

Synthesis and Characterization of Interpenetrating Polymer Networks (IPNs) from Acrylated Soybean Oil and α -Resorcylic Acid: Part 1. Kinetics of Network Formation

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ABSTRACT: Interpenetrating polymer networks (IPNs) using an epoxy phase synthesized from chemically modified α -resorcylic acid, and an acrylate phase employing acrylated soybean oil are the main focus of this study. Part 1 details the epoxidation of α -resorcylic acid with epichlorohydrin in alkaline medium, as well as the study of the polymerization and network formation of the generated epoxy-acrylate interpenetrated systems. The epoxy content of the epoxidized α -resorcylic acid was measured by means of a titration using HBr in acetic acid solution, and the functionalization was studied by FTIR. From the obtained results, mainly calorimetry and gel time determination, it was clear that each phase is affected by the presence of the other, altering the rate and extent at which each individual reaction takes place; and that the two noncompeting reactions (step and free radical polymerizations) occurred at very close temperatures, with a very small gap of around 10 °C between the onsets of the reactions. This evidence leads to the conclusion that the IPNs are formed by a simultaneous process in which both of the networks are formed at approximately the same temperature.

KEYWORDS: Conversions, interpenetrating polymer networks, kinetics, phenolic acids, vegetable oils

1 INTRODUCTION

The synthesis of bioplastics also goes hand in hand with the improvement of the current commercially available materials. To expand the physical and chemical performance of polymeric materials, multicomponent macromolecular systems have been proposed and extensively used for several decades [1]. Amongst several types of systems, interpenetrating polymer networks or IPNs are a particular class of hybrid polymer consisting of two (or more) crosslinked polymers, in which the macromolecular networks are held together by permanent entanglements with only a few covalent bonds between the polymers [2]. IPNs are an intimate combination of two or more polymers in network form, where at least one of the polymers is polymerized and/or crosslinked in the immediate presence of the other [3]. These multicomponent polymer systems seek to combine the best properties of two or

more different polymer networks in order to achieve a material with better properties compared to their not-interpenetrated counterparts. It has been found that the network interlock has measurable influences on the curing behaviors and on the mechanical properties of the resulting materials [4].

According to Nabeth *et al.* [5], from the point of view of bond formation, two different mechanisms can be distinguished: a) Stepwise reactions (polycondensations or coupling reactions), and b) Initiated chain reactions when the functional group has to be activated. The network formation mechanism plays an important role in the network build-up. Irrespective of the conversions at the gel point given by the functionality of the monomers, polycondensation driven networks present common features after rescaling with respect to the gel point. Conversely, typical chain polymerizations yield different structures. Thus, the study of the polymerizations stands up as a key concept to understand the final properties of the interlaced networks constituting one homogenous single system.

According to the chemistry of preparation, IPNs can be classified into [6, 7]: (i) Simultaneous IPN, when the precursors of both networks are mixed and

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the two networks are synthesized at the same time by independent, non-interfering reactions. (ii) Sequential IPNs, in which polymer network I is synthesized first and then monomer II, plus crosslinking agents and catalyzers, are swollen into network I and polymerized *in situ*. In the last decades, few research groups have focused their work on the synthesis and characterization of IPNs from natural products, beginning with the pioneering work of Sperling and his coworkers, who developed IPNs from castor oil-based elastomers and styrene monomers [8]. This fact stands up as a key finding, giving the opportunity to perform research in a field lacking recent developments. Also, other naturally functionalized triglyceride oils and their use in producing semi-IPNs was reviewed by the same group [9]. After this work, other groups have used castor oil as a source of polyurethanes to prepare oil-based IPNs [10, 11]. Other oil-based IPNs include the use of oligomerized soybean oil- [12], tung oil- [13], and canola oil-based polyol with primary terminal functional groups [14]. It is worth highlighting that most of these oil-based IPN structures are not completely, but partially, derived from biological raw materials and fossil fuels. IPNs between commercial resins, such as epoxy, and elastomeric materials of natural origin are known in the literature. Examples include acrylate and methacrylate monomers derived from vernonia oil combined with bisphenol A-type resin [15], and a flexible methacrylate network based on camelina oil combined with a rigid aliphatic glycidylether modified bisphenol-A-based liquid epoxy resin [16].

Due to their abundance, price, and unsaturated hydrocarbon nature, it has been proposed that the vegetable oils are currently the most employed materials in the chemical industry of renewable materials [17]. However, the resulting polymers have intrinsically low glass transition temperature (T_g) because they are structurally assembled by long and flexible hydrocarbon chains. The flexibility of the polymer backbone may be markedly increased with the insertion of aromatic groups that stiffen the chain by impeding rotation, since more thermal energy is then required to set the chain in motion [18]. This feature is especially useful in the field of thermosetting materials, because the presence of rigid aromatic structures confers to the materials the thermomechanical properties required in their industrial and high-performance applications.

