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Epoxy resin coatings modified by ionic liquid. Study of abrasion resistance

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Abstract. In the present study, an epoxy resin coating containing a uniformly dispersed 9 wt% of the ionic liquid 1-octyl-3-methylimidazolium tetrafluoroborate (EP+9%[OMIM]BF_4) has been applied by spin coating on a neat epoxy substrate, and its abrasion resistance under multiple scratch has been compared with that of neat epoxy coating. EP+9%[OMIM]BF_4 presents the lowest surface damage after 15 successive scratches. The ionic liquid-modified coating reduces instantaneous penetration depth in a 13% and residual depth in a 22% with respect to EP, and increases viscoelastic recovery (after 30 seconds) in a 7.6%. The lubricating effect of the ionic liquid reduces the coefficient of friction up to the tenth scratch number. EP and EP+9%[OMIM]BF_4 have also been obtained in the form of spin-coated films with similar visual transparency. Dynamic-mechanical characterization of the films under a tensile configuration confirms that the addition of the ionic liquid increases the ductility and reduces the glass transition temperature of the epoxy resin.

Keywords: *coatings, films, epoxy resin, ionic liquid, abrasion*

1. Introduction

As in many other scientific and technological fields, it can be said that ionic liquids (ILs) are making a deep impact in the development of new thermoset polymers, with special emphasis on epoxy resin materials [1, 2]. Epoxy resins modified by the addition of ILs are the object of wide interest for their improved properties and potential applications. Room-temperature ionic liquids play multiple roles when used as additives of epoxy thermosets [3], ranging from catalysts and curing agents [4] to plasticizers or precursors of conducting [5–7] and more sustainable materials [8].

Very recent studies are focusing on the effect of different fillers on the tribological performance of epoxy-based bulk materials, coatings and films [9–14]. From the point of view of improving the poor tribological performance or epoxy resin, ILs have shown their ability to reduce the brittleness of the bulk epoxy matrix materials, reducing friction coefficients and protecting against wear [15–20].

The first dispersion of a room temperature IL in an epoxy resin matrix with the purpose of improving its tribological performance was that of the short alkyl chain 1-ethyl-3-methylimidazolium tetrafluoroborate [20], which is not miscible with the epoxy network but distributes into microcavities. A higher compatibility with the epoxy matrix was achieved by increasing the length of the alkyl chain from two to eight carbon atoms, using 1-octyl-3-methylimidazolium tetrafluoroborate ([OMIM]BF_4) [15–18]. In the case of bulk epoxy resin containing [OMIM]BF_4, the IL increases the immediate surface damage by scratch due to the reduction in hardness and glass

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transition temperature, and to the increase in ductility [21]. However, the IL induces a self-healing of the abrasion damage plastic deformation up to 96% after 22 hours [15] for a 9 wt% [OMIM]BF_4.

In the present study, we have used the spin coating technique [22, 23] to obtain epoxy resin coatings and films containing 9 wt% [OMIM]BF_4.

The need for new epoxy coatings with improved abrasion resistance and lower friction coefficients is a very active field at the present moment [24]. Very recent results have shown the feasibility of the spin coating method for applying epoxy resin nanocomposites containing protic or aprotic ionic liquids and dispersions of graphene in ionic liquids as protective coatings, for the friction and wear [25] reduction of mild steel substrates [26].

The aim of the present work is to use epoxy resin substrates to develop new gradient composition materials, where the additive is concentrated exclusively where it is needed, that is, at the surface layer, without modifying the bulk epoxy substrate. Neat epoxy resin (EP) and EP+9%[OMIM]BF_4 have been also obtained in the form of spin-coated films in order to determine the effect of the additive on the properties of the epoxy resin.

