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UV-cured epoxy coating reinforced with sepiolite as inorganic filler

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Abstract Epoxy coatings containing sepiolite as inorganic reinforcement was obtained by UV-induced polymerization. An increase in epoxy group conversion was achieved in the presence of the inorganic filler; this was due to the strong interactions between the high density of silanol groups present on the sepiolite surface and the carbocationic growing chain. Improved properties of the cured coatings were achieved such as higher T_g, higher modulus, higher surface hardness. Interface-dominated materials are obtained since the high interfacial area plays a major role in the final composite properties.

Introduction

Fillers play important roles in modifying the desirable properties of polymers and reducing the cost of their composites. In coating applications fillers can improve toughness, mechanical properties, scratch resistance as well as reducing gas permeability and enhancing flame retardancy. Polymer properties can indeed be tailored by changing the volume fraction, shape, and size of the filler particles [1–3]. A further improvement of the mechanical properties can be achieved by using filler materials with a larger aspect ratio such as short glass fibers [4–6].

In recent years the use of nanofillers have attracted significant interest, both in academic and industrial fields, because they often exhibit dramatic improvement in thermal and mechanical properties of polymer matrix already at a very low filler loading [7]. In fact, the exfoliation of nanofillers having very high surface area frequently improves, even at low loadings (<5 wt%), the physical and mechanical properties of polymers [8–10]. Higher modulus, optical transparency, increased strength, enhanced barrier properties, higher thermal stability are typical features of polymer nanocomposites [11–13], which can be very important in order to enhance the polymer coating performance.

Most of the literature regarding nanocomposites is devoted to lamellar-layered silicates [14–16]; the most used is montmorillonite (MMT). Owing to the nanometer-sized particles obtained by dispersion, these nanocomposites exhibit markedly improved mechanical, thermal, optical, and physico-chemical properties when compared with the pure polymer or conventional (microscale) composites as firstly demonstrated by Kojima et al. [17] for nylon-clay nanocomposites. Improvements can include, for example, increased moduli, strength and heat resistance, decreased gas permeability, and flammability.

Recently, attention has been devoted to the use of sepiolite as inorganic fillers for polymeric matrix [18–20]. Sepiolite is a layered hydrated magnesium silicate characterized by a needle-like morphology, very high surface area (BET 374 m^2/g) [21] and a very high density of silanol groups (2.2 groups per 100 $Å^2$) [22] on surface. Sepiolite has a structure similar to the layered structure of MMT, formed by two tetrahedral silica sheets enclosing a central sheet of octahedral magnesia except that the layers lack continuous octahedral sheets. The discontinuous nature of the octahedral sheet allows for the formation of rectangular-aligned channels; these nanostructured tunnels

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account in large part for the high specific surface area. In addition, it has good mechanical strength and thermal stability. These properties make sepiolite ideal for reinforcement of polymer materials and it has been either used for the reinforcement of elastomers [23], thermoplastic, and thermoset polymers [24–26].

In this study sepiolite has been dispersed as inorganic fillers in an UV-curable epoxy resin. The UV curing technique is getting an increasing importance in the field of coatings due to its peculiar characteristics [27]: it induces the polymer formation with a fast transformation of the liquid monomer into a solid film with tailored physical-chemical and mechanical properties. It can be considered an environmental-friendly technique, due to the solvent-free process, and it is usually carried out at room temperature, therefore it guarantees the saving of energy. Furthermore, the cationic photopolymerization process of epoxy systems presents some advantages compared to the radical one [28]: lack of inhibition by oxygen, low shrinkage, good adhesion, and mechanical properties of cured films. The cationic UV-induced ring opening polymerization process has been studied and the properties of cured films evaluated and correlated with their structure.

Experimental

Materials

The 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate epoxy resin (CE) was purchased by Aldrich and used as epoxy-based system. A mixture of triarylsulfonium hexafluorophosphate salts (PI, Omnicat 432) was given by IGM resin, Netherlands. The structures of the reactive components are reported in Table 1. The inorganic filler was sepiolite (provided by Tolsa SA Spain), a layered-hydrated magnesium silicate characterized by a needle-like morphology, very high surface area (BET 374 m^2/g) and a very high density of silanol groups (2.2 groups per 100 $Å^2$) on surface.

