



Are ionic liquids effective curing agents for preparing epoxy adhesives?

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ABSTRACT

This work compares for the first time the efficacy of using different ionic liquids (ILs) as epoxy hardeners in epoxy-based adhesives. Several phosphonium and imidazolium-based ionic liquids were tested as epoxy hardeners, and the thermal and mechanical properties and the lap shear strength of the cured epoxy resins were studied at different IL concentrations. Both the chemical structure and the concentration of ILs were found to impact the final properties of the epoxy resin, but among the ten different ILs studied, three of them cured the epoxy resin effectively and produced similar and even better mechanical properties and lap shear strength than those obtained with traditional amine-based curing agents. These results constitute an important step towards sustainability thanks to the non-volatility of ILs and the significantly lower amount needed for effectively curing epoxy resins.

1. Introduction

Epoxy resins are widely used owing to their excellent mechanical properties, chemical resistance, thermal stability, and adhesive properties. Thus, they are used as coatings, adhesives, and high-performance composites, and other applications. However, traditionally used curing agents are toxic and volatile, which has led to a search for more sustainable candidates. Among others, ionic liquids (ILs) have been successfully used to meet this need.

Ionic liquids are salts that melt at temperatures below 100 °C. Their low vapour pressure, flame resistance, ionic conductivity, and thermal and chemical resistance are particularly interesting properties. In addition, they are highly versatile because different anions and cations can be combined to produce ILs with customized properties. As a result, they can be used in a wide range of applications. For instance, their non-volatility means they can be used as green solvents in organic chemistry [1,2], biochemistry [3] and polymer synthesis [4,5]. They can also be used as catalysts [5–8], electrolytes [9–11], cellulose solvents [12], extraction mediums [13], and lubricants [14]. In polymer science, ILs have been used in gas separation membranes [15], ionic gels [16] and also as plasticizers [17–21]. They are also used as compatibilizers in thermoplastic blends [22–25] or as nanofiller dispersing aids in thermoplastics [26–31] and epoxy resins [32–36]. They have further been employed as combined compatibilizing and dispersing agents [29,

37–39].

Regarding epoxy resins, not only can ILs act as co-curing agents in combination with traditional curing agents [40–42], but a number of imidazolium [43–49] and phosphonium-based [43,50–54] ionic liquids, among others, have also successfully cured resins when used alone. In phosphonium-based ionic liquids, the anion of the IL can initiate the homopolymerization of the epoxy [50–52]. Nguyen et al. [51] reported that more basic anions are more reactive. For imidazolium-based ionic liquids, different mechanisms have been reported in the literature, with the curing reaction being initiated either by the cation [40,46,49] or by the competition between the cation and the anion as reported by Binks et al. [55]. When the imidazolium cation is responsible for initiating the curing reaction, the first step is its decomposition. For this reason, the stability of the ionic liquid is a key factor. Maka et al. [46] demonstrated that anions with higher basicity favour decomposition of the cation.

Even though the use of ionic liquids as effective curing agents for epoxy resins has been widely studied, fewer papers have dealt with the mechanical properties of IL-cured epoxy resins. Moreover, these latter studies have mainly focused on a specific IL concentration [49,53] rather than studying the effect of different concentrations [45]. Regarding the mechanical properties of IL-cured epoxy resins, Nguyen et al. [53] observed that some phosphonium-based ionic liquids produced flexural modulus and fracture toughness results that are comparable to amine-cured ones. Lower crosslinking densities have been seen

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Table 1
Chemical structure of the ionic liquids used as potential curing agents of the epoxy resin.

IL	Structure	IL	Structure
IL-P-TMPP		IL-I-Cl	
IL-P-DCA		IL-I-DCA	
IL-P-TFSI		IL-I-TFSI	
IL-P-Cl		IL-I-BF4	
IL-P-DEP		IL-I-PF6	

to result in tougher materials whereas highly crosslinked ones are associated with brittleness. Finally, Maka et al. [45] reported that while a minimum amount of IL is necessary to obtain samples with high tensile and flexural strength, an excess of IL can cause a decrease in these properties due to a potential plasticizing effect.

One of the main applications of epoxy resins is in the production of adhesives. However, only one study in the literature examines the use of ionic liquids in epoxy-based adhesives [45]. The authors involved reported that the use of 1 phr of 1-ethyl-3-methylimidazolium chloride led to a lap shear strength value of 20 MPa, but that higher concentrations caused it to drop. Nevertheless, to the best of our knowledge, no work has analysed the effect of using different ILs on the adhesive properties of epoxy resins.

This work describes for the first time the use of different ionic liquids as curing agents in epoxy adhesives, as well as the impact of the type and concentration of these ILs on the lap shear strength. To this end, ten different imidazolium and phosphonium-based ionic liquids were tested as potential epoxy resin curing agents and the three best performers were selected for the study. The thermal and mechanical properties of samples cured with these ILs were studied. In addition, the effect of the chemical structure and the concentration of the ILs on the adhesion strength was analysed with lap shear tests, and the results were compared with those of epoxy adhesives cured with conventional hardeners.

2. Materials and methods

2.1. Materials

The epoxy resin was a diglycidyl ether of bisphenol A (DGEBA) (Nazza, Eurotex, Spain) with an epoxy equivalent weight of 184-190 g/equivalent, viscosity of 11500-13500 mPa s and pot life of 30 min at 25 °C.

The different IL candidates for use as potential curing agents for the epoxy resin are depicted in Table 1 along with their chemical structure. The tributyl(ethyl) phosphonium diethylphosphate (IL-P-DEP) and trihexyltetradecylphosphonium chloride (IL-P-Cl) were kindly supplied by Cytec, Inc (Princeton, NJ, USA). The trihexyltetradecylphosphonium dicyanamide (IL-P-DCA) was purchased from IOLiTec-Ionic Liquid Technologies GmbH (Heilbronn, Germany). The 1-ethyl-3-methylimidazolium dicyanamide (IL-I-DCA), trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide (IL-P-TFSI), 1-ethyl-3-methylimidazolium chloride (IL-I-Cl), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (IL-I-TFSI), 1-butyl-3-methylimidazolium tetrafluoroborate (IL-I-BF4), trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate (IL-P-TMPP) and 1-butyl-3-methylimidazolium hexafluorophosphate (IL-I-PF6) were purchased from Sigma Aldrich (St. Louis, MO, USA). The curing mechanism proposed in bibliography for epoxy resins using ILs have been discussed in the introduction and are shown in Table 2. The range of IL content studied varied from 1 to 20 phr.