Lignin, whose annual production on earth has been estimated to be in the range of $5\text{--}36 \times 10^8$ tons [19], is undoubtedly the most promising natural source of aromatic monomers for the chemical industry. Modern pyrolysis techniques stand as a sustainable way for aromatics biosourcing by providing low molecular weight fragments of natural lignin, which

can be used as platform chemical for organic synthesis. A vast amount of lignin-based compounds, including phenol and more complex platform chemicals, such as guaiacol and syringol derivatives, have been identified in pyrolysis oils [20, 21]. Tannins have also been explored as a source of aromatic monomers to produce thermosetting resins [22].

In Part 1 of this project, the formulation of interpenetrating polymer networks, comprising epoxy and acrylate phases, is studied. It mainly focuses on the study of the polymerization and network formation, which can answer the question of how the presence of one network affects the curing behavior and final morphology of the other. Triglycidyl ether of α -resorcylic acid (or epoxidized α -resorcylic acid), crosslinked with a commercial multifunctional amine (through stepwise mechanism) was employed as the epoxy phase of the system. The acrylate phase was prepared by reacting acrylated epoxidized soybean oil (AESO), slightly diluted with methyl methacrylate to reduce its high viscosity, with a free radical initiator (through chain reaction mechanism) to generate the crosslinked acrylate network. Acrylated epoxidized soybean oil (AESO) is synthesized from the reaction of acrylic acid with epoxidized soybean oil, and it has been extensively studied and used in the surface coating area [23]. The AESO has been blended with styrene to improve its processability and controls the polymer properties in order to reach a range acceptable for structural applications [24]. The mechanical performance of acrylated oils has been extensively studied by La Scala and Wool [25].

The triglycidyl ether of α -resorcylic acid was obtained from chemical modification of α -resorcylic acid, and it was employed as a representative model to produce a highly crosslinked and stiff epoxy network, bearing a high density of rigid aromatic structures. The use of this compound as a raw material to synthesize epoxy resins has been very limited. The only reference found in the literature about an epoxy resin synthesized using resorcylic acid is disclosed in a Japanese patent, where the making of an epoxy resin from β -resorcylic acid, an isomer of the α -resorcylic, is presented and discussed [26]. α -Resorcylic acid is a constituent of peanuts (*Arachis hypogea*), chickpeas (*Cicer arietinum*), red sandalwood (*Pterocarpus santalinus*), and hill raspberry (*Rubus niveus*) [27]; and it has been found as a secondary metabolite in cultures of the fungus *Sporotrichum laxum* ATCC 15155 [28].

In the future, large-scale production of compounds structurally resembling α -resorcylic acid could be achieved by applying common organic reactions and industrial transformation processes to the biorefinery products of lignocellulosic materials simulating the petrochemical field, in which the raw products obtained

from fossil deposits are transformed into high value chemicals. From the literature review, it was found that most of the current IPNs are not fully, but partially, prepared from biological raw materials and fossil fuels. The novelty of the present study is not only derived from the selection of the macromolecular components, which includes the use of a derivative of α -resorcylic acid as a precursor for the epoxy phase that has not been reported in the literature, nor its interpenetration with an acrylated oil. Also, this study aims to provide a response to the need for IPNs prepared from formulations including a higher contribution of biological materials, but also for the final properties that can be generated when associating the phases in the IPN structure.

2 EXPERIMENTAL

2.1 Materials

α -Resorcylic acid (α -RA, $\geq 98\%$), epichlorohydrin (99.0%), sodium hydroxide ($\geq 98\%$), benzyltriethylammonium chloride ($\geq 98\%$), 33 wt% HBr in glacial acetic acid, methyl methacrylate, and 2,2'-Azobis(2-methylpropanitrile) (AIBN) were acquired from VWR (US). Jeffamine T-403 polyetheramine by Huntsman, trifunctional primary amine, average molecular weight of approximately 440, and amine hydrogen equivalent wt (AHEW) of 81 g/eq [29], was purchased from VWR (US). Acrylated epoxidized soybean oil or AESO (Figure 1), viscosity 18000–32000 cps (at 25 °C) and molecular weight of approximately 1800–7200 g/mol was purchased from Sigma-Aldrich (USA) [30]. R represents the fatty acid chains modified with the acrylate group. The average number of acrylate groups per triglyceride has not been determined by the supplier or Sigma-Aldrich. However, it has been established that it contains, on average, 4.5 double bonds that can first be converted into epoxy groups and then into acrylate moieties [31].