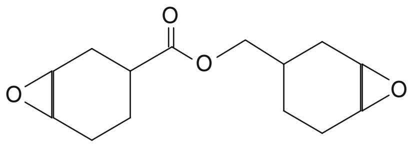
Samples preparation

The formulations were prepared by adding the inorganic filler to the epoxy resin in the range between 3 and 7 wt%. To all the formulations, 2 wt% of cationic photoinitiator was added. The obtained solutions were sonicated for 15 min and when homogeneous dispersion were achieved, they were coated on glass substrate and UV-irradiated (low-pressure Hg lamp, Italquartz, Milano, Italy) for 2 min at a light intensity of 30 mW/cm^2. Transparent-cured films on the average thickness of 100 μm were obtained.

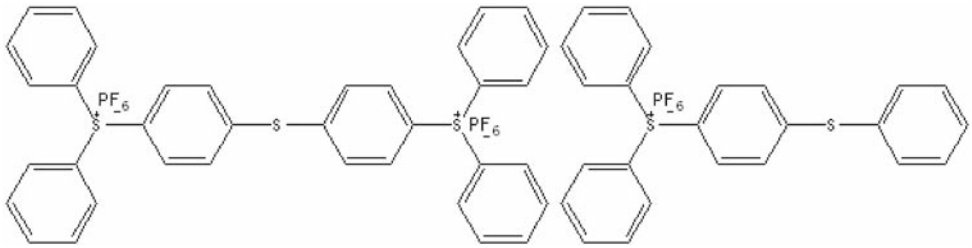
Characterization techniques

The kinetics of the photopolymerization was determined by real-time FT-IR spectroscopy, employing a Thermo-Nicolet 5700. The formulations were coated onto a silicon wafer. The sample was exposed simultaneously to the UV beam, which induces the polymerization, and to the IR beam, which analyzes in situ the extent of the reaction. Because the IR absorbance is proportional to the monomer concentration, conversion versus irradiation time profiles can be obtained. Epoxy group conversion was followed by monitoring the decrease in the absorbance, due to epoxy groups, in the region 760–780 cm^{-1}. A medium pressure

Table 1 Chemical structures of the chemical components of the photo-curable formulation



CE



PI

mercury lamp (Hamamatsu Omnicure) equipped with an optical guide was used to induce the photopolymerization (light intensity on the surface of the sample is about 30 mW/cm^2). All the polymerization reactions were performed at room temperature at constant humidity (RH = 25–30%); the samples were stored for at least 24 h before properties evaluation.

Gel content was determined on the cured films by measuring the weight loss after 24 h extraction with chloroform at room temperature, according to the standard test method ASTM D2765-84.

Dynamic mechanical thermal analysis (DMTA) was performed with a Rheometric Scientific MKIII (UK) instrument, at a frequency of 1 Hz in the tensile configuration.

Thermogravimetrical analysis (TGA) was performed using a LECO TGA-601 instrument in the range between 30 and 700 °C, with a heating temperature of 10 °C/min in air.

The pendulum hardness (Persoz, ASTM D4366) was measured from the damping of the oscillation of the pendulum. Pendulum hardness values are expressed in seconds and are related directly to the softness of the samples. The shorter the damping time, the lower is the hardness.

Samples were prepared for TEM observation by Argon ion polishing system GATAN PIPS, working at 3.5 keV at an angle of 7°. They were examined in a 300-keV transmission electron microscope (TEM) Philips CM30. TEM micrographs were processed with a slow scan CCD camera and analyzed with the Digital Micrograph program. The TEM observations were always performed using a very low electron flux in order to avoid any structural modification of the sample induced by the electron beam.

Results and discussion

Photopolymerization process investigation

The photopolymerization kinetics was monitored by real-time FT-IR. The conversion curves as a function of irradiation time for the pristine epoxy resin and in the presence of increasing sepiolite content were investigated. While the plateau value gives the final epoxy group conversion, the slope of the curve gives an indication of the polymerization rate. In Fig. 1, the conversion curves for the pure CE resins is reported and compared with the conversion curve for the formulations containing sepiolite in the range between 3 and 7 wt%.