The thermal stability of the ionic liquids was studied by thermogravimetric analysis (TGA) in a TA TG-Q-500 thermogravimetric analyser (TA Instruments, New Castle, DE, USA). The tests were performed from 40 °C to 800 °C at a 10 °C/min rate in an oxygen atmosphere.

Two different amines were also used as reference traditional curing agents: 2,2'-dimethyl-4,4'-methylenebis(cyclohexylamine) (Aradur), commercially sold as ARADUR 2954 (Huntsman, The Woodlands, TX, USA) and 4,4'-diaminodiphenyl sulphone (DDS) (Sigma Aldrich, St. Louis, MO, USA). The stoichiometric proportion was used in both cases.

2.2. Preparation of samples

As common in the processing of epoxy resins, in order to avoid bubbles during the curing process, DGEBA was degassed in a vacuum oven at 80 °C for an hour prior to the addition of the curing agent. Next,

Table 2
Homopolymerization initiation mechanisms using ILs as curing agents for epoxy resins.

IL type	Initiation mechanism	Ref	
		[55]	Anionic polymerization Homopolymerization
		[46,55]	
		[55]	
		[49]	
		[50–52]	

Table 3
Experimentally optimized curing protocols for each curing agent.

Curing agent	Curing protocol
IL-P-TMPP	2 h 80 °C/2 h 120 °C/1 h 150 °C/1 h 170 °C
IL-P-DCA	2 h 120 °C/2 h 140 °C/1 h 170 °C
IL-I-DCA	2 h 110 °C/1 h 140 °C/1 h 170 °C
DDS	3 h 150 °C/2 h 170 °C/1 h 210 °C
Aradur	2 h 80 °C/2 h 120 °C/1 h 170 °C/1 h 200 °C

the resulting mixtures were mechanically mixed at 50 °C using a Heidolph RZR2000 digital rod stirrer (Heidolph Instruments, Schwabach, Germany) for 5 min, until completely homogeneous mixtures were obtained. Specimens for DMA and mechanical testing (i.e., three-point bending tests and Charpy impact tests) were obtained as follows: the mixture was poured into the corresponding silicone moulds and the corresponding curing protocol for each curing agent (Table 3) was applied. In the case of the specimens for the lap shear tests, the mixture was placed between two substrates, covering an area of 12.5 × 25 mm and the corresponding curing protocol was applied. Table 3 only shows the curing protocols of the selected ionic liquids and of the reference traditional amine-based curing agents.

2.3. Characterization

2.3.1. Thermal properties

Differential scanning calorimetry (DSC) studies were carried out using a Perkin-Elmer DSC-7 calorimeter (Waltham, MA, USA) calibrated using an indium standard as a reference. To evaluate the curing ability of the different ILs, the uncured mixtures were heated from 30 °C to 250 °C at a rate of 10 °C/min under a nitrogen atmosphere. The curing enthalpy

was determined from the area of the exothermic peak.

The conversion (α) and curing rate (ν) were measured by DSC isothermal scans and calculated as per equations (1) and (2), respectively. The enthalpy of the completely cured samples (ΔH_{Total}) was calculated by adding the released heat of consecutive isothermal scans carried out at increasing temperatures until no heat release was observed.

$$\alpha = \frac{\Delta H_{isothermal}}{\Delta H_{Total}} \quad (1)$$

$$\nu = \frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_{Total}} \quad (2)$$

Dynamic mechanical analysis (DMA) was carried out on rectangular specimens (30 × 8 × 2 mm) using a TA Q800 viscoelastometer (TA Instruments, New Castle, DE, USA) in single cantilever bending mode. The heating rate was set at 4 °C/min, the frequency at 1 Hz and the applied temperature interval was –100 °C–250 °C. To calculate the crosslinking densities (ν_e) the elasticity theory was used [46,53], as per equation (3):

$$\nu_e = \frac{E_r}{3RT_r} \quad (3)$$

where E_r is the storage modulus at T_r , T_r is a temperature at which the material is in a rubbery state ($T_r = 245$ °C was selected in the present work) and R is the ideal gas constant ($R = 8.314$ J/mol K).

2.3.2. Mechanical properties

The mechanical properties were measured using three-point bending tests in an Instron 5569 universal testing machine (Instron, Norwood, MA, USA). The samples were moulded according to the ISO 178 standard (80 × 10 × 4 mm). A span of 64 mm and a crosshead speed of 2

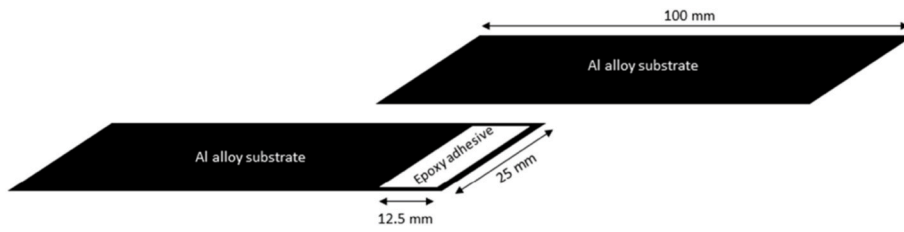


Fig. 1. Scheme of the specimens used for lap shear tests.