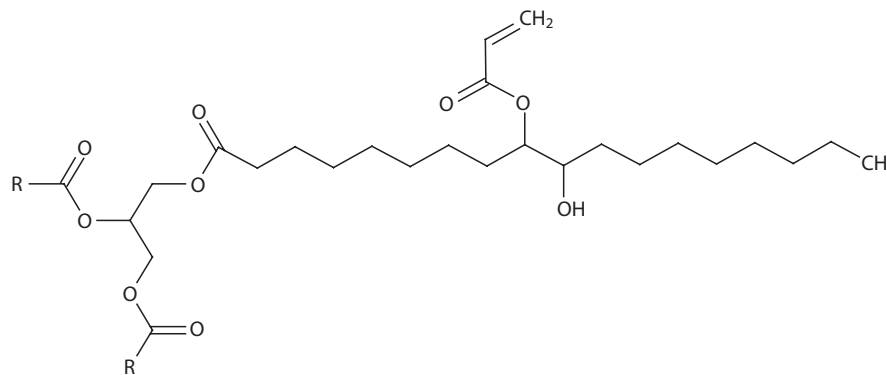


Figure 1 Chemical structure of the acrylated soybean oil.

2.2 General Procedure for the Glycidylation of α -Resorcylic Acid

The glycidylation of α -resorcylic acid was conducted following the method and conditions established by the Fulcrand group [32, 33]. The described process leads to the synthesis of epoxyalkylaryl ethers by the reaction between compounds containing acid hydroxyl groups and haloepoxyalkanes in the presence of a strong alkali. A reactor was loaded with the desired amount of α -resorcylic acid (containing 3 moles of $-\text{OH}/\text{mol}$ of compound) and epichlorohydrin (5 moles epichlorohydrin/mole $-\text{OH}$). The mixture was heated at 100 °C and benzyltriethylammonium chloride (0.05 moles $\text{BnEt}_3\text{NCl}/\text{mole } -\text{OH}$) was added. After 1 h, the resulting suspension was cooled down to 30 °C, and an aqueous solution of NaOH 20 wt% (2 moles NaOH/mole $-\text{OH}$, and also containing 0.05 moles of $\text{BnEt}_3\text{NCl}/\text{mole } -\text{OH}$, was added dropwise. Once the addition of the alkaline aqueous solution was completed, the mixture was vigorously stirred for 90 min at 30 °C, and then the reaction was stopped. After that, the mixture was poured into an extraction funnel and the organic layer was separated. Through numerous liquid-liquid extractions with deionized water, the organic phase was abundantly washed until neutral pH was reached, and then vacuum concentrated. The crude resulting product was purified by silica gel chromatography using petroleum ether/ethyl acetate (30/70) solvent system.

2.3 Characterization of Starting and Modified Materials

2.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

With the aim of studying the functional groups present in the product, FTIR was performed. Infrared spectra of the starting materials and epoxidized products were

measured by attenuated total reflection (ATR) method using a Thermo Nicolet 6700 Fourier transform infrared spectrometer connected to a PC with OMNIC software analysis. All spectra were recorded between 400 and 4000 cm^{-1} over 64 scans with a resolutions of 16 cm^{-1} .

2.3.2 Epoxide Equivalent Weight Determination

Epoxide equivalent weight (EEW, g/eq) of the epoxy products was determined by epoxy titration according to Pan, Sengupta and Webster [34]. Basically, a solution of 0.1 M HBr in glacial acetic acid was used as a titrant agent, 1 wt% crystal violet in glacial acetic acid was used as indicator, and toluene as solvent for the sample. The EEW was calculated using Equation 1:

$$EEW = \frac{1000 \times W}{N \times V} \quad (1)$$

where W is the sample weight (g), N is the molarity of HBr solution, and V is the volume of HBr solution used for titration (mL).

2.4 Synthesis of IPNs

The IPNs consist of a phenolic-based epoxy resin combined with the triglyceride-based acrylate resin. The epoxy phase was prepared by mixing the triglycidylated derivative of the α -resorcylic acid (TRA) or epoxidized α -resorcylic acid with the commercial hardener Jeffamine T-403, a well-known trifunctional amine, in a 10/7 weight ratio. The components of the acrylated phase, acrylated soybean oil, methyl methacrylate (added to reduce the high viscosity of the acrylate oil in the amount of 20 wt% of the total weight of acrylated oil) and AIBN as initiator (1 wt% of the total weight of the acrylate phase) were mixed separately and then added to the epoxy phase precursor solution in different weight percentages. After mixing these solutions, all samples were placed in glass molds and then cured in the oven following the next heating sequence: 50 $^{\circ}\text{C}$ for 1 h, 60 $^{\circ}\text{C}$ for 1 h, 75 $^{\circ}\text{C}$ for 2 h, 120 $^{\circ}\text{C}$ for 12 h, and finally 180 $^{\circ}\text{C}$ for 1 h.