The reactivity of pure epoxy resin is relatively high at the beginning, showing afterward a conversion slow down reaching a final conversion of around 55%. The slow down of the photopolymerization rate is due to a vitrification effect caused by the formation of a polymer network characterized by a high T_g value. The quick viscosity increase induces a decrease in the reactive species mobility with a reduction on photopolymerization rate. A large number of unreacted epoxy groups remain trapped within the glassy polymer network.

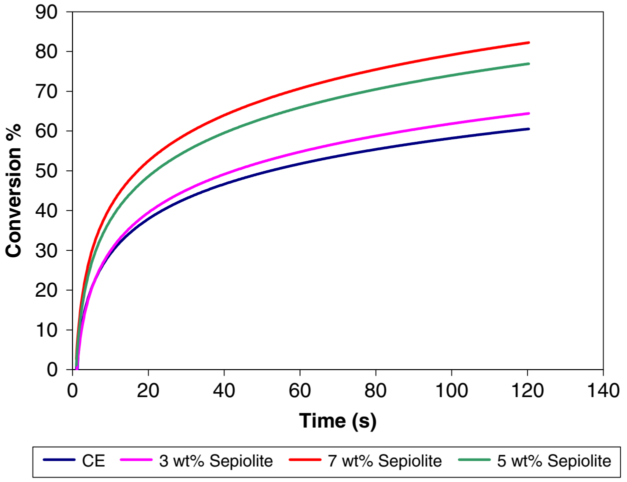


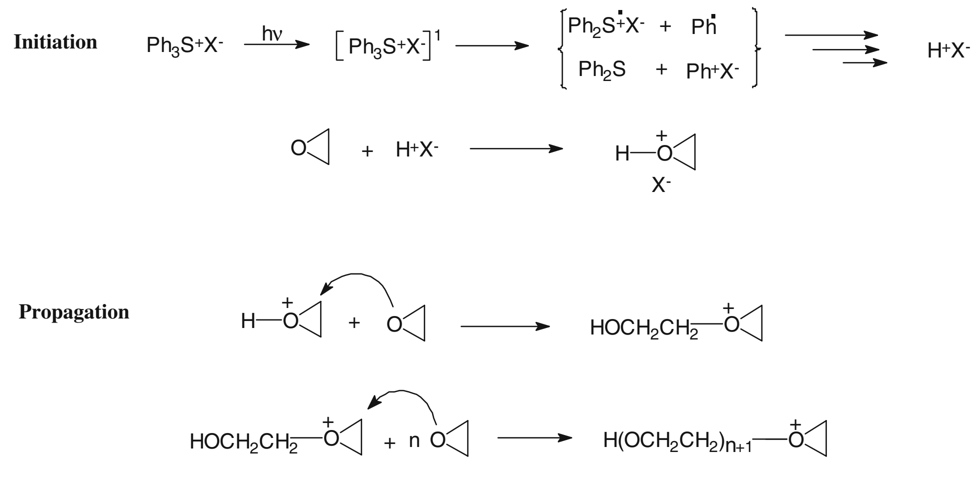
Fig. 1 Real-time FTIR kinetics conversion curves for the UV-curing of CE containing different concentrations of sepiolite as inorganic filler

Quite surprisingly it was observed that by increasing the sepiolite content into the photo-curable formulation, an increase in photopolymerization rate and in epoxy group conversion was reached. Since the cationic UV-curing process is sensitive to the viscosity showing a decrease in cationic chain propagation by increasing the viscosity of the medium, it would have been expected a decrease in epoxy ring opening polymerization by adding the sepiolite to the epoxy resin, because of the resultant viscosity increase.

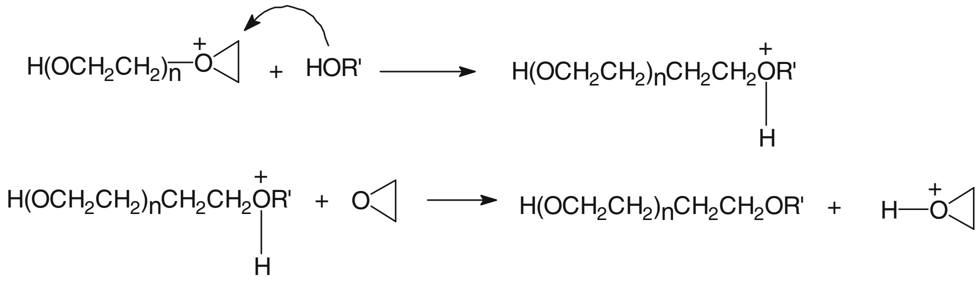
In order to explain the results showed by real-time FT-IR analysis, it has to be taken into account the well-known effect of the hydroxyl-containing additives in cationic UV curing.