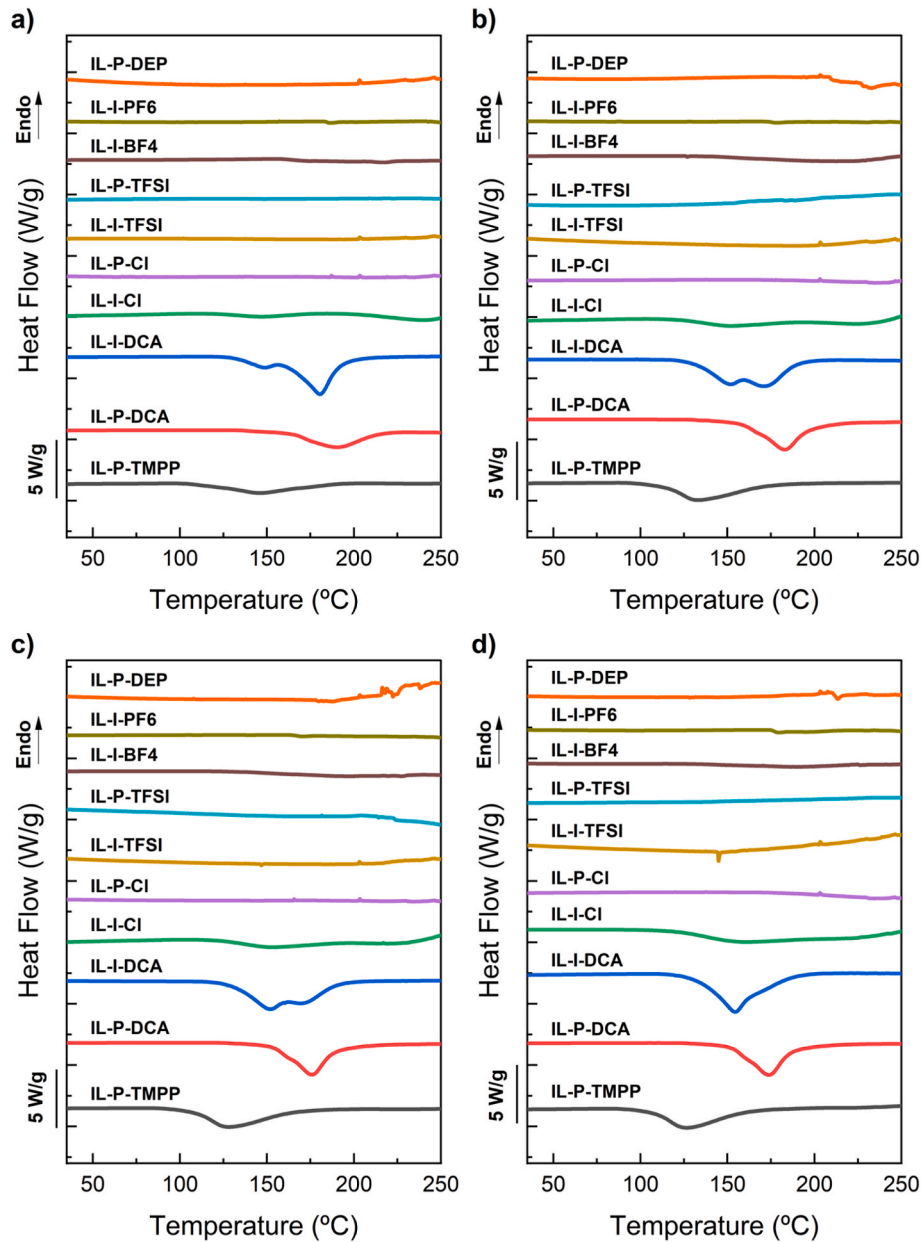


Fig. 2. DSC thermograms of the studied ionic liquids in concentrations of a) 5 phr, b) 10 phr, c) 15 phr and d) 20 phr.

mm/min were used to carry out the tests. For each composition, at least 5 specimens were analysed. The flexural strength (σ_F) and deformation at break (ε_F) were calculated following equations (4) and (5). The flexural modulus (E_F) was calculated from the slope of the tangent line of the linear zone within the elastic limit of the stress-strain curve (equation (6)).

$$\sigma_F = \frac{3F_{max}L}{2bh^2} \quad (4)$$

$$\varepsilon_F (\%) = \frac{6sh}{L^2} \times 100 \quad (5)$$

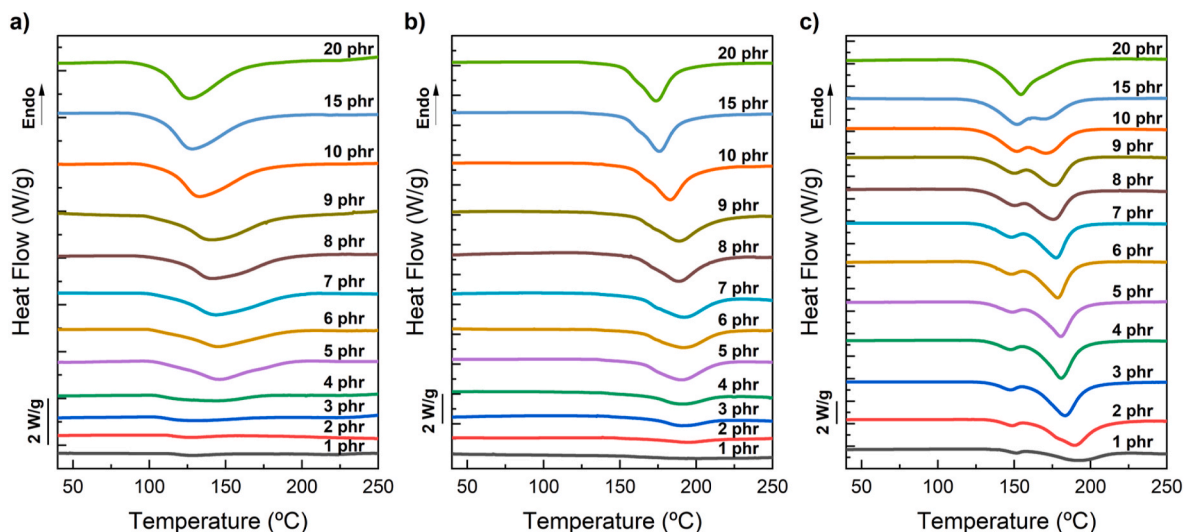


Fig. 3. DSC thermograms of the selected ILs in concentrations from 1 to 20 phr: a) IL-P-TMPP, b) IL-P-DCA and c) IL-I-DCA.

$$E_f = \frac{\sigma_{f2} - \sigma_{f1}}{\epsilon_{f2} - \epsilon_{f1}} = \frac{FL^3}{4sbh^3} \quad (6)$$

where, F_{max} is the maximum load, F the load, L the span, s the deflection, b the width and h the thickness of the specimen.

Charpy impact tests were carried out on notched specimens using a Ceast 6548/000 impact tester (Instron, Norwood, MA, USA) and a pendulum of 2 J. The samples were moulded according to the ISO 179-1 standard (80 × 10 × 4 mm). The notches were 2.54 mm deep with a radius of 0.25 mm. A minimum of eight impact specimens were tested for each reported value.