2.5 Characterization of Networks

2.5.1 Kinetics of Gelation

The characteristic peaks in the infrared region for the acrylic unsaturation (1638 cm^{-1}) and epoxy ring (915 cm^{-1}) respectively were used to calculate the conversion of the acrylic and epoxy groups. The band at approx. 2960 cm^{-1} , assigned to the C-H stretch absorption, was used as a reference because it does not suffer any chemical modification during the process.

The progress of curing reaction was evaluated using Equation 2:

$$\text{Conversion (\%)} = \left[1 - \frac{\left(\frac{A_{pol}}{A_{ref}} \right) t}{\left(\frac{A_{pol}}{A_{ref}} \right) 0} \right] * 100 \quad (2)$$

where $A_{pol} = 915 \text{ cm}^{-1}$ or 1638 cm^{-1} peak areas, $A_{ref} = 2960 \text{ cm}^{-1}$ peak area, $t =$ reaction time, and $0 =$ initial moment of reaction (uncured mixture) [35].

2.5.2 Determination and Measurement of the Extent of Reaction at the Gel Time

Gel time was determined following the method described by the ASTM D2471-99 [36]. For each system, at least three sets of experiments were performed. The extent of the reaction at the gel point can be calculated by means of two theories. According to Carothers [37], the critical extent of the reaction, P_c at the gel point is given by

$$P_c = 2 / f_{avg} \quad (3)$$

where f_{avg} represents the average functionality of the system, and is given by

$$f_{avg} = \frac{\sum N_i f_i}{\sum N_i} \quad (4)$$

and where, N_i is the number of molecules of monomer I with functionality f_i .

Flory and Stockmayer [38] also developed another relationship, correlating the extent of conversion at the gel point for stoichiometric mixtures,

$$P_c = 1 / [(f_{w,epoxy} - 1) (f_{w,amine} - 1)] \quad (5)$$

where $f_{w,epoxy}$ represents the weight average functionality of the epoxy monomers, and $f_{w,amine}$ represents the weight average functionality of the amine monomers.

2.5.3 Thermal Properties

The thermal properties of the IPNs, as well as the parent resins, were investigated by differential scanning calorimetry (DSC) on a TA DSC Q2000. Nitrogen was used as the purge gas and the samples were placed in aluminum pans. For each material sample, the thermal properties were recorded at 5 $^{\circ}\text{C}/\text{min}$ in a heat/cool/heat cycle from 30 $^{\circ}\text{C}$ to 300 $^{\circ}\text{C}$.

3 RESULTS AND DISCUSSION

3.1 Synthesis of Triglycidylated Ether of α -Resorcylic Acid

Regarding the coupling of epoxy groups to the α -resorcylic acid, it was found that the treatment of

this compound with epichlorohydrin in alkaline aqueous medium (see Figure 2), in the presence of benzyltriethylammonium chloride as a phase transfer catalyst, allowed the total glycidylation of this phenolic acid to generate the triglycidylated derivative of α -resorcylic acid or TRA (also referred to as ERA, a short version of epoxidized α -resorcylic acid).

The reaction yield of the triglycidylated derivative of α -resorcylic acid, after purification through silica gel chromatography, was around 80%. The remaining 20% probably corresponds to mono and di glycidylated products of α -resorcylic acid, as well as unreacted α -resorcylic acid and mechanistically possible dimerization products of the newly formed glycidylation compounds. Since this work is mainly focused on the preparation of IPNs, no further identification or characterization of the reaction products was performed. The mixture of glycidylated products was used to produce the interpenetrated systems. Because phenols are more acidic than alcohols, they can be converted to phenolates through the use of a strong base. These intermediates are strong nucleophiles and can react with primary alkyl halides to form ethers. According to the literature [39], once the phenolate anions are formed, they can react with epichlorohydrin following two competitive mechanisms: one-step nucleophilic substitution (mechanism $\text{S}_{\text{N}}2$) with cleavage of the C-Cl bond and a two-step mechanism based on ring opening of epichlorohydrin followed by intramolecular cyclization (through $\text{S}_{\text{N}}1$ mechanism), with the release of chloride, to reform the epoxy ring. Titration with HBr showed that the resulting mixture after modification has an average molar epoxy content of $(9.0 \pm 0.5) \times 10^{-3}$ moles per gram of resin, which corresponds to an epoxy equivalent weight = 111 gr/eq. The presence of epoxy groups was confirmed by FTIR (Figure 3).

