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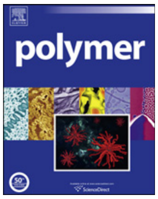

Scratch resistant tough nanocomposite epoxy coatings based on hyperbranched polyesters

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ABSTRACT

Advanced multifunctional coatings were prepared by UV curing of epoxy based formulations containing hyperbranched polymers (HBP) and an epoxy functionalized alkoxysilane additive. The addition of HBP to the UV curable epoxy resin induced an important flexibilization of the glassy epoxy network with an increase in toughness of the cured polymeric coatings. Adding the functionalized alkoxysilane into the UV curable formulations, as inorganic precursor of silica phase, an improvement on surface hardness was obtained without strongly affecting the flexibilization and the toughness achieved by the addition of the HBP additive. The increase on surface hardness was accompanied with an increase in scratch resistance and modulus. Advanced scratch resistant and tough nanocomposite epoxy coatings were obtained by properly selecting the components of the formulation.

1. Introduction

Today, multifunctionality in a coating formulation is essential since coatings do not only provide just a certain amount of protection towards the environment or optical appearance to a surface, but they should also provide additional functions like low abrasion and low wear, high chemical stability, high or low adhesive properties, and many others.

One approach towards these multifunctional coatings is the introduction of a specific nanostructure, either organic or inorganic in nature. The first comprises latex particles [1], core shell particles [2], or globular macromolecules of star or dendritic type [3]. This approach is especially promising in increasing the toughness of a thermoset coatings.

Hyperbranched polymers (HBP) belong to a group of macromolecules called dendritic polymers, which have peculiar and often unique properties [4]. They possess a highly branched backbone, which gives access to a large number of reactive groups; their structure gives them excellent flow and processing properties, and they are characterized by lower viscosity than those of linear polymers of comparable molecular weight. Such properties make HBP extremely interesting for coatings [5–8] and UV-curing applications [9–12], and for this they have attracted a great deal of attention for application e.g. for powder coatings [13], high solid coatings [14], flame retardant coatings [15] and barrier coatings for flexible packaging [16]. In general, advantageous results of the use of these HBP in the reactive formulations are a tunable viscosity, a high reactivity in combination with low volatility and often improved toughness, without affecting either the viscosity of the uncured coatings or the thermomechanical properties of the cured material. In addition, there is an opportunity for tunable multifunctionality in the hyperbranched component, e.g. combination of reactive epoxy groups and long alkyl group in one macromolecule which can enhance on the one hand the curing rate and introduces additionally low-energy surface properties.

Star-shaped and hyperbranched polymers have been successfully studied for coating applications [17]. UV curable systems were especially promising where it was possible to use phenolic end groups of hyperbranched polyesters as transfer agents, e.g. in the cationic photocuring process of epoxies. The curing rate, conversion, as well as modulus and thermal stability, and especially

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impact resistance can be improved simply by adding unmodified hyperbranched polyester to the coating formulation.

On the other hand, the incorporation of inorganic nanosized materials provides access to coating systems with higher hardness and improved scratch resistance but often leads to a much reduced toughness and thus, limited long term stability.

Hybrid organic-inorganic nanocomposites have drawn considerable attention, in recent years, because they combine both the advantages of an organic polymer (flexibility, lightweight, good impact resistance and good processability) and inorganic materials (high mechanical strength, good chemical resistance, thermal stability and optical properties) [18].

A combination of both features – addition of HBP for toughening improvement and formation of inorganic domains generated *in situ* for enhanced surface scratch resistance - seems to be a very promising approach towards new, multifunctional technical coatings. However, the final performance of the coating will be governed by the complex interplay of the different components in a coating formulation and finally, by the degree of dispersion of the inorganic nano-objects in the matrix and the specific interface interactions.