2.3.3. Lap shear tests

The lap shear strength was measured by means of lap shear tests. The aluminium 2024-T351 alloy substrates which measured 100 × 25 × 1.6 mm were acquired from Rocholl GmbH (Eschelbronn, Germany). Fig. 1 shows a scheme of the specimens used for the tests, as well as the dimensions of the joints. Prior to the application of the resin, no other preparation of the substrates was performed except washing them with fresh acetone, and the epoxy resin was applied at room temperature and 50% relative humidity 60 min after degreasing. The samples were prepared according to the ASTM D-1002 standard, and had an adhesion area of 12.5 × 25 mm and a nominal thickness of 0.1 mm. The samples were tested at room temperature in an Instron 5569 (Norwood, MA, USA) in tensile mode, using a constant rate of 1 mm/min. The lap shear

strength was calculated as the ratio between the maximum force (F_{max}) and the adhesion area, as shown in equation (7). At least 10 specimens were analysed for each composition.

$$\text{Lap shear strength} = \frac{F_{max}}{\text{adhesion area}} \quad (7)$$

3. Results and discussion

3.1. Thermal properties

The ability of ILs with different chemical structures to cure DGEBA was evaluated by DSC. Ten ionic liquids were tested at different concentrations (5, 10, 15 and 20 phr). Fig. 2 shows the heat flow vs temperature curves for the different ILs and the different concentrations. As can be seen, regardless of the concentration employed, only IL-P-TMMP, IL-P-DCA, IL-I-DCA and IL-I-Cl showed the characteristic exothermic peak related to the heat released during the curing reaction. Therefore, only IL-P-TMMP, IL-P-DCA, IL-I-DCA and IL-I-Cl acted as effective curing agents of DGEBA and produced solid specimens which were further verified when samples for testing were prepared.

IL-P-TMMP [50,51,53], IL-P-DCA [43,52], IL-I-DCA [43] and IL-I-Cl [45] have previously been described as effective curing agents of DGEBA. IL-P-DEP [51,53] and IL-I-BF4 [46,47] have also been reported as being capable of initiating the epoxy-ring opening, producing the

Table 4

DSC parameters of epoxy resins containing different concentrations of the selected ILs: T_o , onset temperature, T_{max} , temperature at peak maximum, and ΔH , curing enthalpy.

IL (phr)	T_o (°C)	T_{max} (°C)	ΔH (J/g)	T_o (°C)	T_{max} (°C)	ΔH (J/g)	T_o (°C)	T_{max} (°C)	ΔH (J/g)
	IL-P-TMPP			IL-P-DCA			IL-I-DCA ^b		
1	*	*	10	*	194	47	140/165	151/191	175
2	*	*	12	160	195	72	135/166	149/190	458
3	*	*	39	163	191	102	133/163	147/184	518
4	*	144	71	161	190	132	133/162	147/181	543
5	112	146	220	159	190	281	131/162	148/181	547
6	112	145	214	159	191	277	131/161	148/181	562
7	112	143	291	160	192	314	130/160	148/178	562
8	113	142	322	158	189	389	130/159	149/176	560
9	113	141	353	157	189	428	130/159	149/176	557
10	112	133	386	155	183	453	130/160	151/173	596
15	106	128	427	152	176	461	130/163	152/170	631
20	104	127	440	150	174	486	134	155	647

*Calculation not possible due to very broad peaks.

^b The enthalpy is calculated as the area under the two peaks.

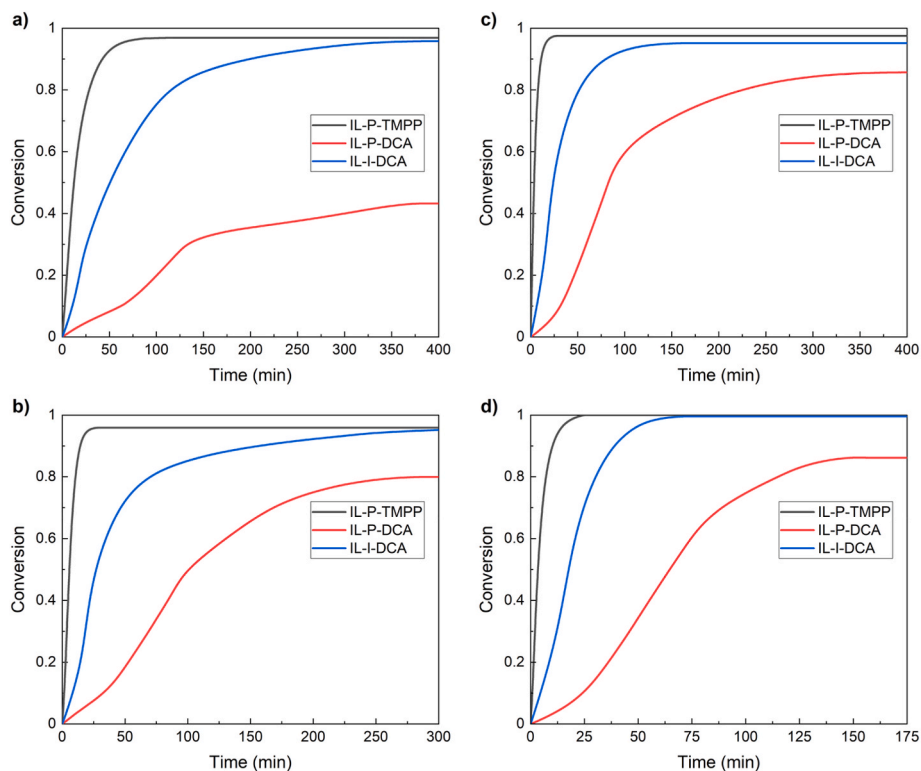


Fig. 4. Conversion of the curing reaction of the DGEBA cured with the selected ILs at different concentrations: a) 5 phr, b) 10 phr, c) 15 phr and d) 20 phr.