The α -resorcylic acid structure was characterized by the presence of a strong IR absorption band at 3200 cm^{-1} . The carbonyl exhibited a strong peak at 1750 cm^{-1} . The spectrum of the epoxidized α -resorcylic acid presented similar absorption bands to those exhibited by its non-modified counterpart. The most remarkable difference between them was the disappearance of the weak peak

at 3200 cm^{-1} (attributed to the presence of hydroxyl groups). The lack of this absorption peak in the FTIR spectrum of the epoxidized α -resorcylic acid is related to the removal of the -OH functional groups due to the glycidylation reaction. The presence of absorption bands is also evident at 1227.5 cm^{-1} and 1050 cm^{-1} , due to the presence of -C-O-C- groups formed during the reaction; as well as the characteristic bands for oxirane rings at 847.5 cm^{-1} and 910 cm^{-1} .

3.2 Kinetics of Gelation

The reaction between epoxy and amine groups of the Jeffamine T-403 is a step-growth reaction. As a first approach to study the reactions, the gel times at $65 \text{ }^\circ\text{C}$ were measured. In order to study how the presence of one system influences the crosslinking behavior of the other, a hypothetical epoxy system (in which the acrylate phase has no initiator) and a hypothetical acrylate system (in which the epoxy phase has no curing agent) were prepared and measured, along with the experimental system (containing all the components to allow the polymerization of the monomers). The resulting gel times, as a function of the weight fraction, are shown in Figure 4. As can be seen, all the systems reached the gel point in less than approx. 60 minutes when tested at $65 \text{ }^\circ\text{C}$; and this parameter changed as a function of the epoxy/acrylate ratio. It was observed that the gel time of the hypothetical systems increased when enlarging the content of the other phase. In other words, the gel point of the acrylate phase was delayed when the concentration of the epoxy phase in the mixture was enlarged, and vice versa. Based on these findings, it is suggested that there is a dilution effect of the reactants by the components of the other non-reacting phase, decreasing the reaction rate and therefore inducing the delay in the gelling time [40]. Regarding the experimental system, in which all the reacting components were included, it is interesting to observe that for the epoxy-acrylate weight percentages of 25–75 and 50–50, the gel times were considerably reduced when compared to those shown by the hypothetical systems. The other ratios

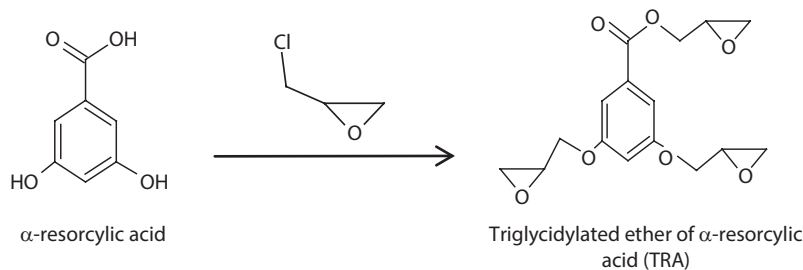


Figure 2 Glycidylation reaction of α -resorcylic acid with epichlorohydrin.

