Journal of
Materials Chemistry C

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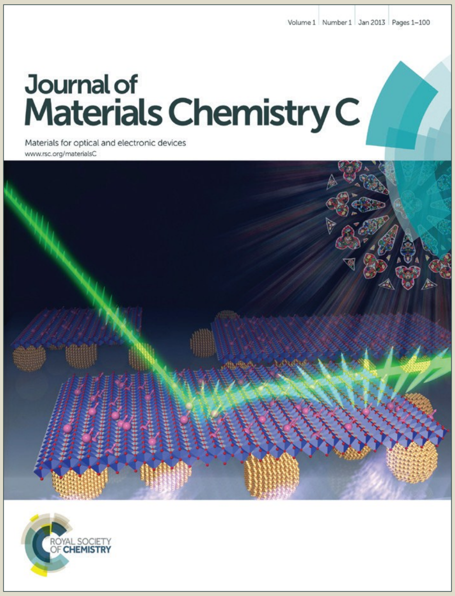

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COMMUNICATION

Transient mechanochromism in epoxy vitrimer composites containing aromatic disulfide crosslinks

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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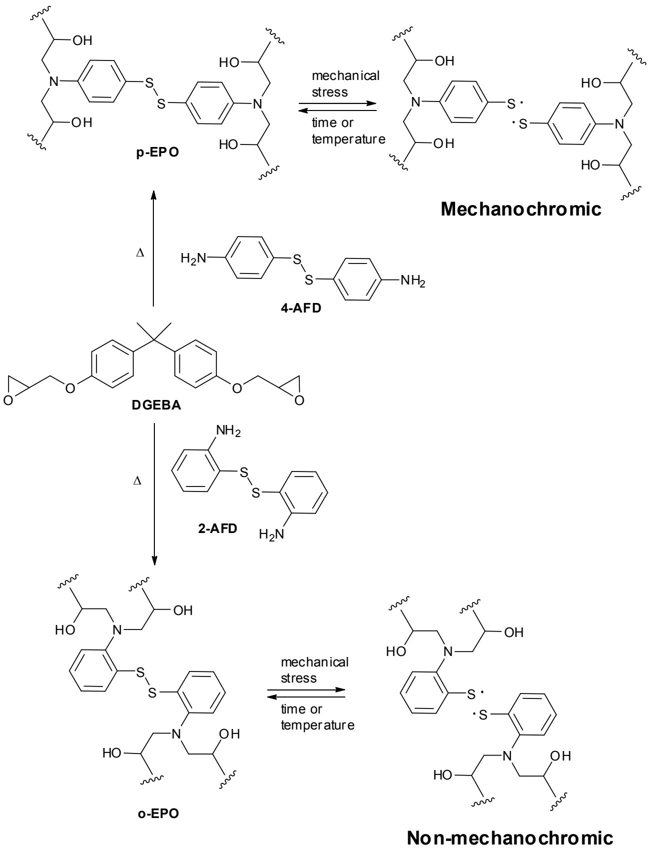
4-Aminophenyl disulfide (4-AFD) has been recently reported as a hardener for the design of reprocessable, repairable and recyclable epoxy networks. Now we show that such hardener is also responsible for a mechanochromic effect, due to an intermediate radical species formed upon damage, as confirmed by theoretical studies.

During the next few years, fiber-reinforced polymer composites (FRPCs) are foreseen to grow exponentially in sectors such as automotive, aerospace, construction, energy or sports. This is mainly due to their light weight and excellent mechanical and environmental performance. On top of that, recent developments in reversible polymer networks[1-4] which are based on dynamic covalent chemistries,[5] have boosted the flourishment of a new era of thermoset materials with properties that were inconceivable to date, such as processability, recyclability, self-welding and reparability. To date, very few examples of FRPCs based on reversible polymer networks have been described. Recent examples include polyimine-based carbon-fiber composites developed by Taynton *et al.*[6] and epoxy-based glass-fiber composites by Chabert *et al.*[7] In many cases, the dynamic functionality is introduced into the polymer network *via* the hardener, which can contain a reversible chemical bond. However, to the best of our knowledge a dynamic hardener has never been reported to create new additional functionalities into a polymer network or FRPC. Here we report how 4-AFD (Scheme 1), a dynamic hardener which is useful for the creation of dynamic epoxy networks or *vitrimers*, can endow an additional mechanochromic functionality to the resins and composites made thereof. The field of polymer mechanochemistry has grown very rapidly over the last decade,[8, 9] in part due to its importance in monitoring material failure.[10] Thus, the possibility of having a dynamic hardener which on top of giving vitrimer behavior also gives mechanochromic properties, could offer significant advantages in the composite field.



