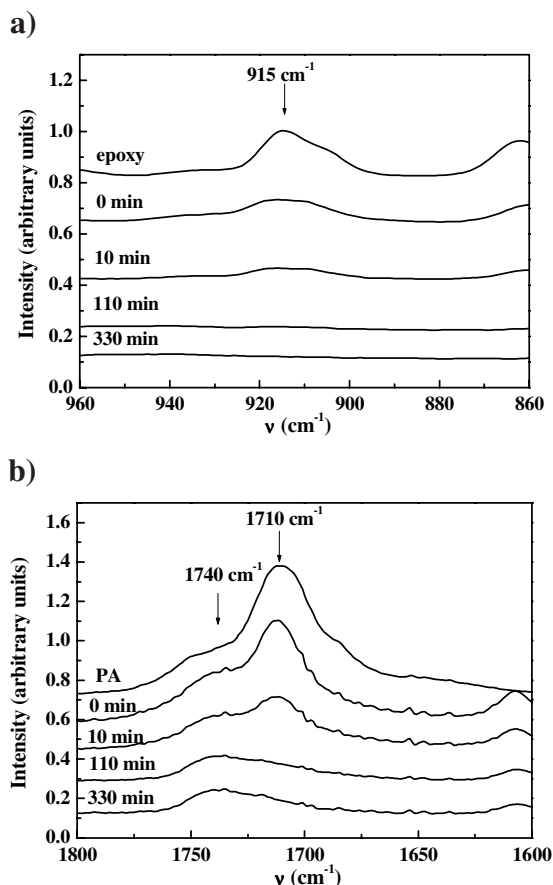


Figure 4. FTIR spectra as a function of reaction time at 90 °C for a formulation with E/PA = 1; (a) region of the epoxy ring, (b) region of C=O (epoxy = DGEBA, PA = palmitic acid).

is less indicative of the conversion degree because of the partial superposition of the absorption peaks of reactants and products. The C=O group of PA exhibits two absorption bands: one at 1710 cm⁻¹ characteristic of a carboxylic acid dimer, and another at 1740–1750 cm⁻¹ assigned to a carboxylic acid monomer, Figure 4(b).^[17] While the peak at 1710 cm⁻¹ shows a significant decrease during reaction, the other one remains superposed to the peak of the ester group produced by a reaction, located at about 1740 cm⁻¹.^[17] Although quantitative estimations are difficult from these spectra, it may be stated that a significant conversion of the epoxy groups took place after 330 min at 90 °C and, consequently the same should have happened with the carboxyl groups for the stoichiometric formulation.

Fourier-transformed infrared spectroscopy spectra were also obtained for several formulations with variable amounts of E/PA, during reaction at 90 °C. In every case, after 6 h reaction at 90 °C no trace of the epoxy groups at 915 cm⁻¹ was found in the FTIR spectra. Therefore, the reaction products were synthesized at 90 °C for 6 h for any E/PA initial ratio.

The product distribution at the end of the reaction was followed by SEC. Figure 5 shows an SEC chromatogram with the peaks of PA at 23.5 min and DGEBA ($n=0$) at 25.0 min. Very small peaks of the epoxy monomers with higher molar masses are also present at 23.9 min (DGEBA, $n=1$) and 22.5 min (DGEBA, $n=2$) (see also the magnification shown in Figure 7).

Figure 6 shows the SEC chromatograms of reaction products obtained with E/PA = 1 and E/PA = 1.4. The main peak at 20.4 min present in the spectra of the stoichiometric formulation, Figure 6(a), must be assigned to a DGEBA molecule that was reacted at both the ends with PA, as this was the main product expected for E/PA = 1. This product can be identified as DGEBA(PA)₂(OH)₂ (this indicates

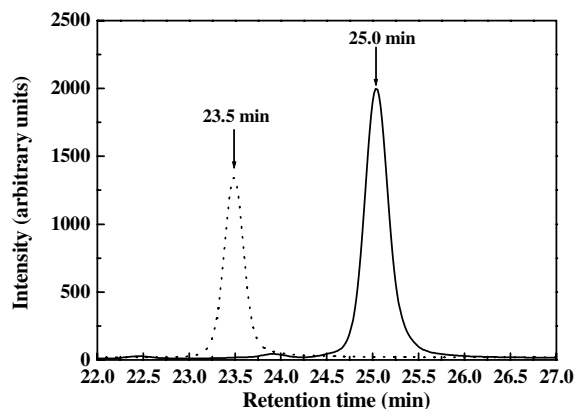


Figure 5. SEC chromatogram showing the peaks of DGEBA ($n=0$) at 25.0 min and of PA at 23.5 min. Very small peaks of the epoxy monomers of higher molar mass are present at 23.9 min (DGEBA, $n=1$) and at 22.5 min (DGEBA, $n=2$) (see the magnification in Figure 7).