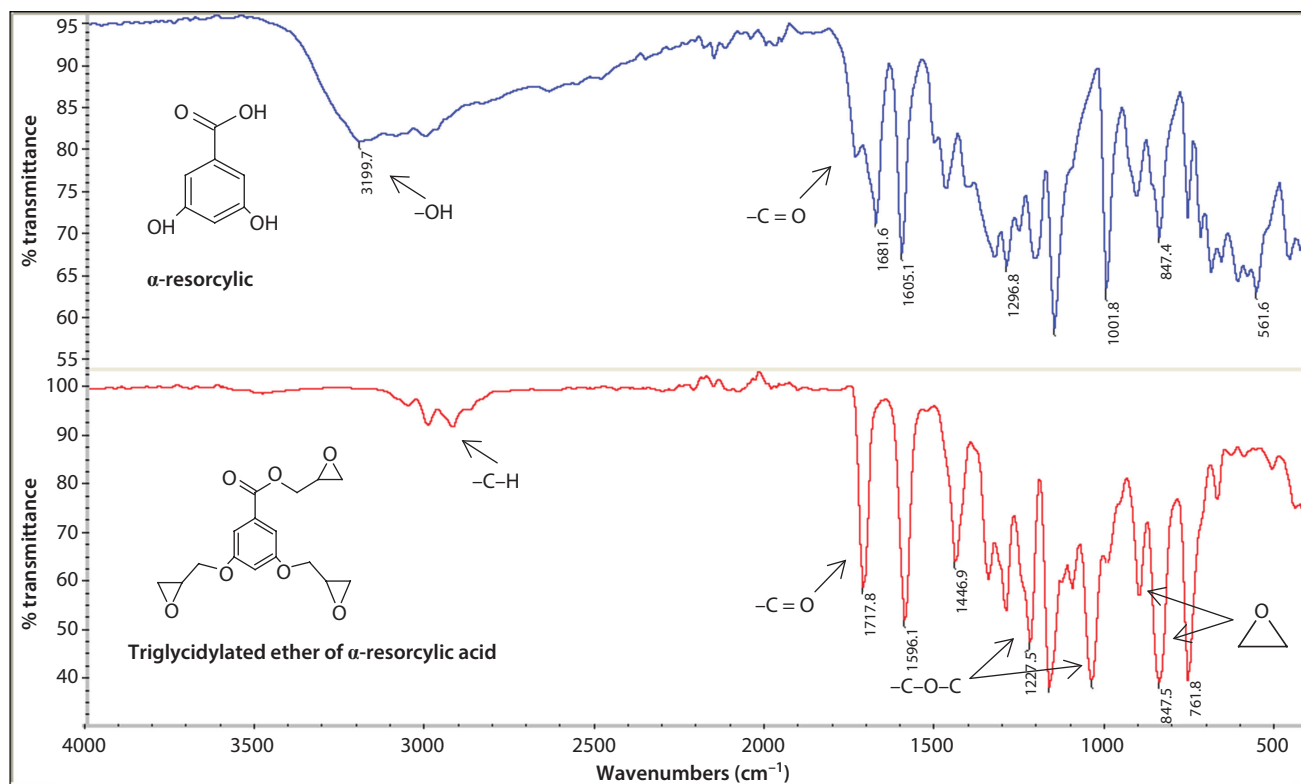


Figure 3 FTIR spectra of α -resorcylic acid and epoxidized α -resorcylic acid.

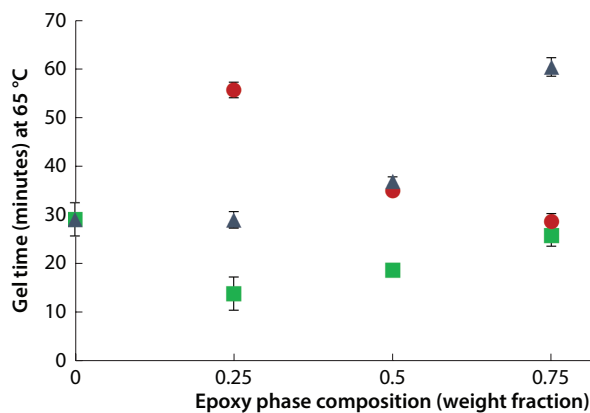


Figure 4 Gel times at 65 °C for the studied hypothetical epoxy system (●), hypothetical acrylate system (▲), and the experimental system (■).

showed gelling times similar to the hypothetical counterparts. The epoxy 75–acrylate 25 system reached the gel point at a similar time (~27.5 minutes) to that shown by the hypothetical epoxy system (no initiator in the acrylate phase); denoting that the gelling of this system is dominated by the epoxy phase.

As demonstrated by the DSC studies (detailed in the following section), the condensation reaction of the epoxy monomers with the crosslinking agent (amine

in this case) is highly exothermic. It is important to mention that this is an expected behavior, because the ring-opening reaction of the highly strained three-member ring occurs with extreme ease, and is thermodynamically favorable. On the other hand, it has been clearly stated by theory that the radical chain polymerization rate is dependent on the initiator concentration [37]. Usually, thermal homolytic dissociation of initiators is the most widely used method of

generating radicals to start the polymerization. Taking these facts into account, it is likely that the decrease in the gelling time for the epoxy-acrylate weight percentages of 25–75 and 50–50 is due to a phenomenon of autocatalysis. The ring-opening reaction of the highly strained three-member epoxy ring releases extra energy in the system, favoring the dissociation of the initiator, and therefore increasing the polymerization rate that leads to gelation at some point of the reaction. This behavior, combined with the gelling of the epoxy phase, might have maximized the rate at which the systems reached the gel point.

The theoretical extent of the reaction at the gel point was calculated by means of the Carothers and Flory-Stockmayer approaches. According to Carothers, Equation 3 yields an average functionality of 4.01 for an equimolar α -resorcylic acid/Jeffamine T-403 mix. Equation 2 then yields $P_c = 0.499$. According to Flory and Stockmayer, taking $f_{w,epoxy} = 3$, and $f_{w,amine} = 6$, Equation 4 yields $P_c = 0.316$. The extent of the reaction, at 65 °C, was followed by studying the disappearance of the oxirane absorption band at 825 cm^{-1} (the measurements were performed three times). The observed P_c value for a stoichiometric mixture of epoxidized α -resorcylic acid and multifunctional amine was 0.43 ± 0.10 . Experimental values falling approximately midway between the two calculated values have been observed in many other similar systems [37]. The extent of the reaction at the gel point for the remaining IPNs is shown in Table 1.