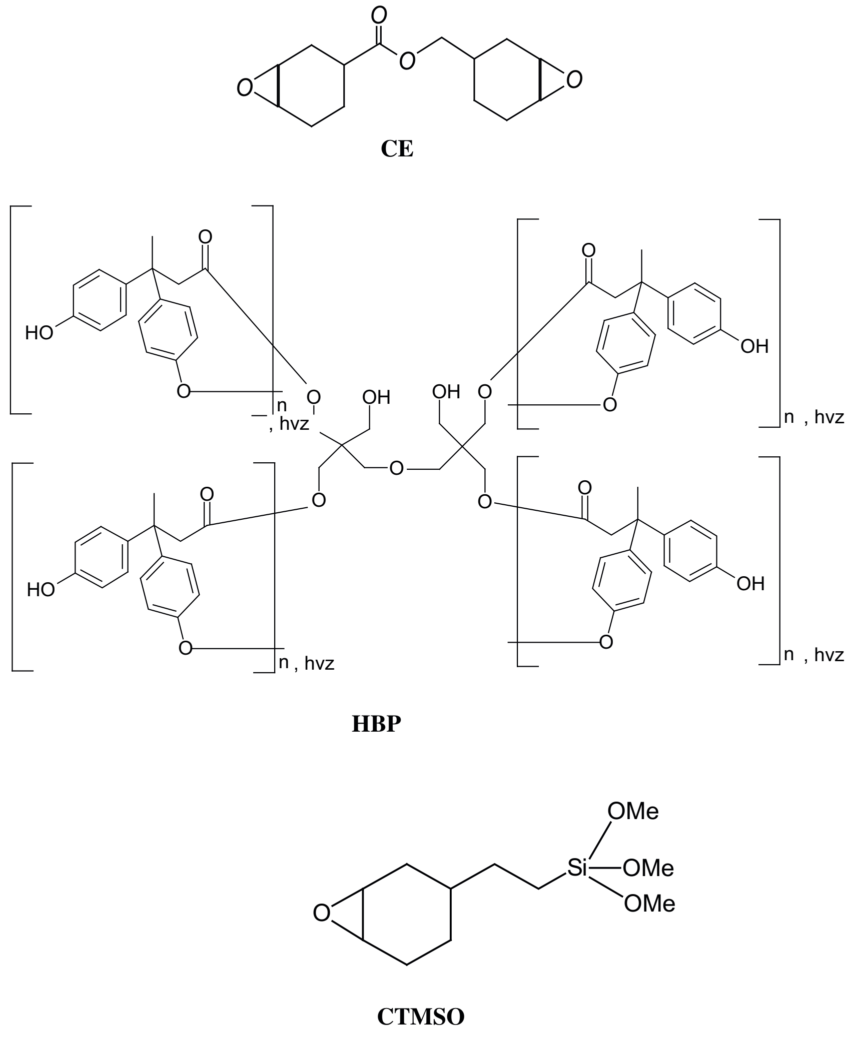
Many nanocomposites based on conventional linear polymers have been prepared and characterized so far, but only a few and only very recent studies have been reported about the use of HBP in combination with inorganic nano-objects [19–21]. The presence of a large number of functional end groups and the peculiar globular shape of the HBPs seem to be advantageous in the preparation of nanocomposites, as they can allow better interaction of the organic phase with the inorganic particles, and thus one can expect this field to be exploited further.

The aim of this paper was the combination of the toughening effect of phenolic HBP together with the effect of silica generated *in situ* via a sol–gel process by using an epoxy functionalized alkoxysilane as inorganic precursor. The cured films were characterized in term of their dynamic-mechanical properties, toughness and surface hardness: the obtained properties were discussed in relationship to the achieved morphologies.

2. Experimental

2.1. Materials

The bis-cycloaliphatic diepoxy resin 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexyl carboxylate, (CE, from Aldrich) was used as base resin. The epoxy functionalized alkoxysilane [2-(3,4-epoxycyclohexyl)ethyl]trimethoxysilane (CTMSO, from Aldrich) was used as inorganic precursor of the silica filler. The HBP ($M_n = 4000$ g/mol, $M_w = 5500$ g/mol, PD = 1.38 by GPC; $T_g = 55$ °C) was synthesized on purpose as previously reported [9]. Triphenylsulfonium hexafluoroantimonate (Cyracure UVI6974, as 50%



Scheme 1. Chemical structures of the materials employed.