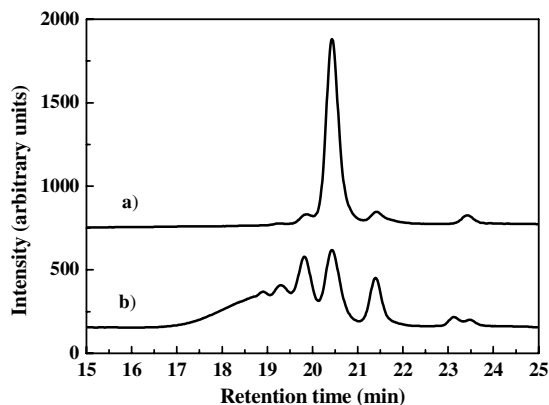


Figure 6. SEC chromatograms of reaction products obtained after 6 h at 90 °C for formulations with E/PA = 1 (a), and E/PA = 1.4 (b).

that the two PA units are joined to a DGEBA molecule generating two OH groups). A small fraction of peaks of lower and higher molar masses are also present in the SEC chromatogram that can only be assigned to products arising from the transesterification of DGEBA(PA)₂(OH)₂; Figure 1, reaction (2). The small fraction of these products is explained by the low catalytic activity of BDMA for the transesterification reaction after the completion of the epoxy-acid reaction and in the absence of free epoxy groups. The situation changes completely for the formulation synthesized with E/PA = 1.4, Figure 6(b). Now, the peaks assigned to compounds produced by the transesterification of DGEBA(PA)₂(OH)₂ appeared with much higher intensities at the same retention times than for the stoichiometric formulation. Moreover, at retention times comprised between 23 and 24 min two peaks were clearly evidenced. A magnification of this region is shown in Figure 7 (curve c) together with the peaks of PA (curve b) and of DGEBA ($n = 0, 1,$ and 2) (curve a).

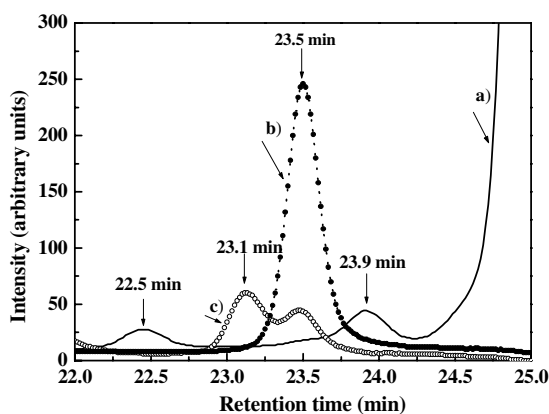


Figure 7. Magnification of the SEC chromatogram of the reaction product synthesized with E/PA = 1.4 (curve c), compared with SEC chromatograms of PA (curve b) and DGEBA ($n = 0, 1,$ and 2) (curve a).

Based on the fact that only products arising from the transesterification reactions of DGEBA(PA)₂(OH)₂ can be present in Figure 6(a), peaks shown in Figure 6(b) at the same locations must be assigned to the same products. Therefore, peaks at 19.2, 19.7, 20.4, 21.3, and 23.1 min were, respectively, assigned to the series of the transesterification products DGEBA(PA)₄, DGEBA(PA)₃(OH), DGEBA(PA)₂(OH)₂ (two isomers), DGEBA(PA)(OH)₃, and DGEBA(OH)₄. The product prepared with E/PA = 1.4 also showed the presence of a small amount of residual PA (peak at 23.5 min) and a high-molar-mass tail assigned to the products derived from the epoxy homopolymerization (products containing two or more DGEBA molecules bonded to PA units). The SEC chromatograms shown in Figure 6(a) and (b) confirm that the main reaction is the epoxy-acid addition, followed by the transesterification reactions and the epoxy homopolymerization. The transesterification is particularly important in the formulations containing an epoxy excess due to the high catalytic activity of the alkoxide anion generated by reactions (3) and (4) of Figure 1.^[5,6]

An indirect confirmation of the assignment of peaks was made by performing a similar polymerization replacing PA by behenic acid, CH₃(CH₂)₂₀COOH. Due to the increase in molar masses, the peaks appeared shifted to the higher retention times except for the small peak at 23.1 min that was present exactly at the same position. This confirms the assignment of this peak to DGEBA(OH)₄. It was also verified that no peak appeared at 23.1 min during the homopolymerization of DGEBA in the absence of a fatty acid.

The reaction product synthesized with E/PA = 1.6 was not completely soluble in THF although it remained in the liquid state at 90 °C. Therefore, the reaction could not be followed by SEC for E/PA ratios equal to or higher than 1.6.