2. Experimental

2.1. Materials

The ionic liquid additive used is 1-octyl-3-methylimidazolium tetrafluoroborate [OMIM]BF_4 (>98% purity; Fluka, Germany) (Figure 1). Neat epoxy resin (EP) substrates (25×25×10 mm) were obtained by adding 28 wt% of the hardener composed by a mixture of amines [16, 20] to bisphenol A epichlorhydrin, and stirring for 3 minutes at room temperature, as previously described [20]. EP coating was obtained by deposition of the same mixture of prepolymer and hardener on a previously cured neat epoxy resin substrate by spin coating (Spin Coater 150i infinite de POLOS TM, SPS-Europe B.V. The Netherlands), at 2500 rpm/s, for 60 seconds. EP+9wt%[OMIM]BF_4 surface layer was obtained by adding the corresponding IL proportion to the prepolymer and stirring for 3 minutes, before adding the hardener, and spin-coating the mixture on the neat epoxy substrate. Coated

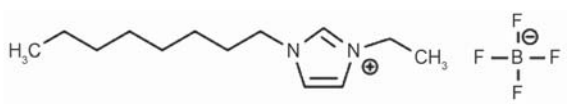

Figure 1. Ionic liquid 1-octyl-3-methylimidazolium tetrafluoroborate.

samples were then cured at 60 °C for 2 hours, and postcured at room temperature for 24 hours.

Films of EP and EP+9wt%[OMIM]BF_4 were spin-coated on polystyrene (PS) discs, with a diameter of 40 mm and an average surface roughness (R_a) of 0.17±0.018 µm, under the same conditions used for the coatings deposited on epoxy substrates. The films were cured following the same procedure described above for the coatings. Cured films were then removed from PS substrates and their thickness was measured with a micrometer.

2.2. Multiple scratch test

Multiple scratch abrasion tests (25 °C; 50% HR) were performed on the coatings with a MTR 3/50-50/NI Microtest Scratch tester with a diamond tip indenter (200 µm diameter and 120° cone angle) following the previously described experimental procedure [15]. Each of the 15 successive scratches was performed under the conditions described in Table 1. Friction coefficient, instantaneous penetration depth (*Pd*) and residual depth (*Rd*) values were determined as a function of scratch number. Viscoelastic recovery was calculated from *Pd* and *Rd* values as: $\%R = [(Pd - Rd)/Pd]\cdot 100$. Final values (Tables 2, 3 and Figure 3) are the average of three tests under the same conditions, with standard deviations lower than 5%.

2.3. Characterization techniques

Optical micrographs were obtained with a Leica DMR optical microscope, and SEM micrographs with a Hitachi S-3500N. Surface topography and roughness values (R_a) were determined with a Talysurf CLI 500 (Taylor Hobson) optical profiler. Dynamic mechanical analysis (DMA) of the films was performed with a DMA Q800 (TA Instruments) under tensile configuration, from 25 to 120 °C, at a heating rate of 3 °C·min^{-1}. Results are the average values after three tests.

3. Results and discussion

3.1. Coatings

Cross sections of the coated epoxy resin samples are shown in Figures 2a and 2b. The thickness of the IL-containing coating is lower than that of IL-free EP coating. Surface roughness (R_a) of EP+9%[OMIM]BF_4 coating (0.11 µm) is also lower than that of the EP coating (0.18 µm).