Table 1
relative weight composition of the photocurable formulations.

Sample identification	CE	HBP	CTMSO
CE–HBP 5	0.95	0.05	–
CE–HBP 10	0.90	0.10	–
CE–HBP 20	0.80	0.20	–
CEH–Si 10	0.70	0.18	0.10
CEH–Si 30	0.56	0.14	0.30
CEH–Si 50	0.40	0.10	0.50

solution in propylene carbonate, PI), from Union Carbide ($Ph_3S^+SbF_6^-$) was added as an actual content of 2 wt% with respect to the epoxy content. The chemical structures of the materials employed are reported in Scheme 1.

2.2. Sample preparation

In order to evaluate both the effect of the HBP content on the toughening properties of the cured epoxy network, and the effect of the inorganic precursor content on the surface hardness of the coating, different formulations were prepared and characterized. The HBP was added to the epoxy resin in the range between 5 and 20 wt%. Afterwards, keeping CE/HBP weight ratio constant at 80:20, the epoxy functionalized alkoxysilane was added in the range between 10 and 50 wt% with respect to the CE/HBP formulation. The relative compositions of the investigated photocurable formulations are reported in Table 1. Triphenylsulfonium hexafluoroantimonate was added to all the formulations at 2 wt% with respect to the CE content.

The formulations were coated on glass slides by means of a wirewound applicator and cured with a medium vapour pressure mercury dynamic UV lamp (Fusion, H bulb) with an intensity on the surface of the sample of 350 mW/cm^2 (measured with EIT instrument) and a belt speed of 6 m/min.

When hybrid coatings were prepared, the UV curing was followed by thermal treatment at 80 °C for 4 h in high humid atmosphere (95–98% relative humidity controlled by a saturated solution of aqueous $NH_4H_2PO_4$). The UV induced process leads to the formation of the organic polymer network, by cationic ring-opening polymerization of epoxy group initiated by a photogenerated Brönsted acid. In these acidic conditions, under high humidity, alkoxysilane groups undergo hydrolysis and condensation reaction generating siloxane crosslinks (sol–gel process).

The thickness of the cured films was measured with a Minitest 3000 Instrument (Elektrophysik, Germany); the average value was found to be in the range of 100 ± 10 μm for all the series of samples.

2.3. Sample characterizations

UV cured samples were prepared of 0.5 mm thickness and 2 × 1 cm for Dynamic-mechanical thermal analyses (DMTA); the analyses were performed on a MK III Rheometrics Scientific Instrument at 1 Hz frequency in the tensile configuration. The storage modulus, E', and the loss factor, tan δ, were measured from 0 °C up to the temperature at which the rubbery state was attained. The T_g value was assumed as the maximum of the loss factor curve (tan δ).

The 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 ASTM D2765-84 technical standard.

Impact resistance measurements were performed with an ATS FAAR Charpy pendulum, according to the ASTM D6110-08 technical standard; specimens were prepared by using a silicone mould obtaining specimen of about 2 mm thick; a number of 5 specimens were evaluated for each samples.

Samples were prepared for TEM observation by Ar^+ 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.

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 surface of the sample. The shorter the damping time, the lower is the hardness.

Scratch tests were carried out on a CSM Micro-Combi Tester by using a Rockwell C diamond scratch indenter (tip radius $R = 200$ μm) and progressively increasing the load from 0.1 N to 10 N at a load rate of 3.3 N min^{-1} (loaded scan) and for a scratch length of 3 mm. To measure frictional coefficient, scratch tests at constant load by using a Rockwell C diamond scratch indenter (tip radius $R = 200$ μm) were performed. A pre-scan with a very small load was carried out, during which the starting surface profile was measured and subtracted from the loaded scratch scan profile to determine the depth of surface penetration (Pd). The instrument was equipped with an integrated optical microscope, and a device to measure the tangential frictional force (in the scratching direction), giving the friction coefficient value during scratching. The determination of the critical loads for a coating-substrate system was done by optical methods. Three scratches were carried out in different zones for each specimen and average values of the load at which the scratch track appears (Lc_1) was determined for each analysis.