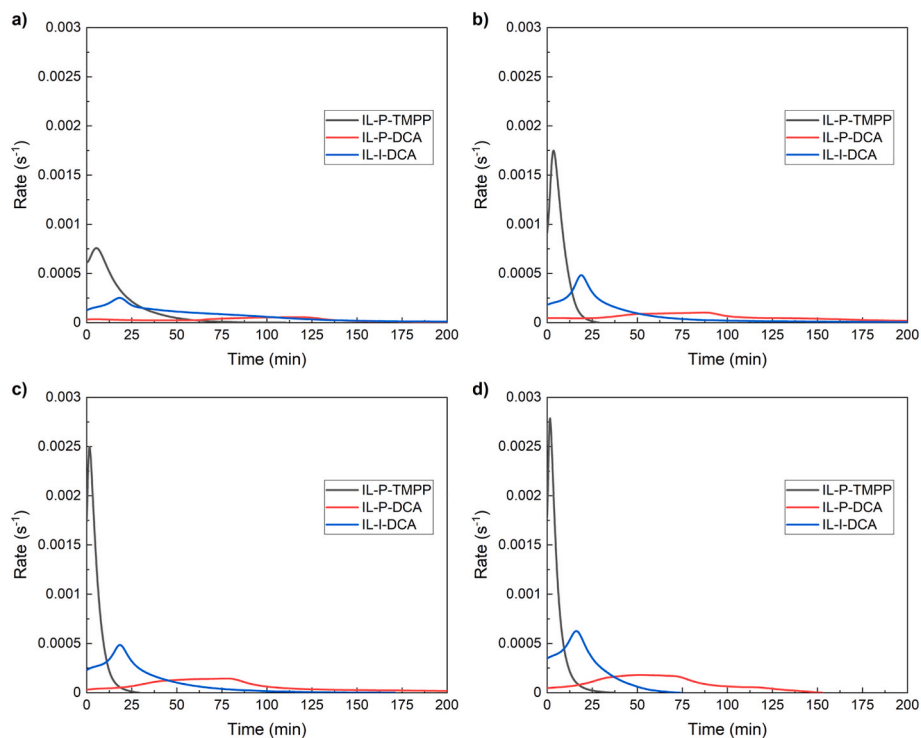


Fig. 5. Curing rate of the DGEBA cured with the selected ILs at different concentrations: a) 5 phr, b) 10 phr, c) 15 phr and d) 20 phr.

characteristic exotherm at temperatures as high as 280 °C. However, temperatures higher than 250 °C were not considered in this work as they are of less technological interest.

As a conclusion, only IL-P-TMPP, IL-P-DCA and IL-I-DCA were selected as effective curing agents for epoxy adhesives. IL-I-Cl was also

ruled out due to the low intensity of the curing reaction-related exothermic peak and the high temperatures necessary for significant curing.

The impact of the concentrations of the selected ILs was also evaluated by DSC. The thermograms of the DGEBA cured with different

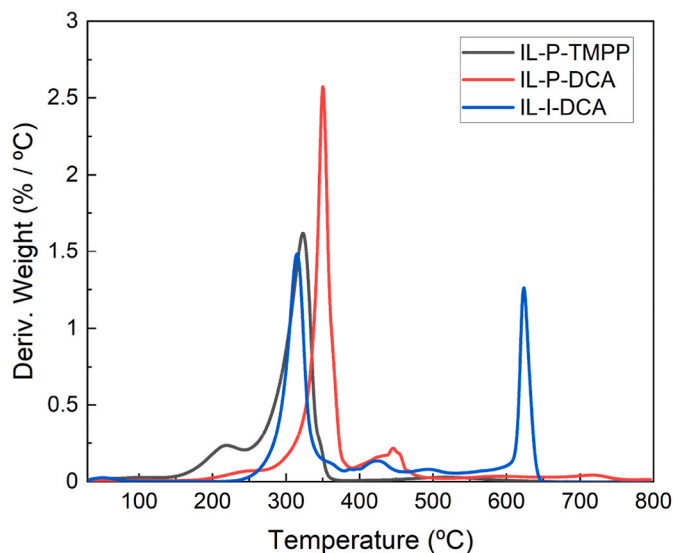


Fig. 6. TGA analysis of the selected ionic liquids.

concentrations of the selected ILs are shown in Fig. 3. The onset and peak maximum temperatures, and the curing enthalpy (ΔH) are presented in Table 4.

As can be seen, at increasing IL concentrations, both the onset and peak maximum temperatures decreased, while the curing enthalpy increased in the three cases. The presence of IL is known to initiate epoxy-ring opening, leading subsequently to homopolymerization [50, 52]. Therefore, higher IL concentrations imply greater numbers of open epoxy rings, giving rise to lower onset and peak maximum temperatures and higher curing enthalpies. As can also be seen, the IL-I-DCA showed a bimodal curve, with two peaks in the exotherm, which could indicate the existence of more than one curing mechanism. As the IL content increased, the first peak became more intense, with the exotherm becoming unimodal at 20 phr. The bimodal character of epoxy resins cured with ILs that contain a dicyanamide anion has previously been reported in the literature [43,46,48], as have ILs containing other cations and anions [40,41,45,46,56].

Isothermal DSC scans of the samples cured with different concentrations of the selected ionic liquids were used to study the conversions and curing rates. Attending to the onset temperatures observed in the non-isothermal scans, an intermediate curing temperature of 110 °C was selected for this study.

Figs. 4 and 5 show, respectively, the conversion and the curing rates of the different ILs at 5, 10, 15 and 20 phr contents, as a function of time. As can be seen, the most reactive IL is IL-P-TMPP, as it showed the highest conversions and curing rates, regardless of the IL content. By contrast, IL-P-DCA showed the lowest conversions and curing rates. As Fig. 5 reflects, higher IL contents resulted in increasingly higher reaction rates.

As previously mentioned, the first step of the curing reaction is the thermal decomposition of the IL [40,43,46]. Therefore, lower thermal stability of the IL should lead to a faster reaction. Fig. 6 shows the TGA curves of the three selected ILs. As can be seen, IL-P-TMPP had the lowest onset degradation temperature, followed by IL-I-DCA and IL-P-DCA, which had the highest. These results are fully consistent with the reaction rates previously discussed, and indicate that the reactivity of ILs is related to their thermal stability [43,46]. In the bibliography, the basicity of ILs has also been related to their reactivity [51,53].

DMA of the cured DGEBA was carried out in order to study the effect of the chemical structure of the IL and its content on the T_g and the crosslinking density. Fig. 7 shows the $\tan \delta$ and storage modulus vs temperature curves of the DGEBA cured with different concentrations of the three selected ionic liquids. Table 5 shows the T_g and calculated

crosslinking density values (equation (3)) obtained from these curves. Some of the curves, and T_g and crosslinking density values obtained at very low IL concentrations are not shown in Fig. 7 and Table 5 because they belonged to non-completely solid, in other words, incompletely cured specimens. Similarly, some of the curves and values of the very high IL concentrations are not shown as exudation of the excess IL from the epoxy resin had taken place.

