

Synthesis and Characterization of Interpenetrating Polymer Networks (IPNs) from Acrylated Soybean Oil α -Resorcylic Acid: Part 2. Thermo-Mechanical Properties and Linear Fracture Mechanics

Bernal Sibaja^{1,2,3}, Camila Pereira Matheus^{1,2}, Ricardo Ballesterro Mendez^{1,2}, Ramsis Farag^{1,2,4}, J. R. Vega Baudrit³ and Maria L. Auad^{*1,2}

¹Chemical Engineering Department, Auburn University, Auburn, AL 36849, USA

²Center for Polymer and Advanced Composites (CPAC), Auburn University, Auburn, AL 36849, USA

³National Laboratory of Nanotechnology (LANOTEC), San José, Costa Rica

⁴Textile Engineering Department, Mansoura University, Egypt

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ABSTRACT: The thermo-mechanical properties and linear fracture mechanics of acrylated soybean oil and the triglycidylated ether of α -resorcylic acid interpenetrated networks as a function of their weight composition are the focus of Part 2 of this article. Thermo-mechanical characterization showed that the obtained materials behave as thermoset amorphous polymers, and that both the modulus and glass transition are extremely dependent on the epoxy/acrylate weight ratio. Modulus values ranged from 0.7 to 3.3 GPa at 30 °C, and glass transition temperatures ranged from around 58 °C to approx. 130 °C. No synergistic effect on these two properties was observed. Interpenetrating networks containing equivalent weight proportions of the parent resins showed the highest fracture toughness of the series, exhibiting a K_{Ic} value of around 2.1 MPa·m^{1/2}. The results showed that the K_{Ic} values did not increase as M_c increased, which seems to suggest that a different mechanism is responsible for the increase in the fracture toughness displayed by IPNs. Also, there seems to be an exponential-type increase in the fracture energy with the $M_c^{1/2}$ for the materials containing the epoxy phase.

KEYWORDS: Fracture toughness, IPNs, mechanical properties, phenolic acids, vegetable oils

1 INTRODUCTION

An interpenetrated polymer network (IPN) is an intimate combination of two or more polymers, where at least one of them is crosslinked in the presence of a network of the other [1]. The formation of IPNs is generally governed by two processes which compete to give a large variety of final properties and degree of mixing: the crosslinking reaction (depending on reaction kinetics) and the phase separation (mainly driven by thermodynamics). Therefore, the final properties and morphology depend on the monomers' or polymers' miscibility and compatibility [2]. Useful properties of polymer components in IPNs are combined in order to overcome the drawbacks of individual components when they form blends. During this process,

the molecular chain dynamics (which determine the properties of these polymers), change dramatically; and this arises as a result of the level of mixing between the components of the system [3].

The interest of studying and preparing interpenetrating polymer networks has been associated with the favorable effect of crosslinking in the miscibility of a multicomponent system. When preparing IPNs, the presence of the crosslinked network (interlacing both polymers) retards the process of phase separation, resulting in some degree of phase mixing. This process is known as "enforced miscibility" [4]. It is generally known that the vast majority of IPNs do not interpenetrate at the molecular level, but rather form different phases finely divided at the nanometer scale. However, these kinds of multicomponent polymeric systems represent an excellent approach for combining the properties of different polymeric materials in a synergetic way. This kind of behavior was described by Li and coworkers in their study on compatibility

*Corresponding author: auad@auburn.edu

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of polymer blends [5]. It was found that even though there is phase separation in IPNs, these materials usually presented highly uniform phase structures, much better than those of the parent polymer blends. This behavior was attributed to the particular network structure of IPNs, where the higher compatibility achieved could be called “force compatibility,” since the enthalpy of mixing does not play a major role in the improvement of miscibility of the system [6].

It has also been found that the network interlock has measurable influences on the curing behaviors and on the mechanical properties of the resulting materials [7], and studies have shown that the incorporation of a second polymer phase can improve both stiffness and impact resistance in polymeric systems [8]. While studying interpenetrated networks based on polyurethane and epoxy resins, Frisch and coworker [9] concluded that in general the properties of the IPNs fall into two categories: a) properties which vary monotonically with network composition (expressed as weight percent of the components), and b) properties which exhibit a maximum or minimum at an intermediate network composition. That network composition in which a maximum in the property is found is the composition at which maximum entanglement is expected. This stands out as a remarkable relation and the maxima or minima can be related to two different physical-chemical phenomena. The maxima in the mechanical properties can be attributed to an increase in the crosslinking density due to interpenetration, since it is known that the tensile strength of a crosslinked material goes through a maximum as the crosslinking density increases. The minima can be attributed to the weakening of the intermolecular forces present in one network due to the presence of the second polymer [5].