The nano-hardness of the coatings was measured by depth-sensing Berkovich nanoindentation instrument (Nano-Indentation Tester, CSM Instruments) on the surface of plain coated samples. The maximum load was fixed at 50 mN (3 indentations per sample, loading/unloading rate of 40 mN/min), corresponding to a maximum indentation depth ≤10% of the thickness of each tested coating, so that the nano-hardness values are representative of the intrinsic properties of the film itself.

3. Results and discussion

We started our investigations by studying the effect of the presence of HBP on the final properties of a UV cured epoxy network. We added the phenolic HBP in the range between 5 and 20 wt% to the CE resin. The formulations were cured by means of UV light in the presence of a suitable cationic photoinitiator.

It was already demonstrated in a previous paper [9], by real-time FT-IR investigation, that the presence of a phenolic HBP additive induces a change on the kinetics of photopolymerization of cycloaliphatic epoxy resin: an increase in epoxy group conversion by increasing the amount of the HBP in the photocurable mixture was evidenced. A complete epoxy group conversion was achieved for the mixture containing 20 wt% of HBP. These results were

Table 2
Properties of UV cured epoxy films containing HBP as additive.

Sample	Gel content %[a]	T_g °C[b]	Impact resistance[c] J/cm^2
CE	100	205	0.95 ± 0.03
CE–HBP 5	100	200	1.03 ± 0.04
CE–HBP 10	100	195	1.16 ± 0.03
CE–HBP 20	99	190	1.18 ± 0.05

[a] Measured after 24 h extraction in chloroform.
[b] Determined as the maximum of tan δ curve from DMTA analysis.
[c] Determined by Charpy pendulum measurements on 2 mm thick samples.

Table 3
Properties of UV–Thermal dual-cured hybrid films containing both the HBP additive and the CTMSO inorganic precursor.

Sample	T_g °C[a]	Gel content %[b]	Impact resistance[c] J/cm^2	Surface hardness Persoz[d]
CE	205	100	0.95 ± 0.03	286
CE–HBP 20	190	100	1.18 ± 0.05	334
CEH–Si 10	205	100	1.13 ± 0.05	363
CEH–Si 30	208	100	1.10 ± 0.04	372
CEH–Si 50	210	96	1.06 ± 0.04	–

[a] Determined as the maximum of tan δ curve from DMTA analysis.
[b] Measured after 24 h extraction in chloroform.
[c] Determined by Charpy pendulum measurements on 22 mm thick samples.
[d] Number of pendulum oscillation.

explained on the basis of a chain transfer mechanism involving the hydroxyl groups present on the surface of the HBP.

In fact, in addition to the usual mechanism for the ring-opening polymerization of epoxides (*activated chain ends mechanism*), Penczek and Kubisa 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 alcohols [22–24]: during the polymerization the growing ionic chain end undergoes a nucleophilic attack by the alcohol to give a protonated ether. Deprotonation of this latter species by the epoxy monomers results in the termination of the growing chain and the proton transfer to the monomer can start a new chain. The polymer has now an alcohol fragment as end group. The effect of the chemical structure of the alcohol added on the occurrence of this chain transfer reaction, during the UV-curing process, has been deeply reported and discussed in the literature [25–28]. The same mechanism can be proposed for the increased epoxy groups conversion observed in the presence of the phenolic group of the HBP additive.

Further confirmation of the interaction between the carbocationic growing chain and the phenolic groups of the HBP additive comes from the very high gel content values (always equal or higher than 99%, see Table 2).

Dynamic-mechanical analyses of the cured films showed a shift of maximum of the tan δ curve towards lower temperature by increasing the amount of HBP in the photocurable formulation (Table 2); this is an indication of a slight decrease of the glass transition temperature [29] achieved in the presence of the hyperbranched additives. The flexibilization of the photocured films might be induced by the chain transfer mechanism involving the phenolic groups: the polyether chain growth decreases and as a consequence, also the crosslinking density of the polymeric network. On the other hand one has to be aware that with the addition of HBP a polymer with a relative low T_g (55 °C) was introduced into the system, which can explain the reduction of T_g due to a flexibilization effect.