As Fig. 7 shows, most of the curves have a single $\tan \delta$ peak, which corresponds to the α -relaxation (T_g) of the cured epoxy resin. In addition, some of the curves present shoulders on the main peak, or even double peaks. The presence of these bimodal peaks has usually been related to incomplete curing of the epoxy resin and/or the existence of areas with two different crosslinking densities [50]. As shown in the bibliography, it could also be an indication of poor miscibility of the ionic liquid [52] or poor distribution of the free ionic liquid [51], but this has only been reported at high IL concentrations, while in the present work bimodal peaks appear at low IL concentrations but disappear at higher concentrations.

As Table 5 also shows, low T_g s, storage modulus and crosslinking densities were obtained at low IL concentrations in all three cases, which is obviously related to a deficient crosslinked network caused by insufficient amounts of the IL curing agent. At increasing IL contents, both the T_g and storage modulus – and consequently the crosslinking density – reached optimum values above which they decreased again. This indicates that maximum crosslinking efficiency was obtained at a certain IL content, above which the reported plasticizing effect of the excess of IL [43,46,50,51] starts to prevail.

When the three ILs are compared, Table 5 shows clearly that IL-I-DCA was able to cure the epoxy resin effectively at low concentrations, since the maximum T_g , storage modulus and crosslinking densities were obtained at 2-3 phr. Further increases in the IL content gave rise to gradual decreases in the three parameters. With respect to the phosphonium-based ILs, in the case of both IL-P-TMPP and IL-P-DCA, higher IL contents – close to 10 phr – were necessary to achieve effective crosslinking of the epoxy resin. It can be seen clearly that there is a critical IL concentration (5 phr in IL-P-TMPP and 4 phr in IL-P-DCA) below which effective crosslinking of the epoxy resin cannot take place. By contrast, as mentioned in the previous paragraph, high IL contents did not further increase the crosslinking effectively, probably due to the plasticizing effect of the excess of IL.

Finally, and as Table 5 also shows, when compared to the epoxy resin cured with the traditional amine-based agents, the IL-cured samples showed higher crosslinking densities than the amine-cured ones, but similar T_g s. Even though the T_g of cured epoxy resins is mainly affected by the crosslinking density, the chemical structure of the amine-based hardener must also be considered, as it becomes part of the final network. That is why the more rigid the structure of the amine, the higher the T_g of the sample [57], pointing to the possibility of obtaining samples with different T_g s but similar crosslinking densities. The literature shows that some ILs lead to higher crosslinking densities than amines [43,51], even aromatic ones [53]. As mentioned, these differences are attributed to the fact that the structure of the amines becomes integrated in the crosslinked network while the curing reaction with ILs occurs via homopolymerization.

3.2. Mechanical properties

The mechanical properties of the epoxy resins cured with the three selected ILs were evaluated by means of flexural and impact tests whose results are shown in Fig. 8. Four different IL concentrations (5, 10, 15 and 20 phr) were studied. In the case of IL-P-TMPP, because of the aforementioned exudation-related issues at higher contents, a maximum concentration of 15 phr was used. Even the 15 phr composition showed some level of exudation, and some black colouring of the specimen was also observed, probably because of the exudation and/or degradation of the excess IL. For this reason, it was eliminated from Fig. 8. Similar

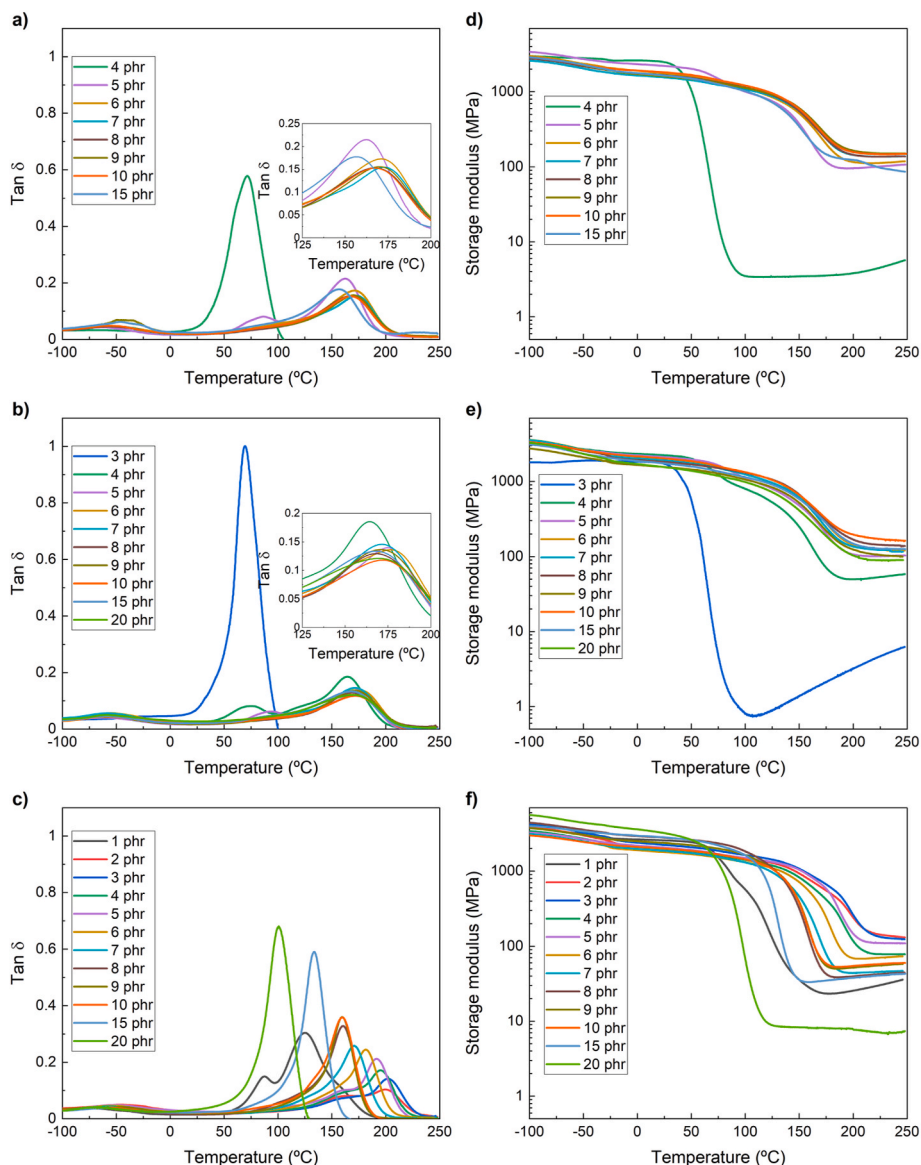


Fig. 7. $\tan \delta$ (a) IL-P-TMPP, b) IL-P-DCA and c) IL-I-DCA and storage modulus (d) IL-P-TMPP, e) IL-P-DCA and f) IL-I-DCA vs T curves obtained by DMA for the DGEBA cured with varying contents of the selected ILs.

results at similar IL contents were observed by Nguyen et al. [51]. Epoxy resins cured with traditional amine-based curing agents were also obtained and tested for comparison purposes, and the results are included as a reference (the continuous line indicates the average value while the shaded areas indicate the standard deviation).