From a synthetic point of view, IPNs can be prepared following two pathways: a) a sequential IPN in which one network is swollen and polymerized in the presence of the other; and b) simultaneous IPN, in which both of the networks' precursors are synthesized at the same time by independent, non-interfering routes [10]. In Part I of this project, the chemical modification of α -resorcylic acid with epoxy moieties, as well as the kinetics and morphology of interpenetrated polymer networks from the system composed of acrylated soybean oil and the triglycidylated ether of α -resorcylic acid were studied and reported. From the obtained results, it was clear that each constituent is affected by the presence of the other, altering the rate and extent at which each individual reaction takes place; and that the two non-competing 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 synthesized at the same time. It has been established that the simultaneous polymerization method is expected to yield a higher degree of interpenetration since it is easy to obtain a homogeneous mixture when low molecular weight monomers are mixed [11].

Part 2 of this project focuses on the thermo-mechanical properties and linear fracture mechanics of the acrylated soybean oil and the triglycidylated ether of α -resorcylic acid IPNs. The evaluation of the thermo-mechanical properties and the study of the networks by means of the rubber elasticity theory allows determining if the properties are either varying as a function of the composition, or exhibit a maximum in the properties as a function of the crosslinking density or molecular weight between crosslinks.

2 EXPERIMENTAL

2.1 Materials

Triglycidylated ether of α -resorcylic acid, trifunctional epoxy, epoxy equivalent weight (EEW) of 111 g/eq, and molecular weight of 215 g/mol, was obtained from α -resorcylic acid; and was used as the epoxy phase. The synthesis and characterization of this compound is presented and discussed in Part 1 of this project. 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, was purchased from VWR (US). 2,2'-Azobis(2-methylpropionitrile) (AIBN) and methyl methacrylate were also acquired from VWR (US). Acrylated epoxidized soybean oil (AESO), viscosity 18000–32000 cps (at 25 °C), and molecular weight of approximately 1800–7200 g/mol, was purchased from Sigma-Aldrich (USA). R represents the fatty acid chain 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 be first converted into epoxy groups and then into acrylate moieties [12].

2.2 Synthesis of IPNs

The IPNs consisted of combining a phenolic-based epoxy resin 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, whose synthesis was described in Part 1 of this project, 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 °C for 1 h, 60 °C for 1 h, 75 °C for 2 h, 120 °C for 12 h, and finally 180 °C for 1 h. The extent of curing was measured by Soxhlet extraction [13].

2.3 Characterization of Networks

2.3.1 Scanning Electron Microscopy (SEM)

An SEM study was performed for the purpose of obtaining a topological characterization of the materials. The fractured surfaces of pre-chilled samples in liquid nitrogen were studied by scanning electron microscope (Zeiss EVO 50 variable pressure scanning electron microscope with digital imaging and EDS). The SEM was operated at an accelerating voltage of 20.00 kV and a probe current of 6×10^{-10} A. Samples were sputtered with gold prior to SEM observations with an EMS 550X auto sputter coating device with carbon coating attachment. Sputter coating was performed at a current of 25 mA for 2 minutes.

2.3.2 Thermo-Mechanical Properties of the Networks

Dynamic mechanical analysis (DMA) on a TA Instruments RSA III was carried out to assess the thermo-mechanical properties by three-point bending. The tests were performed at temperatures ranging from 25 °C to 250 °C with a heating rate of 10 °C/min. The frequency was fixed at 1Hz and a sinusoidal strain-amplitude of 0.1% was used for the analysis. The dynamic storage modulus (E') and $\tan \delta$ curves were plotted as a function of temperature. To be able to explain the effects of the co-monomers on the mechanical properties, it is useful to calculate the crosslinking density (n , mol/m³). The crosslinking density can be estimated from the experimental data using the rubber elasticity theory. Thermosets behave as rubbers above glass transition temperature (T_g). At small deformations, rubber elasticity predicts that the modulus storage (E') of an ideal elastomer with a network structure is proportional to the crosslinking density according to the following Equation 1 [14]:

$$E' = 3nRT = 3RT\rho/Mc \quad (1)$$

where E' is the rubbery storage modulus, R is the gas constant (8.314 J/mol K), T is the absolute temperature (K), ρ is the density of the sample (g/m³), and Mc is the molecular weight between crosslinks (g/mol). The temperature and rubbery modulus were determined for the calculation of the equation at $T_g + 30$ °C. The temperature at which the peak of the $\tan \delta$ presents a maximum was considered as the glass transition temperature of the material.

2.3.3 Linear Elastic Fracture Mechanics

In order to characterize the fracture toughness of the graft-IPNs synthesized in terms of the critical stress intensity factor, K_{Ic} , quasi-static fracture tests were performed following the method described by ASTM D5045-14 [15]. The cured IPN sheets were machined into rectangular coupons of dimensions 70 mm × 20 mm and 2.8 mm thickness. An edge notch of 3 mm in length was cut into the samples and the notch tip was sharpened using a razor blade. An Instron 4465 universal testing machine was used for loading the specimen in tension and in displacement control mode (crosshead speed = 1 mm/min). The load-deflection data was recorded up to crack initiation and during stable crack growth, if any. The crack initiation toughness or critical stress intensity factor, K_{Ic} , was calculated using the load (F) recorded at crack initiation. For each system, at least three sets of experiments were performed at laboratory conditions. The mode-I stress intensity factor for a single edge notched (SEN) tensile strip using linear elastic fracture mechanics is given by Equation 2 [16]:

$$K_{Ic} = \frac{F\sqrt{\pi a}}{Bw} f\left(\frac{a}{w}\right) \quad (2)$$

where,

$$f\left(\frac{a}{w}\right) = \left[\begin{array}{l} 1.12 - 0.23\left(\frac{a}{w}\right) + 10.6\left(\frac{a}{w}\right)^2 \\ - 21.7\left(\frac{a}{w}\right)^3 + 30.4\left(\frac{a}{w}\right)^4 \end{array} \right] \quad (3)$$

and a is the edge crack length, w is the specimen width, B is the specimen thickness and F is the peak load. All data are expressed as means ± standard deviations. Statistical analysis was performed by one-way analysis of variance (ANOVA) in conjunction with Tukey's post hoc test for multiple comparisons using Minitab 17 software. The critical energy release rate, G_{Ic} , can be related to the stress-intensity factor, K_{Ic} , in plane strain conditions by Equation 4 [17]:

$$G_{IC} = \frac{(K_{IC})^2}{E} (1 - \nu^2) \quad (4)$$

where ν is the Poisson's coefficient and E the Young's modulus of the material. For all formulation, ν was taken equal to 0.33 [18].

3 RESULTS AND DISCUSSION

3.1 Scanning Electron Microscopy (SEM)

The fracture surfaces of the thermosets were studied by scanning electron microscopy (SEM). The results of the morphological study are shown in Figure 1.

As shown, the fracture surfaces of the parent resins are characterized by smooth and homogeneous microstructures without any plastic deformation. Both the 100 wt% epoxidized resorcylic acid and the 100 wt% acrylated soybean oil formulations possess a fracture surface and an internal structure of a brittle material, revealing a highly glassy surface, where crack marks, ridges, and planes are dispersed all over the surface. The IPNs 75/25 wt% and 50/50 wt% epoxy-acrylate are also characterized by a highly glassy surface. In the 25/75 wt% epoxy/acrylate, the brittle character of the material seemed to decrease, and the surface exhibits some degree of ductility and plastic deformation.

As it will be discussed in the mechanical and fracture studies, this sample showed the highest value for the critical energy release rate, denoting its ability to dissipate energy due to its more ductile character. It was also evident from the thermo-mechanical evaluation that this IPN presented the least brittle character of the series, which was evident by its relatively high molecular weight between crosslinks. It is important to highlight that the morphology of the samples is consistent with the thermo-mechanical characterization, which revealed a glass behavior under room conditions. Even though the starting materials seemed to be heterogeneous in their chemical nature, there is no indication of phase separation and no clear boundary between the phases. This indicated that the interpenetration occurred at micro- or nanosize level [19], denoting that phase separation was kinetically controlled by permanent interlocking of entangled chains.