This increased flexibilization can be responsible for the toughening achieved for the epoxy based coatings containing HBP as additive. The toughness measurements put in evidence a slight increase of the impact resistance by increasing the amount of HBP in the photocurable monomer mixture (see values in Table 2). This toughness effect can be related to the decrease of T_g values and can be attributed to the plasticization effect induced by the HBP incorporation into the epoxy network.

The subsequent step was the preparation of organic-inorganic hybrid coatings based on the CE–HBP 20 formulation, therefore keeping the CE:HBP ratio constant at 80:20, and increasing the amount of the alkoxysilane additive, [2-(3,4-epoxycyclohexyl)-ethyl]trimethoxysilane (CTMSO), as inorganic precursor in the photocurable formulation.

The organic polymer network was obtained, under UV irradiation, by cationic ring-opening polymerization of epoxy groups initiated by a photogenerated Brönsted acid. Under these acidic conditions alkoxysilane groups react during a thermal post-treatment at 80 °C under a highly humid atmosphere and generate silanol groups that after condensation can form siloxane crosslinks. Therefore, both the ring-opening polymerization and the sol–gel reaction of CTMSO can be acid catalyzed by the UV degradation of an onium salt, as recently reported in literature for other cationic UV-cured hybrid systems [30,31]. The inorganic precursor CTMSO can further act as a coupling agent copolymerizing on the one hand with the organic matrix through its epoxy group, and condensing on the other hand to form a silica network after hydrolysis of its methoxy groups. All the formulations investigated gave rise to photocured films characterized by a high gel content values (equal or higher than 96%, see Table 3) indicating the formation of a completely insoluble network and therefore confirming the efficiency of the dual-cure process.

The dual-cured hybrid films were optically transparent; this can be taken as a preliminary indication that the organic-inorganic phase separation is on the scale smaller than 400 nm. The formation of inorganic domains in the nanometer range was further confirmed by TEM analysis.

In Fig. 1 the bright field TEM micrographs for cured films obtained from the mixture containing 50 wt% CTMSO are reported. These images clearly show a good and homogeneous dispersion of

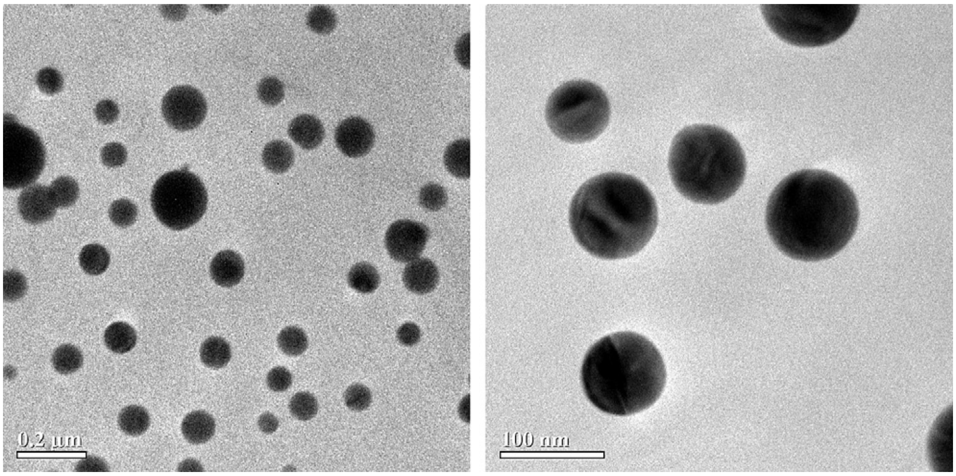


Fig. 1. TEM micrographs for the dual-cured epoxy films obtained from the formulation containing 20 wt% of HBP and 50 wt% of CTMSO (formulation CEH–Si 50).