Scheme 1. Synthetic procedure and chemical structure of dynamic epoxy networks studied in this work, as well as the proposed radical species provoked by mechanical stress.

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† Electronic Supplementary Information (ESI) available: Experimental, characterisation and computational calculation details. See DOI: 10.1039/x0xx00000x

Very recently we developed a dynamic epoxy resin (**p-EPO**, Scheme 1), which was based on reversible aromatic disulfide crosslinks.[11] Due to such reversible disulfides, which were previously applied for the design of dynamic elastomeric materials,[12-14] the epoxy network presented a *vitrimer*-like behavior,[2] i.e., it showed stress relaxation at high temperatures. This permitted to successfully use the resin for the manufacturing of fiber-reinforced thermoset composites which were reprocessable, repairable and recyclable. Recycling of epoxy networks containing 4-AFD crosslinks has also been studied by others.[15-17] The exchange mechanism for these aromatic disulfide moieties was theoretically studied,[18] and it was found to undergo through a radical mechanism, rather than metathesis.

During the manipulation of the mentioned epoxy resin and composites made thereof, a transient mechanochromic behavior was observed. Thus, when the material was machined, the shavings were found to have a green coloration. The same occurred when hitting a composite part with a hammer. It was found that such green coloration disappeared spontaneously after several hours. These observations, and the opportunity that this phenomenon offers to detect damage in composites, encouraged us to further study it, in order to elucidate which chemical species could be involved and why the mechanochromic effect was time dependent.

For that aim, two different epoxy networks were studied (Scheme 1). The first one (**p-EPO**) was our previously reported material, based on diglycidyl ether of bisphenol A (DGEBA) and 4-AFD. Then, a second and very similar epoxy network (**o-EPO**) was synthesized starting from DGEBA and 2-aminophenyl disulfide (2-AFD). The preparation of such networks was performed by mixing DGEBA with the corresponding hardener followed by a curing cycle, as described previously.[11] Glass transition temperature (T_g), degradation temperature (T_d) and stress and strain at break obtained for each epoxy network are shown in Table 1. It is worth noticing that 2-AFD led to an epoxy network with lower T_g. The rest of the properties were comparable between the two vitrimer networks (see Figures S2-S6 in ESI). The corresponding glass-fiber-reinforced composites were prepared by manual lay-up, using a previously described procedure.[11]

Table 1. Thermal and mechanical properties of dynamic epoxy networks **p-EPO** and **o-EPO**.

	T_g (DSC)[ºC]	T_d [ºC]	Stress$^{a)}$ [MPa]	Strain$^{a)}$ [%]
p-EPO	130	300	88	7.1
o-EPO	105	310	84	6.2

$^{a)}$ Values at break, obtained by tension test.

When FRPCs made of **p-EPO** were hit with a hammer, a green[‡] coloration was immediately observed, showing a mechanochromic behavior of the material (Figure 1a). Interestingly, the color disappeared progressively after 24 hours at ambient temperature.[§] Just bending the composite did not lead to any color change; the mechanochromic effect was only observed when resin breaking occurred. In a similar manner, when neat **p-EPO** resin in the form of powder was grinded in a mortar, the same green coloration appeared. In this case, the color also disappeared after 24 hours.

It was postulated that the green coloration could be due to the formation of sulfenyl radicals, promoted by the mechanically assisted excision of the aromatic disulfide crosslinks. Such radicals, for being “frozen” in a high T_g polymer network, could survive several hours before pairing up to form new disulfide bridges, which could explain the progressive disappearance of the color after several hours. To proof that, another FRPC specimen made of **p-EPO** was hit with a hammer, and the resulting piece containing green spots was placed into an oven at 150 °C. At this temperature, the green coloration disappeared in less than 30 seconds. This could be explained as a result of a very high mobility of polymer chains at temperatures above the networks T_g, which would lead to a very fast pairing up of the radical species. In contrast, when a damaged specimen containing green spots was kept in the freezer at –20 °C, the green color was maintained for several days. Following the same logics, this could be attributed to lower chain mobility at these temperatures.