3.2 Thermo-Mechanical Characterization

Figure 2 shows the dynamic mechanical response of IPNs based on epoxidized α -resorcylic acid and acrylated soybean oil. The finding of a well-defined transition from the glassy state to the rubbery state, followed by the rubbery plateau, is consistent with the dynamic mechanical behavior of other thermosetting

polymers, indicating the existence of a stable network structure.

In the glassy region, the systems showed a high modulus (~0.7–3.0 GPa). It is clearly seen that with increasing the acrylated soybean oil content, the stiffness (E') in the glassy state is considerably decreased. Once the glass transition was surpassed, all of the resins exhibited a rubbery plateau modulus that was insensitive to the temperature (~16–65 MPa). The plateau modulus of the IPNs also decreased with increasing the acrylated oil content, which reduces the crosslinking density or n values, as established by the proportionality between E' and this parameter (Table 1). From the plots it is evident that the epoxy parent system is more crosslinked than that of the acrylate parent system, and that the crosslinking is also severely reduced when the acrylate soybean oil content is increased in the systems. The crosslinking effect on T_g is an increasing function of the chain stiffness, which is under the dependence of molecular scale factors, essentially aromaticity. The chain stiffness is expressed by the flex parameter F , which for a given chain of molar mass M_e is given by $F = M_e/N_e$, where N_e is the number of elementary (undeformable) segments; F is essentially an increase function of the content of aromatic nuclei [20]. The α -resorcylic acid-based epoxy matrix is structurally formed by aromatic units; polyfunctional hard clusters that constitute a rigid and densely packed phase that largely reduces the coordinated large-scale motions in the network. It is therefore evident that mixtures richer in the epoxy phase are stiffer, conferring support to the network when stress is applied.

The reduction in the stiffness of the systems is also accompanied by a similar change in the T_g , as evidenced by the shift in the α -transition temperature peak from high to low temperatures. The peaks of the parent resins were relatively narrow, while the IPNs (due to the multitude of components and the great amount of possible relaxation modes acting in triglyceride-based polymers) showed a wider transition [21]. Likewise, all of the systems showed only one $\tan \delta$ peak, indicating that there was no phase separation, and therefore good compatibility between the epoxy and acrylate phase. It is important to mention that there seems to be a decrease in the intensity of the T_g peaks in the $\tan \delta$ plots of the IPNs. This intensity reduction of the T_g peak can be ascribed to some constraint effects on supramolecular level which supports the presence of interpenetration of the two networks [22]. Note that a reduction in T_g is usually due to less tight crosslinking (co-network) which also covers the formation of IPN. Moreover, the peak width at half height is a criterion used to indicate the homogeneity of the amorphous phase. A higher value implies