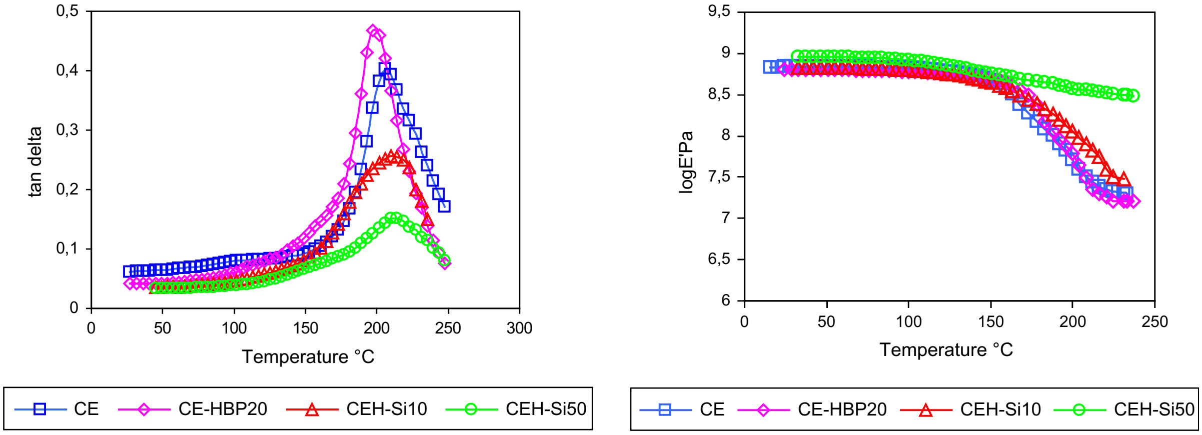


Fig. 2. DMTA curves for CE–HBP 20 cured films and for hybrid dual-cured films obtained in the presence of increasing CTMSO content.

the inorganic phases generated by sol–gel without any macroscopic phase separation which might have occurred during the dual-curing process; the silica domains, generated by the sol–gel process, are embedded in the polymeric matrix on nanometric scale of 25–80 nm. The strong chemical interactions between the organic and inorganic domains through the reacted CTMSO, which acts at the same time as a coupling agent to the organic phase and as inorganic precursor, was crucial to avoid macroscopic phase separation, and thus, it was possible to keep the inorganic clusters domains in the nanometric size.

Dynamic-mechanical analysis performed on the dual-cured films evidenced a tan δ peak broadening with increasing amount of CTMSO and a slight increase on T_g values (See Table 3 and Fig. 2); this is a common behaviour for composites suggesting that the inorganic domains are well molecularly dispersed in the polymer matrix. Furthermore, an increase in storage modulus above T_g in the rubbery plateau is observed in the presence of 50 wt% of CTMSO. Both, the increase in T_g and modulus values, can be attributed to strong and extensive interfacial interactions between the organic and inorganic phases with a restriction of the segmental motion of the polymeric chains.

The T_g increase for hybrid coatings is with 20 °C for CEH–Si 50 lower than expected, especially if compared with previous investigations on hybrid epoxy and acrylic UV cured films which showed a more significant increase in T_g by increasing the inorganic precursor content in the photocurable formulations [32–34]. It is proposed that, in this case, the T_g value of the hybrid can be affected by two opposite factors. The hindering effect of silica clusters on polymer chain motions is expected to enhance the glass transition temperature. In particular, molecularly dispersed silica clusters chemically connected with the polymer network can act as cross-linking units in the polymeric matrix, which significantly hinder the segmental motion of the polymer chains with a T_g increase. On the other hand, the CTMSO inorganic precursor acts as a monofunctional monomer in the cationic polymerization, which reduces the cross-linking density inducing therefore a flexibilization effect. Furthermore we have seen that the HBP additive acts as a flexibilizing agent in the epoxy network. These could be the reasons why only a moderate T_g increase is evident by increasing the inorganic precursor content in the photocurable formulations.

Nevertheless, the inorganic domain formation induces an important increase in surface hardness (see Table 3); this increase can be due to the presence of the silica domains strictly interconnected to the polymer network and to the presence of the silica clusters on the surface of the cured films, as previously evidenced by XPS and Si NMR analyses [35]. The hardness increase is usually related to an increase in scratch resistance, and therefore this result is particularly interesting for coating applications.