Interestingly, when pure 4-AFD was grinded in the mortar no mechanochromic effect was observed. In order to see if the presence of 4-AFD as a filler in a polymer would result in a mechanochromic material, blends of polyethylene and 4-AFD were prepared (5 and 10 wt%) in an internal mixer at 150 ºC during 15 minutes. Such blends did not show any coloration when hit with a hammer (see Figure S7 in ESI).

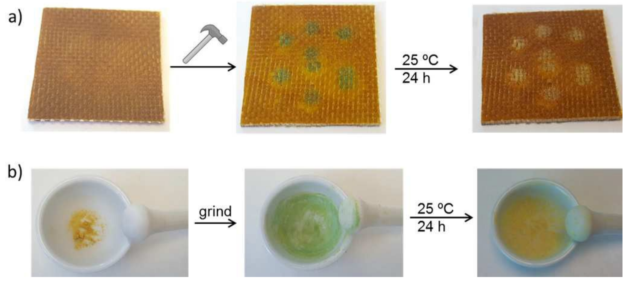

Figure 1. a) Photographic sequence showing the original glass-fiber composite made of **p-EPO** after being hit with a hammer, which resulted in the appearance of green spots, and, after 24 hours at room-temperature, the green color disappeared. b) Photographic sequence showing how cured **p-EPO** resin in the form of powder became green when grinding in a mortar. After 24 hours at room-temperature the green color disappeared.

On the other hand, when FRPCs made of **o-EPO** were submitted to mechanical damage, no coloration was observed (see Figure S1, ESI). In the same way, grinding **o-EPO** in a mortar did not lead to any color formation. Considering that 4-AFD and 2-AFD are isomers which only differ in the relative position of the disulfide and the amino substituents, these results are somehow surprising and led us to perform a theoretical study of the phenomenon.

We studied the spectroscopic properties of the mechanically generated sulfenyl radicals, corresponding to the *ortho* (**o-EPO**) and *para* derivatives (**p-EPO**), by means of computational chemistry. The chemical structures of the studied species are shown in Figure 2a (see ESI for computational details). In the ground state, the radical character was found to be mostly localized in the sulfur atom, for both cases. The values of the spin densities were 0.65 and 0.67 for the *ortho*- and *para*-substituted species, respectively (see Table 2). It is worth noticing that the spin density in the nitrogen atom of the amine group was found to be quite low: 0.11 (*ortho*) and 0.09 (*para*). In the excited state, however, these values change remarkably and the spin density (the radical character) on the S atom decreases to 0.25 and 0.37, and increases for the N atom to 0.33 and 0.23, respectively. This suggests that the charge distribution is reorganized during the excitation. Indeed, inspecting the Mulliken charges (see Table S1, ESI), it was possible to observe how the anionic nature of sulfur increases (corresponding with an increase of the Mulliken charge of this atom), while that of the nitrogen decreases after excitation. This feature appears more evident observing the orbitals involved in the transition, as depicted in Figure 2b.

Table 2. Spin densities (ρ) on sulfur and nitrogen atoms of the $\cdot$S-Ph-N(C_2H_4OH)$_2$ *ortho* and *para* radical species in the ground (G. S.) and excited states (E. S.).

	ρ(S)		**ρ(N)**	
	G. S.	**E. S.**	**G. S.**	**E. S.**
ortho	0.65	0.25	0.11	0.33
para	0.67	0.37	0.09	0.23

The transition corresponds to a $\pi\rightarrow\pi^*$ transition and both orbitals are delocalized along the aromatic ring and the S and N atoms, but the π orbital shows a greater nitrogen character, while the π^* orbital shows a greater sulfur character. Schematically, in the ground state the π orbital is doubly occupied (the π^* is singly occupied) and the electron involved in the transition is delocalized in the ring, with a high contribution of one of the *p* orbitals of nitrogen. In the excited state, this electron is promoted to the π^* orbital, which now is doubly occupied. Therefore, there is an electron transfer from the donor amino group to the sulfur atom, in agreement with the values of Mulliken charges and spin densities.