Regarding the influence of the IL content on the mechanical behaviour, no clear trend was observed in any of the three ILs studied and, although some isolated compositions behaved differently, the values remained constant within the standard deviation of the measurement. This result indicates that the mechanical properties of the IL-cured epoxy resins are not crosslinking density-dependant once a minimum value has been achieved.

When the different ILs were compared, IL-I-DCA was seen to produce the best properties. This superior performance was particularly significant in small-strain mechanical properties, i.e., flexural modulus and strength, but was also observed in high-strain mechanical properties. In any case, it is worth pointing out that the differences between the different ILs were small and in most cases were close to the standard deviation of the measurement.

Finally, when the mechanical performance of the IL-cured epoxy

resins is compared to that of the amine-cured epoxy resins (see Fig. 8), the flexural and impact test results of the former are similar or even higher than the latter, with only a few compositions showing lower values. As already mentioned, IL-I-DCA produced the most favourable results where the mechanical properties of the resulting epoxy resin were at least similar and, in many cases, better than those obtained with the amine-based curing agents.

Therefore, based on mechanical properties, IL-P-DCA, IL-P-TMPP, IL-I-DCA are deemed promising candidates as substitutes for traditional epoxy resin curing agents. Moreover, not only are these ILs capable of delivering comparable properties to amines, but they also represent a step towards sustainability thanks to both their non-volatility and the fact that the amount required for effective curing is much lower.

3.3. Lap shear strength

The lap shear strength of the IL-cured DGEBA samples with different IL contents was studied by lap shear tests. Fig. 9 and Table 6 show the results of the compositions that adhered sufficiently to the aluminium alloy substrate. The compositions that did not adhere sufficiently to the

Table 5

T_g , storage modulus at the rubbery state (245 °C) and crosslinking density (ν_e) values measured by DMA. Only the main peak has been considered.

IL (phr)	T_g (°C)	Storage modulus (MPa)	ν_e (mol/m ³)	IL (phr)	T_g (°C)	Storage modulus (MPa)	ν_e (mol/m ³)	IL (phr)	T_g (°C)	Storage modulus (MPa)	ν_e (mol/m ³)
<i>IL-P-TMPP</i>				<i>IL-P-DCA</i>				<i>IL-I-DCA</i>			
1				1				1	125	36	2753
2				2				2	200	132	10211
3				3	69	6	467	3	202	124	9617
4	72	6	427	4	164	58	4455	4	195	78	6030
5	162	106	8231	5	175	103	8003	5	192	109	8468
6	171	118	9101	6	177	121	9337	6	181	73	560
7	173	138	10659	7	172	116	8980	7	171	47	3622
8	167	138	10682	8	168	138	10668	8	160	44	3436
9	170	151	11672	9	171	100	7747	9	160	58	4478
10	168	149	11509	10	172	163	12616	10	160	60	4625
15	157	87	6745	15	168	125	9706	15	134	43	3295
20				20	169	90	6940	20	101	7	553
25				25	178	86	6674	25	85	7	512

	T_g (°C)	Storage modulus (MPa)	ν_e (mol/m ³)
<i>Aradur</i>	171	19	1477
<i>DDS</i>	223	20	1518

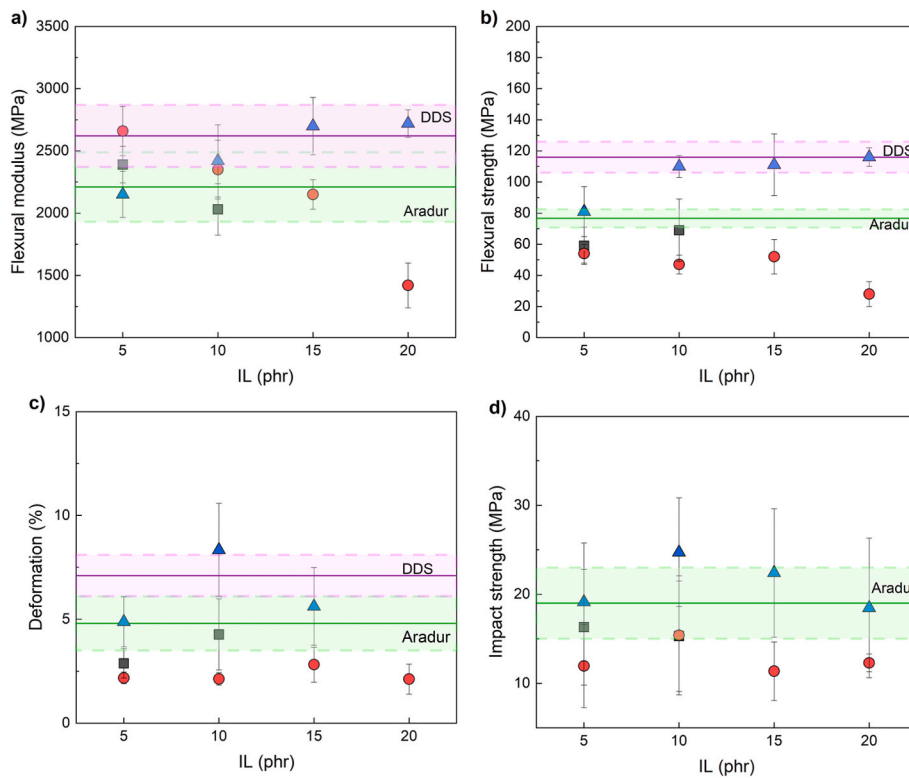


Fig. 8. Flexural modulus (a), flexural strength (b), deformation at break (c), and impact strength (d) of epoxy resins cured with IL-P-TMPP (■), IL-P-DCA (●) and IL-I-DCA (▲). The values for the epoxy resin cured with amine-based curing agents are shown as a reference (continuous line for average value and shaded area for standard deviation). The impact strength of the DDS-cured samples was not measured owing to problems related to specimen preparation. The sample with 20 phr of IL-I-DCA did not break.

substrate due to the low IL content are not shown. The results for the samples cured with the amine-based agents are also shown as a reference.