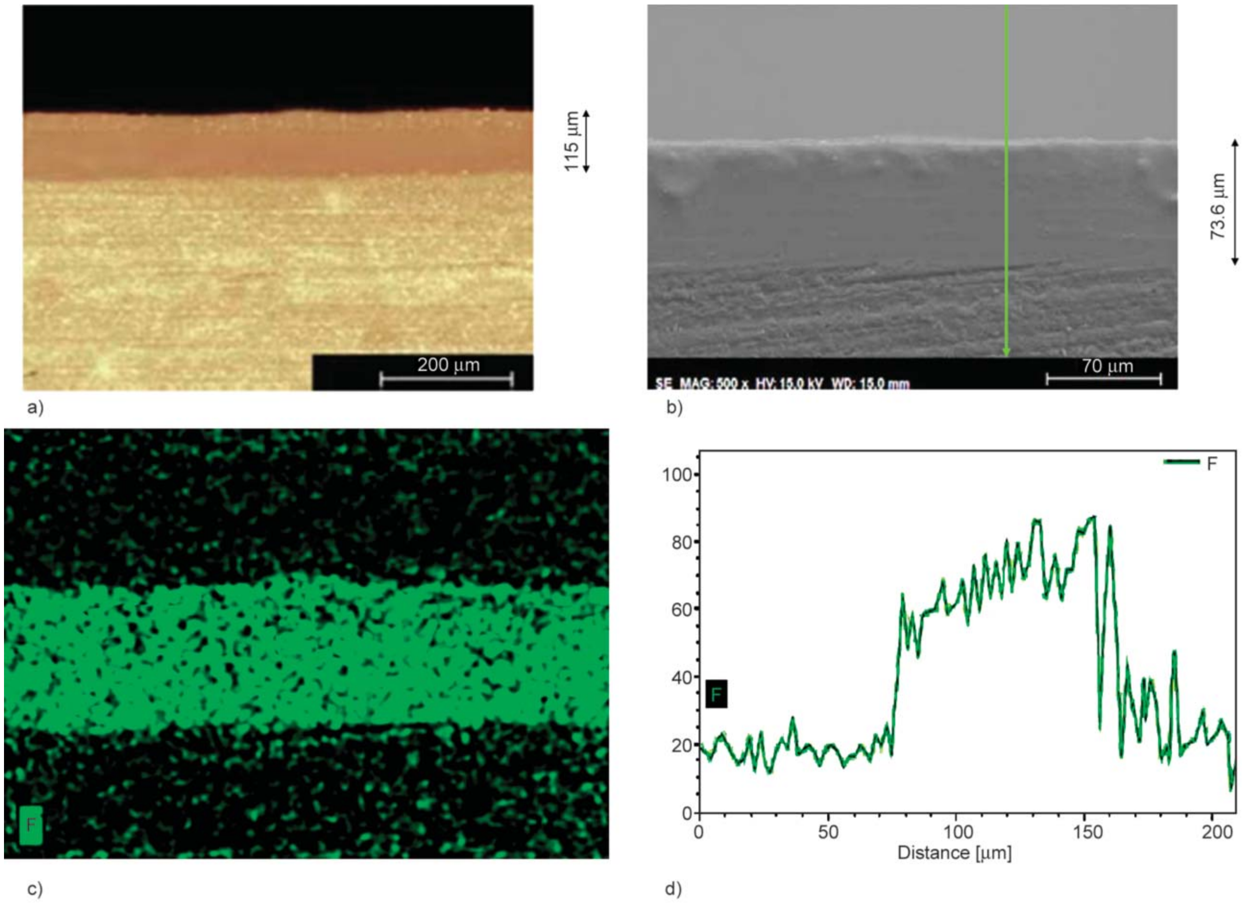

Figure 2. a) Optical micrograph of the cross section of EP on epoxy resin substrate; b) SEM micrograph of EP+9%[OMIM]BF_4 on epoxy resin substrate; c) Fluorine EDX element map for EP+9%[OMIM]BF_4 on epoxy resin substrate; d) EDX fluorine line analysis along the line shown in b).

The concentration and distribution of the IL within the EP+9%[OMIM]BF_4 coating layer has been determined by the fluorine EDX element map (Figure 2c) and the fluorine analysis (Figure 2d) along the line shown in Figure 2b. The results show that the spin coating method has been adequate for the preparation of a homogeneous dispersion of the IL, which is concentrated at the surface layer.

Abrasion resistance results under the experimental conditions summarized in Table 1, are presented as a function of scratch number in Tables 2 and 3 and in Figures 3.

Although under the first single scratch, the instantaneous abrasion resistance of the IL-modified coating is lower than that of EP coating, as a result of the softening effect of the fluid phase, its performance improves with the increase of successive slidings.

Table 1. Multiple scratch test conditions.

Normal applied load	[N]	5
Number of scratches		15
Length	[mm]	5
Velocity	[m·min^{-1}]	5
Temperature	[°C]	25
Relative humidity	[%]	50

Table 2. Results of multiple scratch tests for EP coating.

Scratch number	*Pd* [µm]	*Rd* [µm]	Viscoelastic recovery [%]	Coefficient of friction
1	40.1	16.6	60.9	0.22
2	42.2	20.4	56.2	0.30
3	46.8	23.5	53.8	0.30
4	51.5	25.2	52.2	0.26
5	53.9	28.2	53.6	0.25
6	54.3	29.7	48.9	0.26
7	56.8	29.8	50.9	0.21
8	57.3	30.1	50.2	0.22
9	58.1	30.4	50.3	0.21
10	58.1	30.3	50.6	0.21
11	58.5	30.8	49.9	0.21
12	58.5	31.0	49.7	0.20
13	58.8	31.1	50.1	0.21
14	59.1	31.3	49.8	0.21
15	59.4	31.5	49.7	0.21

Friction coefficient values (Figure 3a), measured simultaneously to abrasion resistance, show that the lubricating ability of the ionic liquid fluid additive [16] reduces friction values, with respect to neat epoxy, from 2 to 7 scratches. However, final friction values as surface damage is more severe, from 7 to 15 scratch numbers, are very similar to those found for the unmodified EP coating.