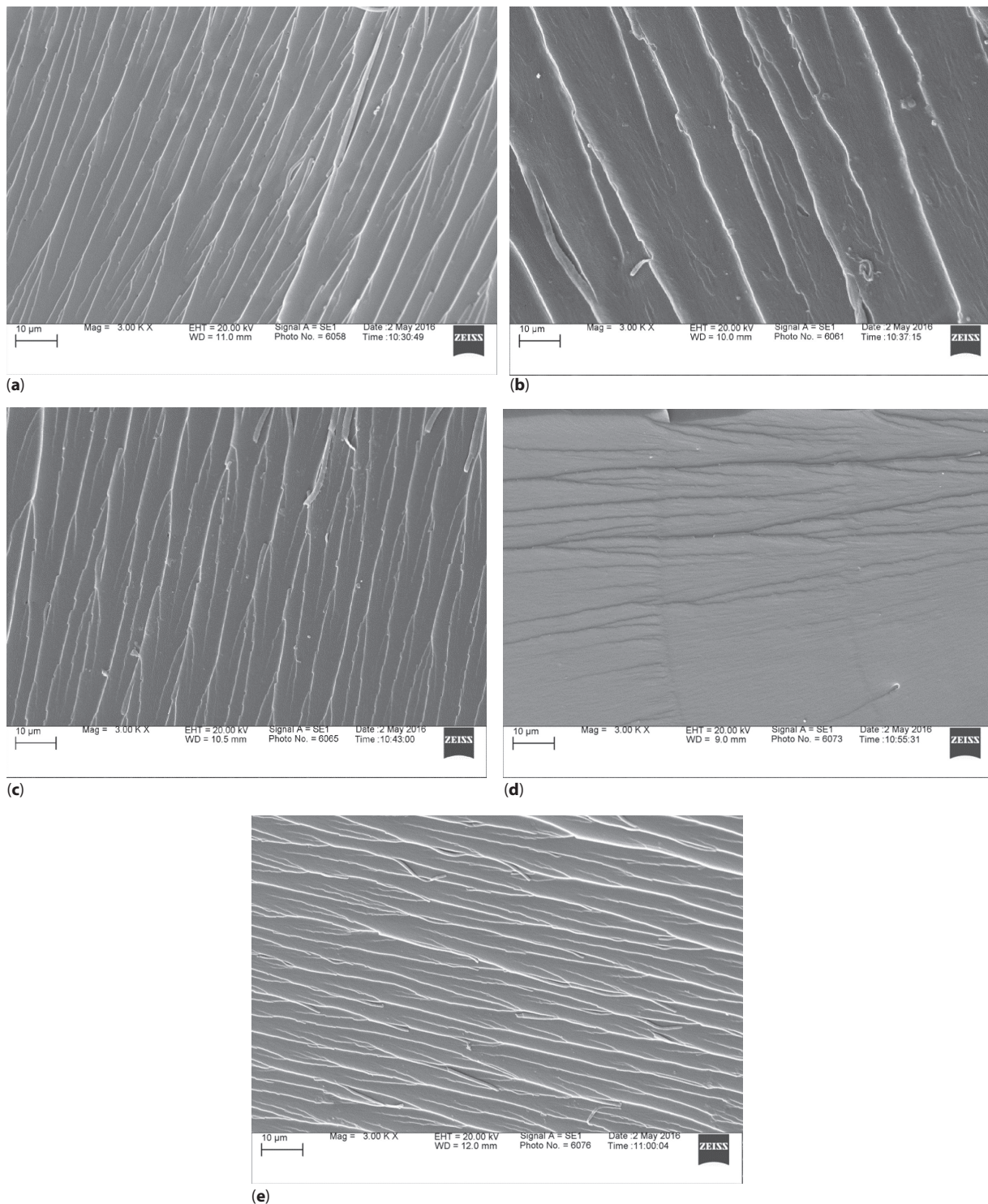


Figure 1 SEM micrographs of the fracture surface of 100 wt% epoxidized α -resorcylic acid (a); IPN 75 wt% epoxy–25 wt% acrylate (b); IPN 50 wt% epoxy–50 wt% acrylate (c); IPN 25 wt% epoxy–75 wt% acrylate (d); and 100 wt% acrylated soybean oil (e).