As can be seen, the conversion of the epoxy phase at the gel point was not deeply affected by the presence of the acrylate phase, and it showed a medium conversion when tested at 65 °C. This parameter ranged from 40% to 55%, and there was no clear trend in its behavior as a function of the epoxy/acrylate ratio. On the other hand, the acrylate phase conversion was impacted by the presence of the epoxy phase. Samples containing 100 wt% and 75 wt% of acrylate reached the gel point

at similar conversions (approx. 20%), but at different times, with the acrylate 75 wt% system reaching the gelation almost two times faster than the acrylate 100 wt%. When increasing the weight content of the epoxy phase in the IPNs, the conversion of the acrylate at the gel point also increased, reaching its maximum (approx. 47%) for the epoxy 75 wt%–acrylate 25 wt%. The rise in the conversion values at the gel point for the IPNs epoxy 50 wt%–acrylate 50 wt% and epoxy 75 wt%–acrylate 25 wt%, could be attributed to an autocatalysis phenomenon in the system, due to the energy release of the ring-opening reaction of the epoxy ring when combined with the amine curing agent, as previously explained. As a general trend, for large epoxy contents, the heat released during reaction might have triggered the conversion of the acrylate phase; however, since its content is low, the gelling is dominated by the epoxy counterpart.

3.2.1 Curing Behavior of IPNs

In order to assess the curing of the epoxy-acrylate IPNs, about 5 mg of each mix was studied by DSC (all measurements were performed three times). Likewise, the samples were cured at 65 °C for 1 hour and then also subjected to calorimetric analysis to evaluate the extension of curing after treatment at the above-mentioned conditions. The DSC of the IPNs, as well as the pure systems, showed only one exothermic peak, corresponding to the curing of the resins. From the results, it was observed that the onset of the curing is shifted to higher temperatures when increasing the amount of acrylate resin in the mixture, ranging from approx. 45 to 55 °C for 100 wt% epoxy to 100 wt% acrylate, with the IPNs falling in between. When analyzing the behavior of the parent resins (epoxy and acrylate) it can be inferred that the polymerization of both systems begins at close temperatures, with the epoxy system starting to react at a temperature around 10 °C lower than the acrylate resin. As a result, there is only one peak observed in the IPNs, which corresponds to the superimposed curing of both resins. From the calorimetry studies, it was also observed that the offset of the curing peaks was around 160 °C. The total heat of polymerization and the residual heat of polymerization (residual heat after curing 1 hour at 65 °C) are displayed in Figure 5.

When analyzing the behavior of the parent resins, it is clear that the ΔH of curing of the epoxy-amine resin is highly exothermic (approx. 67 J/g), being about 2.5 times higher than that shown by the acrylate phase (26 J/g). This means that mixtures richer in the epoxy phase are more exothermic, behavior that is reflected in the experimental results, where the overall or total heat of polymerization associated with the curing peaks is shifted to higher values when increasing the

Table 1 Extent of the reaction at the gel point for IPNs.

IPN	Epoxy phase conversion (± 0.10)	Acrylate phase conversion (± 0.10)
Epoxy 100%	0.43	–
Epoxy 75%– Acrylate 25%	0.40	0.47
Epoxy 50%– Acrylate 50%	0.55	0.43
Epoxy 25%– Acrylate 75%	0.50	0.20
Acrylate 100%	–	0.21