As can be seen in Fig. 9 and Table 6, the results show that, in most cases, adhesion levels similar to those obtained with the best amine-based curing agent (DDS) and better than those of Aradur were achieved. This is a remarkable result and points to IL-cured epoxy resins as effective candidates to replace traditional amine-epoxy adhesives. Moreover, the lap shear strength value of the 4 phr IL-P-TMPP composition was 216% higher than the Aradur-cured epoxy resin and 68% higher than the DDS-cured epoxy resin.

When the impact of the IL content was evaluated individually for the

three ILs in the study, the highest adhesion values were obtained at the lowest concentrations, irrespective of the nature of the IL structure. Moreover, the compositions with the highest adhesion values (4 phr in the case of IL-P-TMPP, 3-4 phr in the case of IL-P-DCA and 1 phr in that of IL-I-DCA) correspond to the lowest crosslinking density values in the adhesion strength range studied (up to 10 phr) for each IL.

Ratna et al. [58] reported that high crosslinking densities decrease the adhesion strength. Moreover, García et al. [59] reported that the T_g of the epoxy network has a significant impact on the adhesive properties, with low T_g structures presenting higher adhesion values, a finding which is fully consistent with the T_g data in this work (Table 5). However, Prolongo et al. [60] have found the opposite: that high T_g leads to

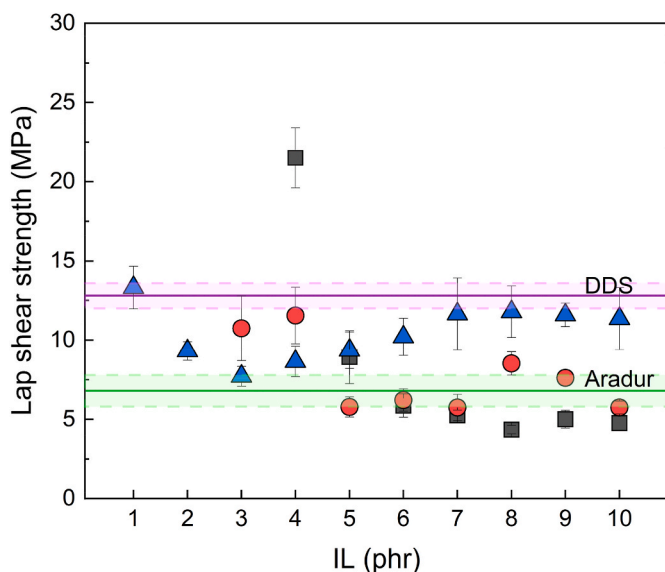


Fig. 9. Lap shear strength for IL-cured (IL-P-TMPP (■), IL-P-DCA (●) and IL-I-DCA (▲) and amine-cured samples. The values for the epoxy resin cured with amine-based curing agents are shown as a reference (continuous line for average value and shaded area for standard deviation).

Table 6

Lap shear strength values of the epoxy resin cured with the selected ILs.

IL (phr)	Lap Shear Strength (MPa)	IL (phr)	Lap Shear Strength (MPa)	IL (phr)	Lap Shear Strength (MPa)
<i>IL-P-TMPP</i>			<i>IL-P-DCA</i>		
1		1		1	13.3 ± 1.3
2		2		2	9.3 ± 0.6
3		3	10.7 ± 2.0	3	7.7 ± 0.6
4	21.5 ± 1.9	4	11.5 ± 1.8	4	8.6 ± 1.0
5	8.9 ± 1.7	5	5.8 ± 0.6	5	9.4 ± 1.1
6	5.9 ± 0.7	6	6.2 ± 0.7	6	10.2 ± 1.2
7	5.3 ± 0.3	7	5.7 ± 0.8	7	11.6 ± 2.3
8	4.3 ± 0.3	8	8.5 ± 0.7	8	11.8 ± 1.6
9	5.0 ± 0.6	9	7.6 ± 0.5	9	11.6 ± 0.7
10	4.8 ± 0.5	10	5.7 ± 0.4	10	11.4 ± 2.0
Lap Shear Strength (MPa)					
Aradur ^a			DDS ^a		
6.8 ± 1.0			12.8 ± 0.8		

^a The values of the epoxy resin cured with amine-based curing agents are also shown as a reference.

enhanced adhesive properties.

Another factor to be considered when discussing the adhesive properties of epoxy resins is the presence of hydroxyl groups. When amine-based curing agents are used, it is known that hydroxyl groups are generated in the structure during the curing mechanism and that this improves adhesion. By contrast, fully cured epoxy networks via homopolymerization show lower lap shear strength values due to the lack of hydroxyl groups at these crosslinking levels [60]. It may be inferred therefore that incomplete crosslinking via homopolymerization leads to some OH groups remaining in the structure, thus favouring higher adhesion values.

It is noteworthy that the optimum IL concentrations for achieving maximum mechanical and adhesive properties differ significantly. The reason for this may be that the specification requirements of materials are also different. While highly crosslinked networks generally favour mechanical properties, adhesive performance is linked to low crosslinking densities because rigidity causes a decrease in the lap shear strength.

In conclusion, ILs are also effective candidates for curing epoxy adhesives since similar – and even significantly higher (in the case of the DGEBA cured with 4 phr of IL-P-TMPP) – lap shear strength values were achieved compared to those obtained when amine-based hardeners were used.

4. Conclusions

Different ILs were tested as prospective hardeners for a DGEBA-based epoxy resin. Based on a calorimetric study, three ILs were selected in order to study the effect of their chemical structure and concentration on the mechanical properties and lap shear strength of the resin. Ionic liquids were seen to be promising candidates for replacing amines as epoxy hardeners for solid parts with competitive mechanical properties (as samples with high T_g values and crosslinking densities even at low concentrations were successfully obtained) and also for epoxy adhesives with comparable or even better lap shear strength. One of the main advantages of replacing amines by ILs is the fact that the amount of IL required is much lower than the corresponding stoichiometric concentration of amines. Thus, the use of ionic liquids is a step towards the production of more sustainable materials.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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