Table 3. Results of multiple scratch tests for EP+9%[OMIM]BF_4 coating.

Scratch number	*Pd* [µm]	*Rd* [µm]	Viscoelastic recovery [%]	Coefficient of friction
1	25.5	8.9	63.4	0.41
2	42.4	17.9	58.2	0.22
3	44.1	19.5	56.1	0.23
4	45.3	20.6	54.8	0.22
5	46.1	21.4	53.9	0.21
6	46.7	21.9	53.2	0.21
7	47.2	22.3	53.0	0.21
8	47.6	22.8	52.4	0.21
9	47.9	22.4	53.3	0.21
10	47.4	22.6	52.6	0.21
11	47.8	22.7	52.7	0.21
12	48.0	23.2	52.0	0.20
13	48.3	23.4	52.0	0.21
14	48.5	23.5	51.8	0.20
15	48.6	23.8	51.4	0.20

Figure 3b shows the evolution of instantaneous penetration depth. After a sharp penetration depth increase from the first to the second sliding, the coating containing the ionic liquid reaches an asymptotic behaviour. In contrast, EP coating needs 7 scratches to reach the asymptote (Figure 3b).

As described by Brostow *et al*. [27], polymers under multiple scratch tests reach asymptotic penetration values after a critical number of slidings on the same path, in a strain-hardening effect. In the present case, neat epoxy requires at least 7–9 slidings to reach such behaviour, while the results for EP+9%[OMIM]BF_4 stabilize after just 3 scratches (Tables 2, 3; Figure 3b). This is attributed to the EP brittleness reduction [28] by the addition of IL. A final 13% reduction of the instantaneous penetration (*Pd*) with respect to EP is found after 15 scratches.

Residual depth (*Rd*) values (Figure 3c), which represent permanent surface damage after viscoelastic