For this reason, the influence of scratch load on mechanical response of the coatings was investigated by carrying out a progressive load scratch test. The beginning of the scratch test as given by Lc_1 values (in the present case the load ranges from 0 to 2500 mN) can be taken as truly representative of the resistance of the investigated materials towards penetration of the indenter before scratching.

The higher scratch resistance achieved for hybrid coatings was confirmed by the analysis of the optical images collected after the scratch test. First critical load (Lc_1) values are reported in Table 4 (the data represent an average of three scratch tests carried out on each sample) for the different investigated samples. The pure CE resin was damaged at very low normal load (0.172 N). The dual-cured hybrid films appeared damaged (see Lc_1 values) at a higher load ranging from 0.721 up to 1.087 N, indicating a significant increase on scratch resistance with respect to the pristine UV cured coating. That evidences a good correlation between the scratch resistance and the SiO_2 content achieved by the condensation of the siloxy groups of CTMSO.

These results are also in agreement with DMTA and Persoz hardness investigations, where an increase of the T_g values and surface hardness was observed for the hybrid materials.

At last, the hybrid coatings showed a noticeable reduction of the friction coefficient (close to 50%) in respect with pristine CE cured system. The values of friction coefficient are reduced by the increase of the inorganic precursor. The friction coefficient is interrelated to the scratch resistance and low friction coefficients are accompanied with a good scratch resistance, as was also put in evidence in previous investigations [36,37].

Finally, nanoindentation experiments confirmed the same trend, with an increase on modulus of hybrid coatings by increasing the inorganic precursor content in the UV curable formulation. The

Table 4
Scratch resistance properties and moduli of the dual-cured films.

Sample	Lc_1 (mN)[a]	Friction coefficient[b]	E (GPa)[c]
CE	172 ± 0.2	0.446 ± 0.06	5.4 ± 0.2
CEH–Si 10	721 ± 0.2	0.339 ± 0.05	5.5 ± 0.4
CEH–Si 30	843 ± 0.2	0.293 ± 0.06	6.1 ± 0.2
CEH–Si 50	1087 ± 0.2	0.265 ± 0.04	–

[a] Determined by scratch resistance measurements as the load at which the scratch track appears.

[b] Determined by scratch resistance measurements.

[c] Determined by nanoindentation test.

data related to modulus values evaluated by nanoindentation test are reported in Table 4.

4. Conclusions

Advanced multifunctional coatings were prepared by a dual cure process including UV curing of epoxy based formulations containing HBP and a sol–gel process of an epoxy functionalized alkoxysilane additives. The strategy that has been followed should combine the toughening effect of HBP and the scratch resistance effect induced by the inorganic domains generated *in situ* via a sol–gel process.

The addition of HBP to the UV curable epoxy resin induced an important flexibilization of the glassy epoxy network with an increase in toughness of the cured polymeric coatings. By further adding the functionalized alkoxysilane into the UV curable formulations, as inorganic precursor of silica domains, an improvement in surface hardness was obtained without strongly affecting the flexibilization and the toughness achieved for the epoxy network containing HBP, which was kept quite good. Inorganic domains in the 20–80 nm range were obtained in this process, as shown by TEM analysis. The increase in surface hardness was accompanied by an increase in scratch resistance, as it was shown by scratch test, and in modulus, as shown by nanoindentation measurements.

In conclusion, by properly adjusting the formulation components, using an epoxy functionalized alkoxysilane additive and a HBP, it is possible to flexibilize the UV cured network which allows preparing high-loading silica hybrid coatings with strong increase in surface hardness and scratch resistance but keeping interesting fracture toughness properties.