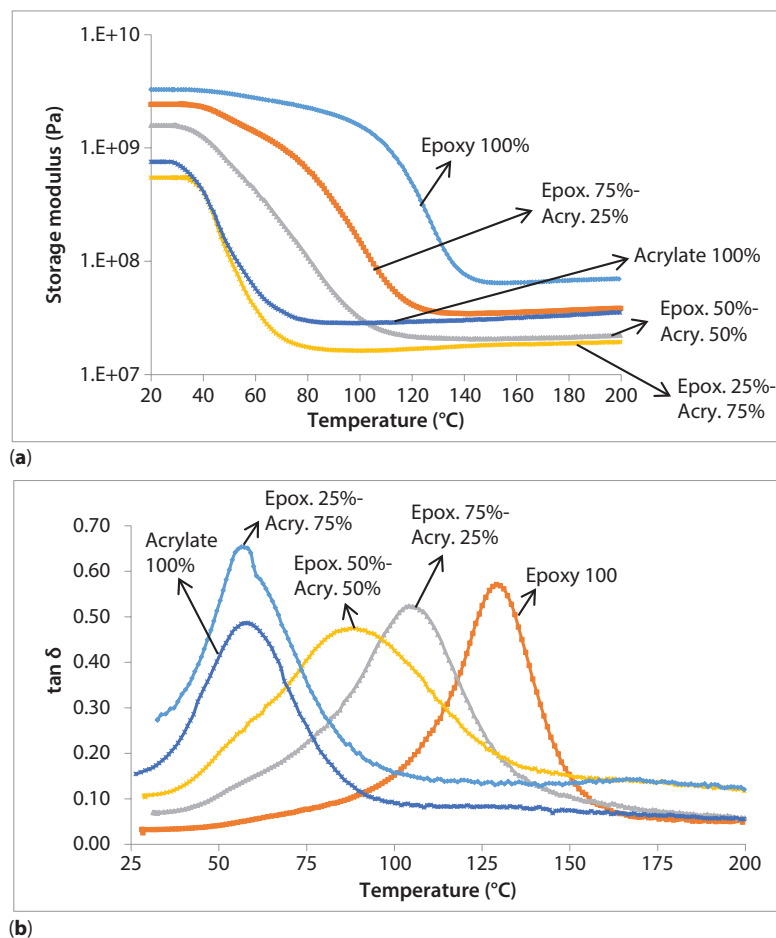


Figure 2 Temperature dependence of the storage modulus (a) and loss factor or $\tan \delta$ (b) as a function of the composition of the IPNs.

Table 1 Mechanical properties of the IPNs.

System	T _g (°C)	E' at 30 °C (GPa)	(g/cm ³)	n (mol/m ³)	M _c (g/mol)
Epoxy 100%	129.10	3.28	1.1301 ± 0.0315	6026	187.53
E75%–A25%	104.18	2.43	1.1293 ± 0.0488	3431	329.12
E50%–A50%	89.11	1.56	1.1169 ± 0.0272	2235	499.71
E25%–A75%	56.41	0.55	1.0984 ± 0.0019	1872	586.89
Acrylate 100%	58.27	0.72	1.0815 ± 0.0084	3185	339.58

higher inhomogeneity of the amorphous phase. In this particular case, the widening of the loss factor peak was observed for the IPNs, especially for the 50/50 wt% mixture. This behavior could be associated with less crosslinked and heterogeneous networks [23].

The resulting thermo-mechanical properties of the systems are listed in Table 1. The crosslinking density (n) and molecular weight between crosslinks (M_c) were estimated from experimental data using the rubber elasticity theory in Equation 1 to be able to explain

the effects of the phases on the mechanical properties of the resulting IPNs.

For the calculation of n , it was assumed that all of the components in the systems entered into the network, which is in reality impossible. However, after the Soxhlet extraction of samples with acetone for 6 hours, it was observed that the total amount of monomers that did not polymerize ranged from 3% to 7% (from Epoxy 100% to Acrylate 100%). These results allowed assuming that the influence of low

incorporation of monomers into the networks can be neglected.

As seen in Table 1, all of the systems behaved as brittle glassy polymers under room conditions. The value of n for the epoxidized α -resorcylic acid cured with Jeffamine T-403 system is approx. 6026 mol/m³, denoting a highly crosslinked network (similar to a diglycidyl ether of bisphenol A (DGEBA) type of epoxy resin, having $n = 5000$ mol/m³) [24]. When acrylated soybean oil is incorporated into the epoxy phase in a low proportion (25 wt%), the n value fell about 2 times; reaching a value of $n = 3431$ mol/m³. As the acrylate weight fraction increases, the crosslinking density still decreases, lowering the thermo-mechanical properties, as evidenced by the numerical decrease of the T_g and modulus. For the 100 wt% acrylate soybean oil system, the crosslinking density reached approx. 3185 mol/m³. It is clear from these results that the acrylated soybean oil phase is plasticizing the epoxy network.

The dynamic mechanic behavior previously described comprises a balance between two factors, crosslinking density and plasticization. As the crosslinking density increases, the more constrained the chain motion is, and thus the stiffer and more thermally resistant the molecular structure is. Plasticization is due to the molecular nature of the triglyceride. The positional distribution of the acrylate groups implies that dangling chain ends remain after crosslinking of the acrylate moieties. Also, the soybean oil contains fatty acids that are completely saturated and cannot be functionalized with acrylates. These inelastically active fatty acid dangling chains do not support stress when a load is applied; therefore, they act as a plasticizing agent, introducing free volume and enabling the network to deform easily when stress is applied to the material. This plasticizer effect is inherent to all natural triglyceride-based materials, and it represents an issue for their potential use in high-performance applications [25].