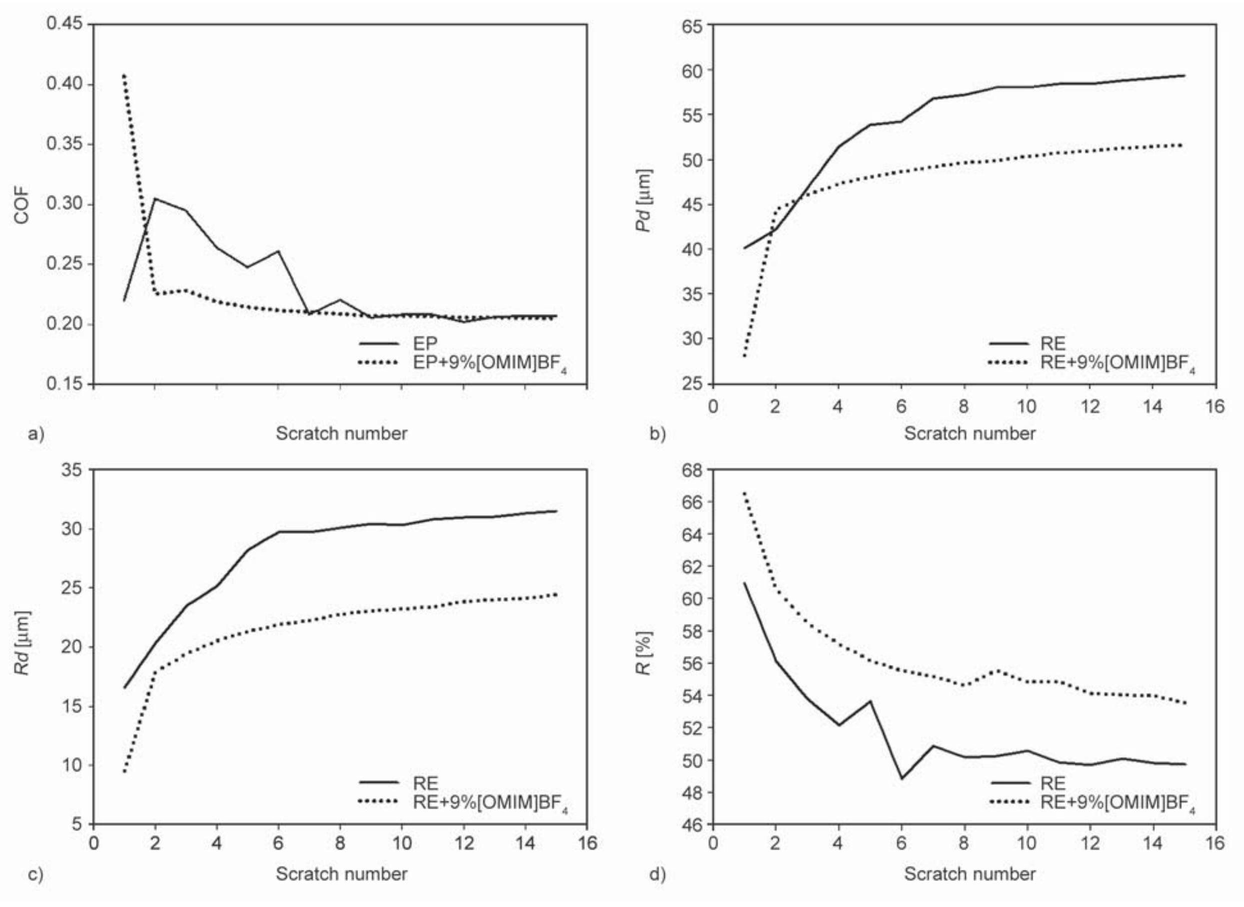

Figure 3. a) Friction coefficient (COF); b) penetration depth (*Pd*) for EP and EP+9%[OMIM]BF_4 ; c) residual depth (*Rd*) and d) viscoelastic recovery (*R* [%]) for EP and EP+9%[OMIM]BF_4 as a function of scratch number.

recovery, are recorded 30 seconds after each sliding, and are shown in Figure 3c. Again, the highest abrasion resistance after 15 scratches is found for the coating that contains ionic liquid, EP+[OMIM]BF_4, with a 22% reduction with respect to EP coating. The best performance of the coating with the ionic liquid fluid phase can be attributed to its ability to present a higher viscoelastic recovery, as shown in Tables 2 and 3, and in Figure 3d. The final increase in viscoelastic recovery after 15 scratches is 7.6%, with the addition of the IL.

Figure 4 shows the profilometry images of the final abrasion scars after 15 scratches. Neat EP coating (Figure 4a) has suffered severe surface damage, with removal of wear debris outside the wear track. In contrast, EP+9%[OMIM]BF_4 coating (Figure 4b) shows plastic deformation without removal of wear debris, and with accumulation of the material pushed by the indenter tip at the end of the abrasion groove.

The results described above for the new coatings are in contrast with those previously described for the scratch resistance of the bulk materials obtained by conventional casting techniques. In the case of bulk EP+9%[OMIM]BF_4, the addition of 9 wt% IL decreases abrasion resistance with respect to neat epoxy resin. However, the bulk-modified EP+9%[OMIM]BF_4 is able to self-heal the surface damage produced by abrasion after a period of 22 hours [15].

The different behaviour of EP+9%[OMIM]BF_4 coating with respect to the bulk material is attributed to the different processing techniques. As it has been described [23], the spin coating method changes the properties of the deposited epoxy layers. In this case, the abrasion resistance found for spin-coated neat epoxy resin is lower than that of the bulk cast material. The best performance of EP+9%[OMIM]BF_4 coating could be due to the concentration of the IL fluid phase at the surface layer which supports the applied load, and induces a change from brittle to more ductile deformation mechanisms.

3.2. Films

EP and EP+9%[OMIM]BF_4 coatings were deposited on polystyrene (PS) substrate, using the same spin coating technique described for EP substrate, but in this case, the surface films were removed after curing. Thickness of EP and EP+9%[OMIM]BF_4 films, measured with a micrometer, are 0.041±0.005 and 0.055±0.007 mm, respectively. Figures 5 show that both films present a similar visual transparency.