The initiation of cationic UV-curing polymerization is a multistep process involving first, the photoexcitation of triarylsulfonium salts, and then the decay of the resulting excited singlet state with the formation of a Bronsted acid, which is the actual initiator of cationic polymerization [29]. Initiation of polymerization takes place by protonation of the monomer, followed by the addition of further monomer molecules, thus resulting in cationic chain growth reaction (see Scheme 1).

In addition to the usual mechanism, shown in Scheme 1 for the ring opening polymerization of epoxides, Penczek and Kubisa [30–32] described a new mechanism for the polymerization of these monomers called *activated monomer mechanism* that takes place when the cationic polymerization of epoxides is carried out in the presence of hydroxyl containing additives. This mechanism is reported in Scheme 2.



Scheme 1 UV-initiated cationic ring opening polymerization process



Scheme 2 Chain transfer process in cationic ring-opening polymerization

The effect on UV-curing kinetics and on chemical structures of polymer networks, due to the chain transfer reaction in the presence of hydroxyl containing additives, has been deeply reported and discussed in literature [33–36]. During the polymerization, the growing ionic chain end undergoes a nucleophilic attack by the hydroxyl group to give a protonated ether. Deprotonation of this latter species by the epoxy monomers results in the termination of the growing chain together with the proton transfer to a new monomer, which can start a new growing chain.

Since the inorganic filler sepiolite is characterized by a high density of surface silanol groups, these can interact with the carbocation growing chain, and therefore the filler will act as multifunctional crosslinker: chemical linkages can be formed between the filler and the polymer networks. Similar results were previously observed by adding silica nanoparticles to an UV-curable epoxy resin [37].

This strong interaction between the organic matrix and the inorganic filler, supposed on the basis of FT-IR investigations, should give rise to an important reinforcement effect to the coating.

The cured films showed a very high gel content value (always above 97%, see Table 2), indicating the formation of a highly crosslinked network and the absence of any extractable oligomers.

Table 2 Properties of UV-cured films

Samples	Epoxy group conversion (%)[a]	Gel content (%)[b]	T_g (°C)[c]	Persoz hardness[d]
CE	55	98	108	154
CE + 3 wt% sepiolite	65	97	115	168
CE + 5 wt% sepiolite	77	96	118	218
CE + 7 wt% sepiolite	81	97	125	197

Epoxy formulations containing 2 wt% of triarylsulfonium hexafluorophosphate as cationic photoinitiator and sepiolite as inorganic filler

[a] Determined by real-time FT-IR spectroscopy

[b] Determined gravimetrically

[c] Determined by DMTA measurements, as the maximum of tan δ curve

[d] Measured with the Persoz pendulum

Dynamic-mechanical and surface hardness characterization

Dynamic mechanical characterization of the UV-cured films was performed by means of DMTA analysis, which allows the evaluation for the elastic (E': storage modulus) and viscous (E': loss modulus) components of the materials in a large temperature interval. In Fig. 2a, b are reported the DMTA thermograms (modulus and tan δ curves) for the cured systems containing an increasing amount of sepiolite. In the T_g region, a strong decrease in E' is evident (Fig. 2a), while the tan δ curve (tan $\delta = E''/E'$: ratio loss modulus/storage modulus) shows a maximum which is assumed as the T_g of the cured films [38] (Fig. 2b).

The data are listed in Table 2 and show an increase in the glass-transition temperature by increasing the amount of the sepiolite in the photo-curable formulation; this is evident by the shift of the maximum of tan δ peak toward higher temperature as shown in Fig. 2b. At the same time an increase in E' modulus is evident in the rubbery region for cured films containing sepiolite.