As revealed by the results, the polymer densities increased slightly with the increase in the epoxy phase content, and ranged from about 1.08 to 1.13 g/cm³. Similar values for triglyceride-based materials have been reported by La Scala and Wool [26]. The rubbery moduli of the systems ranged from approx. 16 to 65 MPa, yielding molecular weight between crosslinks ranging from approx. 188 to 588 g/mol. The M_c , as expected, increased with the increase in the acrylated soybean oil content, because the fatty acid chains increase the free volume of the polymer matrix. Similar values have been obtained by La Scala and coworkers [21].

As a summary of the thermo-mechanical results, α -resorcylic acid-based epoxy system provided a good

alternative to formulate the interpenetrated networks, providing a highly crosslinked and stiff network, due to its ability to react at rather low temperatures and the good resulting mechanical properties. However, no synergistic effect on the thermo-mechanical properties was observed, and contrary to this a reduction in the mechanical performance was observed in the IPN when compared to their parent resins, mainly attributable to the plasticizer effect conferred by the triglyceride-based acrylate matrix.

3.2.1 Linear Elastic Fracture Mechanics

In order to investigate the influence on the introduction of the acrylate phase on the epoxy phase, and vice versa, the fracture toughness of the IPNs and parent resins was evaluated through the critical stress intensity factor, K_{Ic} . Table 2 depicts the obtained results.

According to the statistical analysis of the results, there is significant variation in the fracture toughness of the IPNs when compared to their parent resins ($P < 0.05$). However, Tukey's test indicated that the obtained data can be categorized into three groups of observations, having means that are significantly different. There is statistical evidence to support that the epoxy 50 wt%–acrylate 50 wt% IPN showed the highest fracture toughness of the series (first classification), exhibiting a K_{Ic} value of around 2.1 MPa·m^{1/2}. The second categorization comprises the 100 wt% acrylate, which showed the poorest resistance to fracture (around 0.84 MPa·m^{1/2}). The third group encompasses all of the remaining systems, in which there is no evidence to support that there is a significant difference in the value of this property, meaning that the critical stress intensity factor is not changing as a function of the epoxy/acrylate ratio. The result clearly showed that the inherent fracture toughness of the IPNs is only a weak function of the epoxy/acrylate weight ratio. However, it is important to highlight that the toughenability of the systems depends on the crosslinking density of the matrix. The lower the crosslinking density, the greater the toughenability. Recalling from Table 1, the IPNs epoxy 50 wt%–acrylate 50 wt%

Table 2 Experimental K_{Ic} and G_{Ic} values.

System	K_{Ic} (MPa·m ^{1/2})	G_{Ic} (kJ/m ²)
Epoxy 100%	1.803 ± 0.238	0.88
E75%–A25%	1.593 ± 0.245	0.93
E50%–A50%	2.100 ± 0.027	2.52
E25%–A75%	1.652 ± 0.159	4.45
Acrylate 100%	0.842 ± 0.086	0.88

and the epoxy 25 wt%–acrylate 75 wt%, showed values of n equal to 2235 and 1872 mol/m³, respectively. These systems showed the lowest crosslinking density, and therefore exhibited greater ductility and correspondingly greater toughenability. The effect of reducing crosslinking density has been proposed to be an increase in the main-chain mobility which results in increased ductility [27]. Compared to commercial systems, the IPNs provided a considerably higher fracture resistance. For commercial diglycidyl ether of bisphenol A (DGEBA) type of epoxy resin crosslinked with Jeffamine T-403, K_{Ic} was found to be approximately 0.80 MPa·m^{1/2} [28]. Regarding commercial polymethylacrylate (PMMA), previous investigations performed by this group indicated a value of around 1.1 MPa·m^{1/2} [29].