Critical Gelation Ratio

The formulations with increasing values of E/PA were reacted at 90 °C for 6 h, cooled to room temperature and reheated to 90 °C, to determine if they could reach a liquid state. It was found that an irreversible gel was obtained for the E/PA ratios higher than 3. Therefore, the search of formulations for the hot-melt adhesives was restricted to the range $1 < E/PA < 3$.

Crystallization and Melting of Fatty Ester Chains

The second restriction for a formulation to behave as a hot-melt adhesive is the possibility of producing reversible crystallization and melting of portions of the fatty ester chains. As an example, Figure 8 shows a distribution of the fine crystals present at room temperature in the reaction product obtained using a formulation with E/PA = 1.6. The

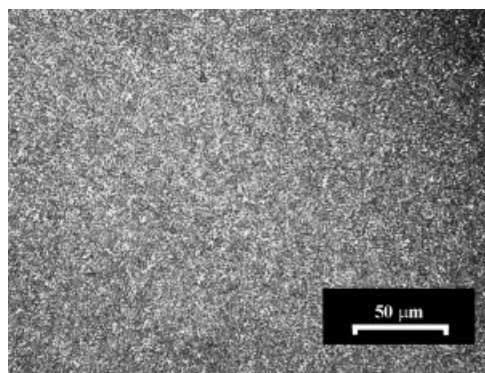


Figure 8. Optical micrograph of the reaction product obtained using a formulation with E/PA = 1.6.

DSC thermogram of this material is shown in Figure 9. Crystals melt at 30 °C with a heat of fusion equal to 30.8 J · g⁻¹.

The heat of fusion may be expressed per unit mass of (CH₂) groups supplied by PA. This leads to a value of 86.2 J · g (CH₂)⁻¹, which may be compared to the value reported for the heat of fusion of a polyethylene crystal,^[18] equal to 293 J · g⁻¹. Therefore, the fraction of CH₂ groups crystallized in the formulation with E/PA = 1.6 was 29.4%.

Similar DSC thermograms were obtained for the reaction products synthesized with the E/PA values comprised between 1 and 2. Figure 10 shows the percent of CH₂ groups of fatty ester chains that could be crystallized as a function of the E/PA ratio. This fraction decreased almost linearly from about 54% for E/PA = 1, to 14% for E/PA = 2. The decrease in crystallinity is associated to the difficulty in aligning the fatty ester chains when increasing the size and the number of branches of species present in the reaction products. The thickness of the fatty ester crystals and consequently the melting temperature should also decrease by increasing the E/PA ratio. The melting temperature

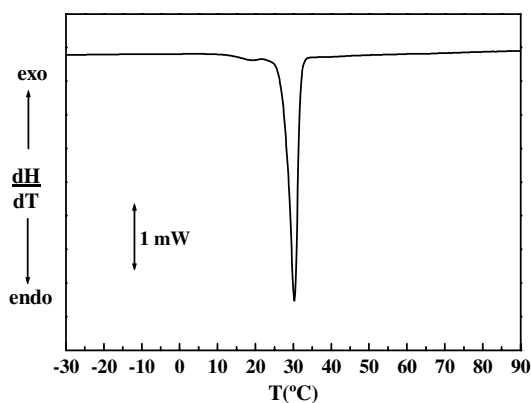


Figure 9. DSC thermogram of the reaction product obtained using a formulation with E/PA = 1.6.

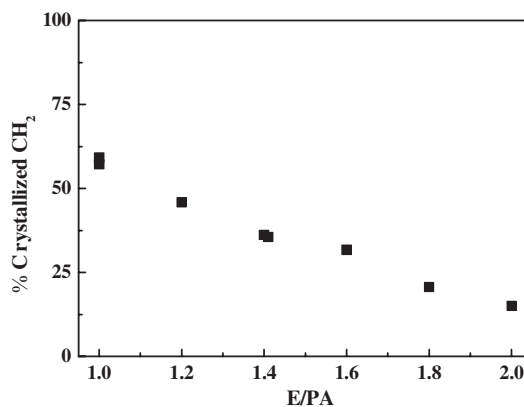


Figure 10. Percent of CH₂ groups of the fatty ester chain that could be crystallized in the reaction product as a function of the E/PA ratio.

varied from 37 °C for the product with E/PA = 1 to 24 °C for the material with E/PA = 2.

Hot Melt Adhesives

The formulations to be tested as the hot-melt adhesives should meet the following criteria: (a) the reversible transformation from a solid to a liquid state by heating above the melting temperature, (b) capacity of crystallizing at room temperature, and (c) excess of epoxy over the fatty acid to take advantage of the outstanding adhesive properties of the epoxy formulations. The window of E/PA ratios where these three criteria were met was comprised between 1.6 and 2. This was the selected range to test adhesive properties.