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References

[1] Sanguansap K, Suteewong T, Saendee P, Buranabunya U, Tangboriboonrat P. Polymer 2005;46:1373.
[2] Ritzenthaler S, Court F, Gyrard-Reydet E, Leibler L, Pascault JP. Macromolecules 2003;36:118.
[3] Hult A, Johansson M, Malmström E. Macromol Symp 1995;98:1159.
[4] Voit B. J Polym Sci Part A Polym Chem 2000;38:2505.
[5] Hult A, Johansson M, Malmström E. In: Roovers J, editor. Advanced polymer science, vol. 143. Springer Verlag; 1999. p. 1.
[6] Malmström E, Hult A. Macromolecules 1996;29:1222.
[7] Hong X, Chen Q, Zhang Y, Liu G. J Appl Polym Sci 2000;77:1353.
[8] Voit B. J Polym Sci Part A Polym Chem 2005;43:2679.
[9] Sangermano M, Priola A, Malucelli G, Bongiovanni R, Quaglia A, Voit B, Ziemer A. Macromol Mater Eng 2004;289:442.
[10] Sangermano M, Di Gianni A, Malucelli G, Roncuzzi C, Priola A, Voit B. J Appl Polym Sci 2004;97:293.
[11] Sangermano M, Di Gianni A, Bongiovanni R, Priola A, Voit B, Pospiech D, Appelhans D. Macromol Mater Eng 2005;290:721.
[12] Sangermano M, Malucelli G, Bongiovanni R, Priola A, Harden A. Polym Int 2005;54:917.
[13] Johansson M, Malström E, Jansson A, Hult A. J Coat Technol 2000;72:49.
[14] Gopala A, Wu H, Xu J, Heiden P. J Appl Polym Sci 1999;71:1809.
[15] Johansson M, Hult A. J Coat Technol 1995;67:35.
[16] Lange J, Stenroos E, Johansson M, Malmström E. Polymer 2001;42:7403.
[17] Schmaljohann D, Voit B, Jansen JFGA, Hendriks P, Loontjens JA. Macromol Mater Eng 2000;275:31.
[18] Mark JE, Lee C, Bianconi PA, editors. Hybrid organic–inorganic composites, vol. 585. Washington: ACS; 1995.
[19] Mori H, Seng DC, Zhang M, Müller AHE. Prog Colloid Polym Sci 2004;126:40.
[20] Choudhury NR. J Sol-Gel Sci Technol 2004;31:37.
[21] Di Gianni A, Tabelsi S, Rizza G, Sangermano M, Halthues H, Voit B. Macromol Chem Phys 2007;208:76.
[22] Penczek S, Kubisa P. In: Brunelle PJ, editor. Ring opening polymerization. Munich: Hanser; 1993. p. 17.
[23] Kubisa P. J Polym Sci Polym Chem 2003;41:457.
[24] Penczek S, Kubisa P, Matyjaszewski K, Szymanski R. In: Goethals EJ, editor. Cationic polymerization and related processes. New York: Academic Press; 1984. p. 139.
[25] Crivello JV, Liu S. J Polym Sci Polym Chem 2000;38:389.
[26] Crivello JV, Acosta Ortiz R. J Polym Sci Polym Chem 2002;40:2298.
[27] Sangermano M, Malucelli G, Morel F, Decker C, Priola A. Eur Polym J 1999;35:636.
[28] Bongiovanni R, Malucelli G, Sangermano M, Priola A. Macromol Symp 2002;187:481.
[29] Nielsen LE. Mechanical properties of polymers and composites. New York: Marcel Dekker; 1994.
[30] Amerio E, Sangermano M, Malucelli G, Priola A, Voit B. Polymer 2005;46:11241.
[31] Chemtob AA, Belon C, Versace DL, Croutxe-Barghorn C, Rigolet S. Macromolecules 2008;41:7390.
[32] Amerio E, Sangermano M, Malucelli G, Priola A, Rizza G. Macromol Mater Eng 2006;291:1287.
[33] Sangermano M, Voit B, Sordo F, Eichhorn KJ, Rizza G. Polymer 2008;49:2018–22.
[34] Malucelli G, Priola A, Sangermano M, Amerio E, Zini E, Fabbri E. Polymer 2005;46:2872.
[35] Amerio E, Malucelli G, Sangermano M, Priola A. e-Polymers 2009;59:1–10.
[36] Amerio E, Fabbri P, Malucelli G, Messori M, Sangermano M, Taurino R. Progress in Organic Coatings 2008;62:129.
[37] Amerio E, Sangermano M, Colucci G, Malucelli G, Messori M, Taurino R, Fabbri P. Macromol Mater Eng 2008;293:700.