The critical energy release rate, G_{Ic} , can be related to the critical stress-intensity factor, K_{Ic} , in plane strain conditions by the Equation 4. The storage modulus was used as an approximation to Young's modulus ($E' \sim E$) to establish some numerical values for the fracture energy. As seen in the table, the parent resins showed equal fracture energies, having values of $G_{Ic} = 0.88$ kJ/m². Unlike the fracture toughness, the fracture energy showed a dependence on the epoxy/acrylate ratio, increasing as the acrylate proportion is enlarged. The highest values were exhibited by the IPNs epoxy 50 wt%–acrylate 50 wt% and the epoxy 25 wt%–acrylate 75 wt%, with $G_{Ic} = 2.5$ kJ/m² and $G_{Ic} = 4.5$ kJ/m², respectively. The variation of G_{Ic} as a function of this relation reflects both the increase in the toughness, due to its direct proportionality with K_{Ic} , and the decrease in the storage modulus. The introduction of the acrylate phase into the epoxy phase decreased the crosslinking density, favoring the chain flexibility as a consequence of having higher M_c values. It is accepted that thermosetting resins undergo plastic

deformation via shear yielding rather than crazing, and this is attributed to high crosslinking density and small chain contour length, l_c . However, when crosslinking decreases the chain contour length grows and the materials become more ductile and tend to yield, dissipating energy through chain deformations and molecular motion [30].

According to Gremmels and Karger-Kocsis [31], the fracture toughness and energy toughness can be described by the rubber elasticity theory. It is established that under plane strain conditions, K_{Ic} and G_{Ic} change as a function of the molecular weight between crosslinks by linear and square root relations, respectively; both relations were verified. It was found that there is no linear correlation between K_{Ic} and M_c for the systems under study. The results showed that the K_{Ic} values did not increase as M_c increased, which seems to suggest that a different mechanism is responsible for the increase in the fracture toughness displayed by IPNs. It is clear, however, that the high toughenability was correlated with high molecular weight between crosslinks.

On the other hand, a similar approach was used to study the relation between the fracture energy and M_c . Figure 3 depicts the results.

The literature suggests that G_{Ic} generally increases with M_c [18], and some of the obtained results are in agreement with the previous relation. As seen, there seems to be an exponential-type increase in the energy with the $M_c^{1/2}$ for the materials containing the epoxy phase. In this case, the introduction of the flexible acrylate soybean oil phase increases the molecular weight between crosslinks, and therefore increases the fracture energy. However, it is important to mention that the dependency does not hold for the entire set of values, with the 100 wt% acrylate not showing any correlation.

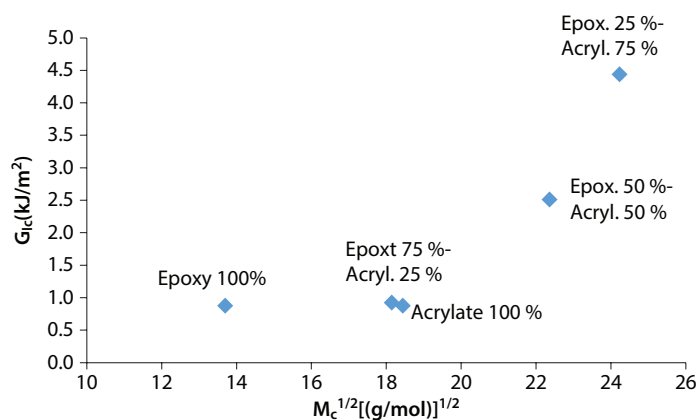


Figure 3 G_{Ic} versus $M_c^{1/2}$ for the studied IPNs.

4 CONCLUSIONS

An epoxy phase synthesized from α -resorcylic acid and acrylate phase using acrylated soybean oil was used to prepare IPNs. The mechanical properties of the IPNs were not superior to those shown by the constituent polymers. For the α -resorcylic acid and soybean oil system, modulus values ranged from 0.7 to 3.3 GPa at 30 °C, and glass transition temperatures ranged from around 58 °C to approx. 130 °C. Both parameters were affected by the epoxy/acrylate ratio, showing an increase as the epoxy proportion was enlarged. Interpenetrating networks containing equivalent weight proportions of the parent resins showed the highest fracture toughness of the series, exhibiting a K_{Ic} value of around 2.1 MPa·m^{1/2}. The results showed that the K_{Ic} values did not increase as M_c increased, which seems to suggest that a different mechanism is responsible for the increase in the fracture toughness displayed by IPNs. Also, there seems to be an exponential-type increase in the fracture energy with the $M_c^{1/2}$ for the materials containing the epoxy phase. Soxhlet extractions indicated a high degree of conversion and incorporation of the monomers into the polymer networks. These materials can be used as thermosetting matrices for the development of composite materials. Likewise, they have potential as partial replacements in the formulation of commercial thermosetting resins, where higher toughenability is required.

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