Figure 11 shows single lap-shear strength values of hot-melt adhesives corresponding to reaction products synthesized with E/PA = 1.6, 1.8, and 2. The value of 2.5 MPa obtained for the formulation with E/PA = 2, lies in the range of values reported for the commercial hot-melt adhesives.^[13–15] Failure modes following the single lap-shear

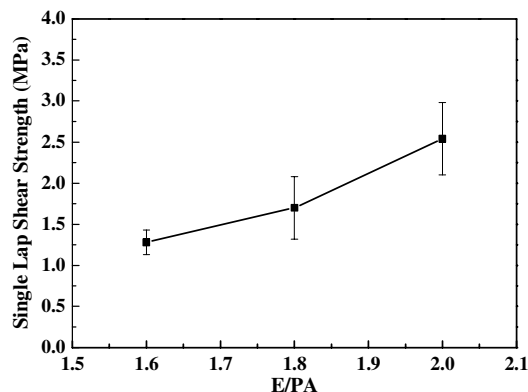


Figure 11. Single lap-shear strength values of hot-melt adhesives corresponding to reaction products synthesized with E/PA = 1.6, 1.8, and 2.

test are divided into interfacial, interfacial-cohesive and cohesive failure. The interfacial failure signifies failure at the adhesive/substrate interface. The interfacial-cohesive failure, also called mixed failure, exhibits both interfacial and cohesive failure in different regions of the tested sample. The cohesive failure occurs when the adhesive remains on both the surfaces. The hot-melt adhesives synthesized with E/PA = 1.6 and 1.8 exhibited interfacial failure, meaning that the amount of epoxy was not enough to obtain a good adhesion with the substrate. An interfacial-cohesive failure was observed for E/PA = 2. This particular E/PA ratio can be taken as a basis to develop the hot-melt adhesive formulations.

An interesting aspect of this new family of hot-melt adhesives is the low processing temperatures and the fact that no tackifier is needed in the final formulation.

Plasticized Epoxy Networks

The materials synthesized with E/PA > 3 were single-phase epoxy networks plasticized by the fatty acid chains covalently bonded to the gel. No crystallization was observed when cooling to room temperature.

Figure 12 shows the glass transition temperature of the plasticized epoxy networks as a function of the PA/E molar ratio in the initial formulation. T_g values decreased from 90 °C for the neat epoxy to 0 °C for the formulation with E/PA = 3. These materials may be useful for particular applications requiring crosslinked epoxies with T_g values in the range of room temperature.

Conclusion

Epoxy-fatty acid formulations combine the outstanding adhesion properties provided by the epoxy with the possibility of crystallizing fatty ester chains. This makes them potential candidates for the hot-melt adhesives, a field dominated by the blends of thermoplastic polymers with

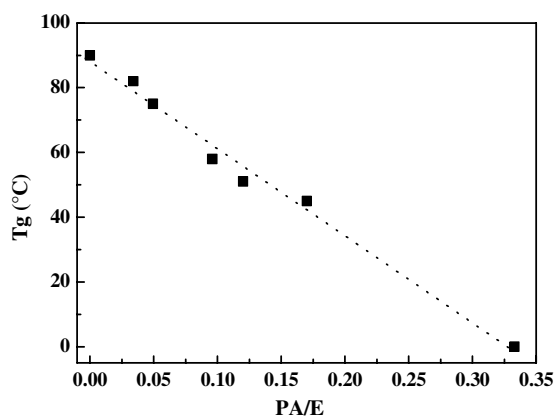


Figure 12. Glass transition temperature of plasticized epoxy networks as a function of the PA/E molar ratio in the initial formulation.

aromatic hydrocarbon resins. The reaction product obtained by the reaction of DGEBA and PA synthesized with a molar ratio of epoxy to carboxylic acid groups, E/PA = 2, exhibited very good properties as the basis of a hot-melt adhesive. It could be reversibly-transformed from a solid to a liquid by heating above the melting temperature of the fatty ester crystals (24 °C), a fraction of fatty ester chains could be crystallized at lower temperatures, and its single lap-shear strength was 2.5 MPa which is in the range of values reported for the commercial hot-melt adhesives.

It was also shown that low amounts of a fatty acid may be used to plasticize the network obtained by the epoxy homopolymerization initiated by a tertiary amine. The plasticizer becomes covalently bonded to the epoxy monomer in a reaction catalyzed by the same tertiary amine used to initiate the epoxy homopolymerization, and does not phase separate or crystallize when cooling. In the range of carboxyl to epoxy molar ratios, PA/E < 0.33, it was possible to vary the glass transition temperature of the resulting network from 0 to 90 °C.

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