The transition wavelengths and their corresponding oscillator strengths are also shown in Figure 2b. It can be observed that the *para*-substituted species absorbs in the visible region of the spectrum (λ = 490.8 nm) while the *ortho*-substituted absorbs near the infrared region (λ = 719.7 nm). Besides, the oscillator strength for the *para* compound is about one order of magnitude greater than that for the *ortho* compound. It is worth noticing that this is a crucial issue, since the oscillator strength is a measure of the probability of the transition, which is related to the intensity of the transition. The larger the oscillator strength is, the larger the intensity. In order to explain this difference in the value of the oscillator strength, we have to recall that this quantity mainly depends on two main factors: firstly, the overlap between the initial and final state wavefunctions and, secondly, the variation of the dipole moment in the transition. In both species the overlap is large, as can be deduced from the orbital shapes depicted in Figure 2b. However, the change in the dipole moment is very different; in the *ortho* species, the amine group and the sulfur atom are close and, thus, the charge transfer that takes place during the transition does not imply a large change in the dipole moment, since both groups are adjacent. Nevertheless, in the *para* species, this variation is more important, as the groups involved in the excitation are farther apart. As a consequence, the oscillator strength, and thus the intensity of the transition, is considerably higher. This would explain the fact that only the *para*-substituted network (**p-EPO**) presents mechanochromism; the intensity of the transition in the *ortho*-substituted network (**o-EPO**) is very weak (and also very redshifted), not being observable to the naked eye.

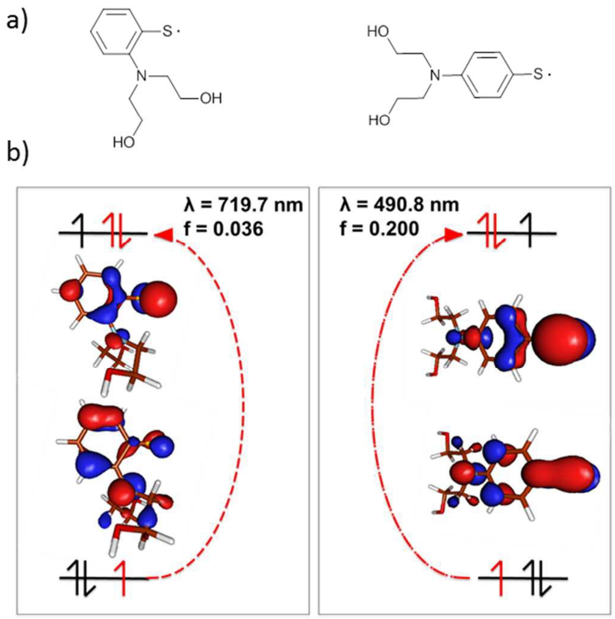

Figure 2. a) Molecular structures of the *ortho* (left) and *para* (right) radical species used in the quantum chemical simulations. b) Graphical representation of the molecular orbitals involved in the electronic transition responsible of the mechanochromic behavior of the epoxy network, along with the corresponding absorbed photon wavelength and the transition oscillator strength. In black and red, orbital occupations for the ground and excited states, respectively.

Conclusions

In this communication we have shown that an epoxy vitrimer containing 4-aminophenyl disulfide presents mechanochromic properties. Such phenomenon is attributed to the formation of sulfenyl radicals, which disappear after 24 hours at ambient temperatures or in a few seconds when heated above T_g, probably due to recombination of such radical species. Interestingly, no mechanochromic effect is observed for a similar epoxy vitrimer system made of 2-aminophenyl disulfide. Theoretical studies show that the different behavior between these two networks could be due a higher change in the dipole moment when sulfur and nitrogen atoms are in *para* positions. This constitutes, to the best of our knowledge, the first example in which a hardener endows a dual smart functionality: vitrimer behavior, as shown in previous work,[11] and mechanochromism. It is foreseen that such mechanochromic effect will have useful practical applications in terms of damage detection, a topic of great importance when dealing with structural materials such as fiber-reinforced polymer composites.

Acknowledgements

This work was partially funded by the Basque Government under the ELKARTEK ACTIMAT 2016 project. Technical and human support provided by IZO-SGI, SGIker (UPV/EHU, MICINN, GV/EJ, ERDF and ESF) is gratefully acknowledged for assistance and generous allocation of computational resources.

Notes and references

‡ The actual color of the mechanochromic species could be blue, the green color coming from the combination of blue and amber.

§ The light colored spots observed after 24 hours recovery are due to irreversible damage, such as delamination and fiber breaking.

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GRAPHICAL ABSTRACT