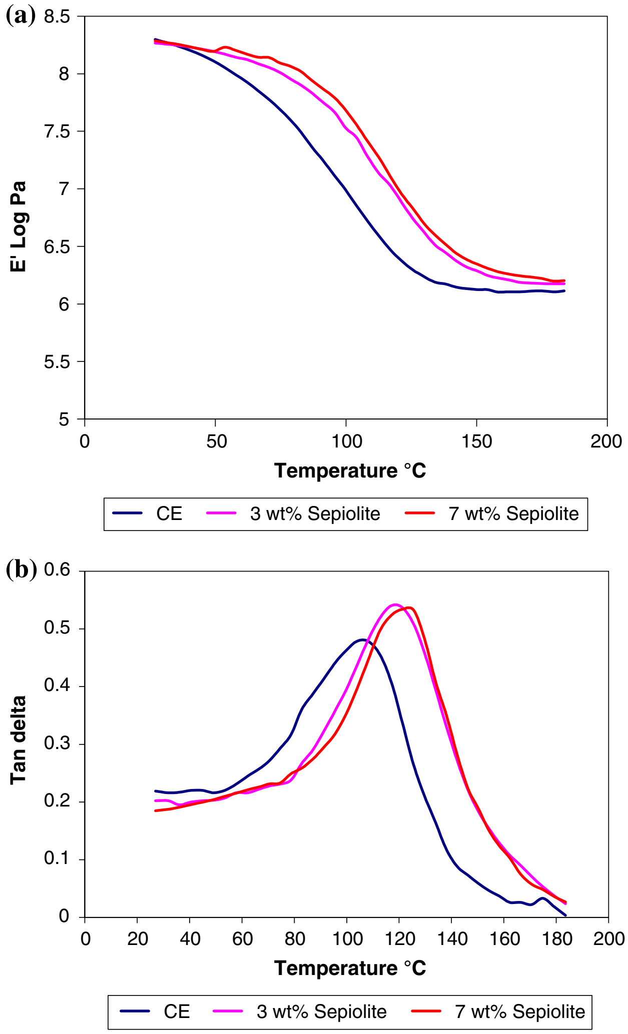


Fig. 2 **a** Storage modulus for the cured samples containing increasing sepiolite content. **b** tan δ values for the cured samples containing increasing sepiolite content

The increase in both T_g values and in modulus can be attributed to strong and extensive interfacial interactions between the organic and inorganic phases. In fact the inorganic sepiolite particles that strongly interact with the polymeric network can restrict the segmental motion of the polymeric chains, and the hindering mobility is the cause of the T_g increase.

Because of the large interactions between the filler and the polymeric chain, a high interfacial region volume fraction is achieved. Such an effect promotes stress transfer from the matrix to the inorganic filler leading to increased strength and stiffness of the composite, which is evidenced by the modulus increase in the rubbery region.

For the same reason, the presence of the sepiolite filler induced also a modification of the surface properties by an increase in Persoz hardness (see Table 2). This hardness increase can be due to the increase in modulus because of the strong interaction between the filler and the polymeric matrix. The hardness increase could induce an increase in scratch resistance of the cured coatings. Scratch test is under progress.

Thermal stability

The thermal stability of the filled systems was determined using a thermogravimetric analyzer and compared with the unfilled epoxy-cured network. The TGA curves of pristine epoxy resin and in the presence of increasing amount of sepiolite are shown in Fig. 3. The TGA values for the 10 and 50% weight loss and for the non-volatile part or char content are reported in Table 3.

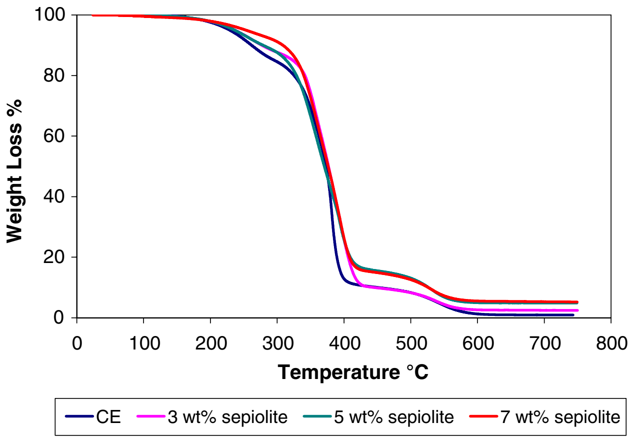


Fig. 3 TGA thermograms for the cured samples containing increasing content of sepiolite

Table 3 Thermal properties of cured films

Sample	10% Weight loss[a]	50% Weight loss[b]	Char content (%)[c]
CE	250	370	0
CE + 3 wt% sepiolite	270	375	2.8
CE + 5 wt% sepiolite	275	380	5.2
CE + 7 wt% sepiolite	310	380	5.7

[a] Temperature at which a 10 wt% loss is reached

[b] Temperature at which a 50 wt% loss is reached

[c] Char content at 700 °C

These data indicate that with increasing amount of sepiolite in the photo-curable formulation, a slight increase in thermal stability of the pure epoxy network is achieved. In all cases the thermal degradation occurs in one step, which is mainly due to the degradation of the crosslinks together with the formation of volatile by-products. The composite materials also show a higher char content as sepiolite content increased.