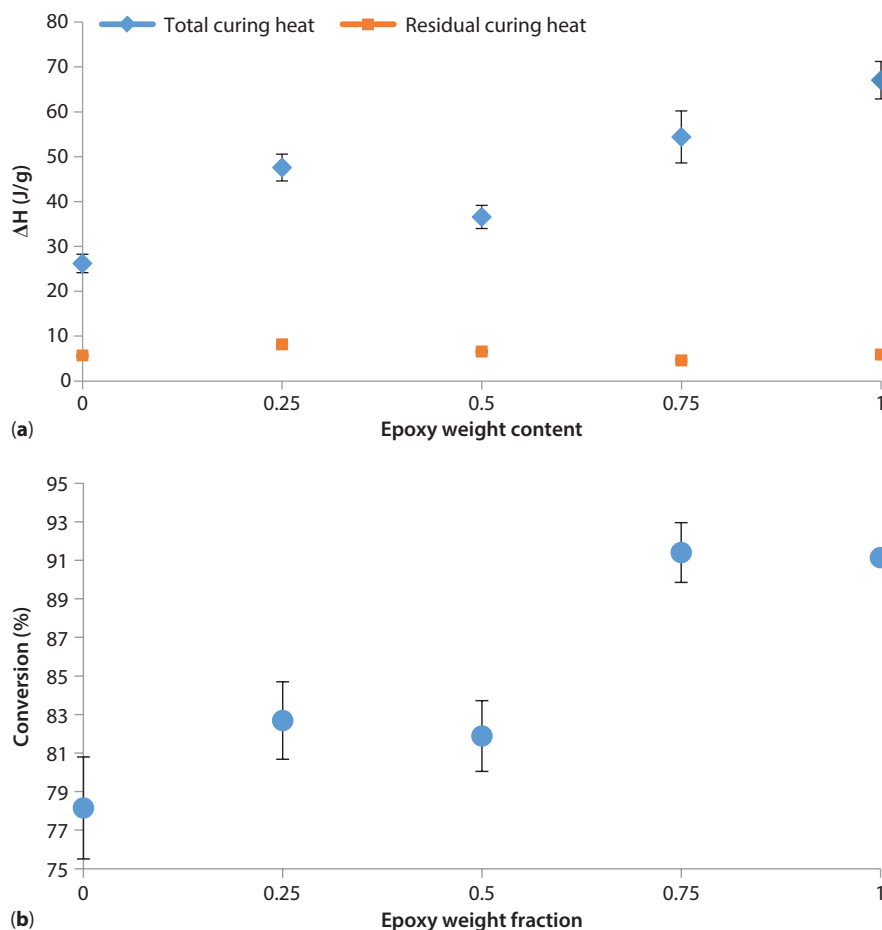


Figure 5 Heats of polymerization (a) and conversions (b) of the IPNs.

content of epoxy phase in the systems. The total heat of polymerization approximately increases as a linear function of the epoxy content; however, this tendency is truncated by the epoxy 25 wt%–acrylate 75 wt%, suggesting that the curing mechanism of each constituent is affected by the presence of the other, probably due to autocatalysis or even chemical interactions between the components [40].

Regarding the residual heat after curing 1 hour at 65 °C, it seems to be not greatly affected by the epoxy/acrylate ratio, and it ranged from around 4.000 J/g to 8.500 J/g. This finding suggests that most of the components are reacted after 1 hour at 65 °C, a fact that is reflected in the conversions (Figure 4b), which ranged from around 78% to 91%. As it happened with the curing heats, the conversions shifted to higher values when increasing the proportion of the epoxy system; probably due to the high chemical reactivity of non-sterically hindered glycidyl ethers, such as epoxidized α -resorcylic acid, towards amines [41].

As previously described, during the epoxy-amine curing process, the general reaction occurs via a

nucleophilic attack of the amine nitrogen on the carbon of the epoxy function. The mechanism proceeds through a S_N2 type reaction, which is in turn highly dependent on the structure and on the reaction conditions. Epoxidized α -resorcylic acid contains oxirane functionalities that are non-sterically hindered, facilitating the nucleophilic attack of the amino group. As a consequence of this feature, the reaction occurs rapidly at relatively low temperatures (~ 45 °C). It is important to mention that etherification products, arising from the polymerization of epoxy groups and hydroxyl groups of acrylated soybean oil at elevated temperatures, might also be present in the final polymer matrix. However, since stoichiometric amounts of epoxy groups and amine comonomers are used, and also due to the low reactivity of the secondary hydroxyl groups [42], the effect of this side reaction on the final product can be neglected.

Based on the results of the conversion and calorimetry studies, it is suggested that the two noncompeting reactions (step and free radical polymerizations) occurred at very close temperatures, with a very small

gap of around 10 °C between the onsets of the reactions. However, it is clear that each constituent is affected by the presence of the other, altering the rate and extent at which each individual reaction takes place.

4 CONCLUSIONS

An epoxy phase synthesized from α -resorcylic acid crosslinked with a commercial amine hardener and acrylate phase using acrylated soybean oil were used to prepare IPNs. The EEW of the epoxidized derivatives of α -resorcylic acid after chemical functionalization was found to be approx. 112 g/eq. Grafting of epoxy functions onto the monomer's structure was confirmed by FTIR. DSC analysis revealed the presence of exothermic peaks related to curing of the systems, and that the curing mechanism of each constituent was affected by the presence of the other. All of the systems reached the gel point in less than approx. 60 minutes when tested at 65 °C; and this parameter changed as a function of the epoxy/acrylate ratio. The experimental P_c value for a stoichiometric mixture of epoxidized α -resorcylic acid and multifunctional amine was 0.430 ± 0.100 ; falling in between that predicted by the Carothers and Flory theories.

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