The EP and EP+9%[OMIM]BF_4 films were then characterized by dynamic-mechanical analysis measured under tensile configuration (Table 4; Figure 6) in order to establish the influence of the ionic liquid additive.

The results show that the addition of IL produces the reduction of the glass transition temperature of the film, thus confirming the plasticizing effect of the ionic liquid.

The strong decrease in the storage modulus (Figure 6a) confirms the increased ductility effect of the ionic liquid additive in the epoxy resin film. The similar maximum values and curve width of the dissipation factor (tan δ) (Figure 6b) for both films are in agreement with a uniform distribution of the IL in the epoxy matrix within the film.

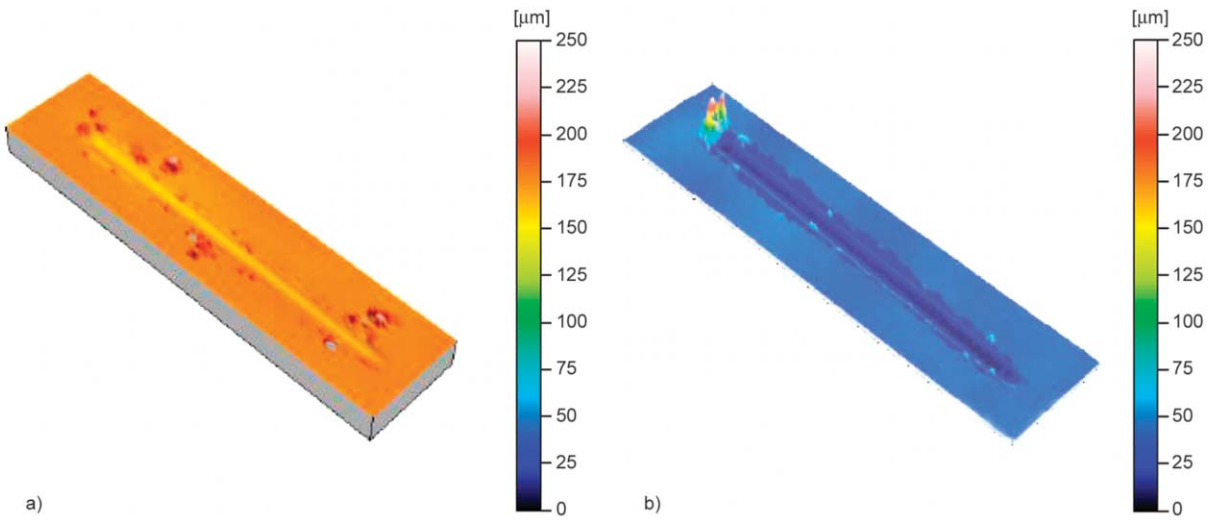

Figure 4. Surface topography of the abrasion scars on: a) EP; b) EP+9%[OMIM]BF_4.