Morphological analysis

TEM analyses were performed on CE samples containing 7 wt% of sepiolite, in order to investigate the morphology of the filler dispersed in the photo-cured network. The bright field TEM micrograph is shown in Fig. 4. It is possible to observe that the filler morphology looks like needles that are well dispersed within the polymeric network; almost all the nanoparticles are separated from each other even if all forming agglomerations. This picture shows that the needle-shape filler is not strongly aggregated on its own, but the sonication process was able to disaggregate the filler into the polymer network precursor; the dispersion was kept during the fast UV polymerization, which assured to freeze the dispersion achieved into the liquid resin avoiding re-agglomeration. The final result on properties' improvements is due to the strong and intense interactions between the inorganic filler and the polymeric matrix; it is possible to speak of "interface dominated" materials [39] since such the high interfacial area plays a major role in the composite final properties.

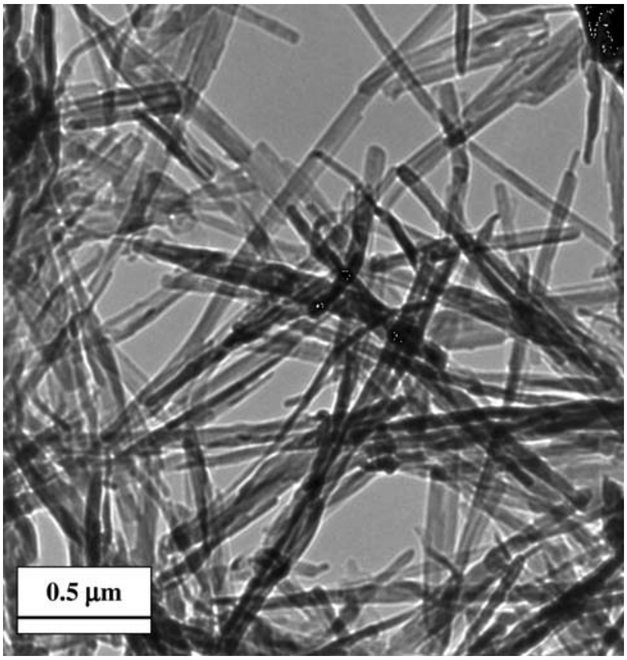


Fig. 4 Bright field TEM micrograph for epoxy UV-cured sample containing 7 wt% of sepiolite

Conclusions

Epoxy coating reinforced with sepiolite as inorganic filler was obtained by UV-induced polymerization. The photocuring process was investigated by means of real-time FT-IR analysis and it was shown that an increase in photopolymerization rate and epoxy group conversion was achieved by increasing sepiolite content. This was attributed to the high density of silanol groups on the sepiolite surface that can interact with the carbocationic growing chain through a very well-known *activated monomer mechanism* which occur in cationic ring opening polymerization in the presence of hydroxyl groups. DMTA analysis put in evidence an increase in T_g values and on modulus of the cured coatings obtained in the presence of sepiolite. A strong and extensive interfacial interactions between the organic and inorganic phases can be expected because of the chemical linkages achieved because of the activated monomer mechanism. This good interaction is evidenced by TEM analysis, which showed the inorganic filler well dispersed within the polymeric network. Even if the sepiolite formed strong agglomerations almost each needle is separated from each other, assuring a strong interaction between the filler and the polymeric matrix.

In conclusion, the results reported in this investigation suggest a strategy to achieve advanced photo-cured epoxy coatings with higher T_g and modulus, increased surface hardness, with an expected increase in scratch resistance, by adding an easily available and low-cost inorganic filler as sepiolite. The properties achieved by this new materials make them attractive for a wide variety of applications in the coating industry.

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