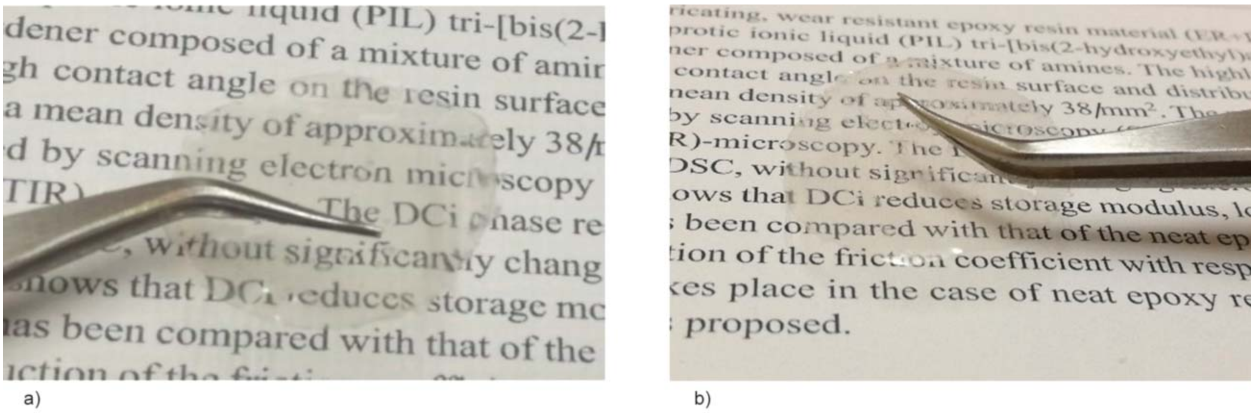

Figure 5. Photographs of the films showing a paragraph of the text of reference [29]: a) EP; b) EP+9%[OMIM]BF_4.

Table 4. Dynamic-mechanical properties of EP and EP+9%[OMIM]BF_4 films.

Film	Storage modulus (onset)		Loss modulus (max.)		tan δ (max.)	
	T [°C]	*E′* [MPa]	*T* [°C]	*E″* [MPa]	*T* [°C]	tan δ
EP	81.26±1.54	1056.00±94.00	83.48±2.43	277.76±6.95	97.08±2.96	1.00±0.05
EP+9%[OMIM]BF_4	74.08±0.42	392.61±40.19	74.94±0.16	112.73±10.68	87.89±0.36	0.97±0.02

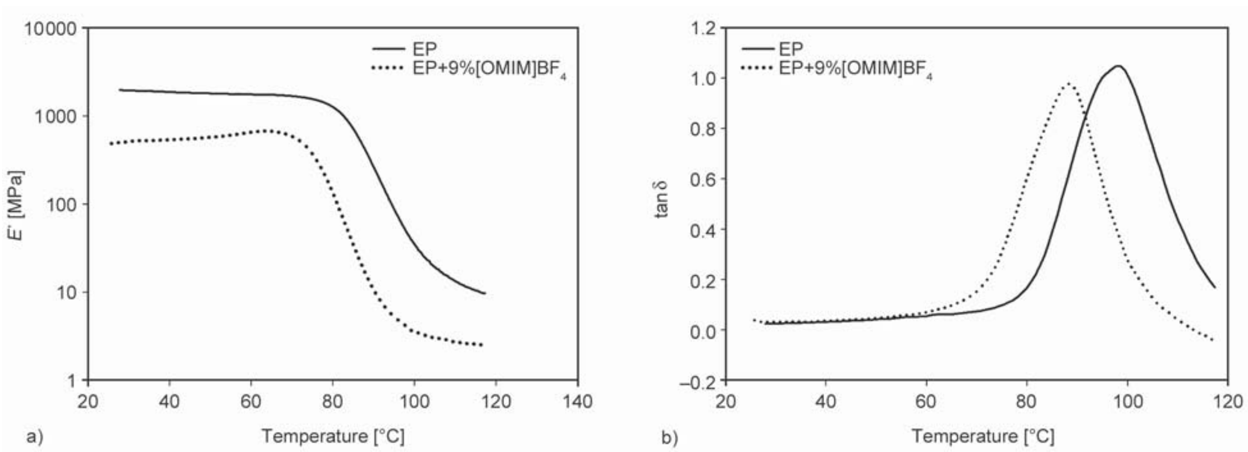

Figure 6. Dynamic-mechanical properties of films under tensile configuration: a) storage modulus; b) tan δ.

4. Conclusions

A spin coating method has been developed to obtain new epoxy resin coatings modified by the addition of ionic liquid. The ionic liquid reduces the thickness and surface roughness of the coating and presents a uniform distribution within the surface layer. The abrasion resistance of the resin coating is increased by the ionic liquid, which induces plastic deformation without material loss after 15 scratches, with lower penetration depth, lower residual depth and higher viscoelastic recovery.

Spin coating has been used to obtain the same materials studied as coatings in the form of films with similar visual transparency. Dynamic mechanical analysis of the films has shown that the ionic liquid reduces the glass transition temperature, thus enhancing chain mobility, while reducing the storage modulus. These results confirm the increased ductility of the epoxy resin. This ductility increase, the plasticizing effect and the lubricating ability of the ionic liquid could explain the different deformation modes under abrasion found for neat epoxy and ionic-liquid modified coatings.

The procedures described here could be used on other substrates for surface protection and tribological applications.

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