

Advances in cationic photopolymerization*

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Abstract: This review discusses cationic UV-curing processes of vinyl ethers, propenyl ethers, and epoxy monomers. Cationic photopolymerization based on photogeneration of acid from onium salts induced by UV light and consecutive polymerization initiated by photogenerated acid was first proposed at the end of the 1970s. The process engendered high interest both in academia and in industry. Cationic photoinduction presents some advantages over comparable radical-mediated processes, particularly the absence of inhibition by oxygen, low shrinkage, and good adhesion, and mechanical properties of the UV-cured materials. Moreover, the monomers employed are generally less toxic and irritant than acrylates and methacrylates, which are widely used in radical photopolymerization. In this overview, particular emphasis is given to our recent contributions to the field of cationic photopolymerization for different classes of monomers.

Keywords: cationic UV-curing; epoxy monomers; propenyl ether; vinyl ether.

INTRODUCTION

UV-induced polymerization of multifunctional monomers has found a large number of industrial applications [1], mainly in the production of films, inks, and coatings on a variety of substrates including paper, metal, and wood. Moreover, it has demonstrated scope for more high-tech applications such as coating of optical fibers and fabrication of printed circuit boards.

Part of the reason for the growing importance of UV-curing techniques, both in industrial and academic research, is a peculiar characteristic [2,3] that induces fast transformation of a liquid monomer into a solid polymer film having distinctive physical-chemical and mechanical properties. It can be considered environmentally friendly owing to the solvent-free methodology, and is usually carried out at room temperature, thus conferring added energy-saving advantages.

During a UV-curing process, radical or cationic species are generated by the interaction of UV light with a suitable photoinitiator.

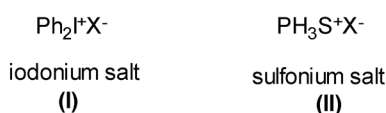
Relatively recent significant advances have been made in the practical application of cationic photopolymerization. These advances include the development of thermally stable photoinitiator systems and cationic photopolymerizable materials. One of the advantages of cationic systems is the absence of air inhibition, a property that eliminates the need for an inert atmosphere during curing and distinguishes cationic from radical polymerization. Cationic polymerization, once initiated, may continue to proceed after the light source has been removed. This process, called the “dark reaction”, is the result of the ability of the relatively long-lived protonic acid or Lewis acid species to continue the polymerization. Free radicals, on the other hand, are extinguished by a variety of termination steps, and no

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new radicals are formed from the photoinitiators in the absence of light. This property further distinguishes cationic from radical polymerization. Furthermore, the cationic photopolymerizable systems are characterized by absence of toxicity or irritation properties and for this reason are good alternatives to acrylate and methacrylate systems usually employed in the radical process. Last but not least, a lower shrinkage is observed in the cationic photopolymerization mechanism, which induces better adhesion properties on different substrates, with respect to the radical one.

Cationic photopolymerization, based on photogeneration of acid from onium salts induced by UV light and consecutive polymerization initiated by the photogenerated acid, was first proposed in 1978 [4].

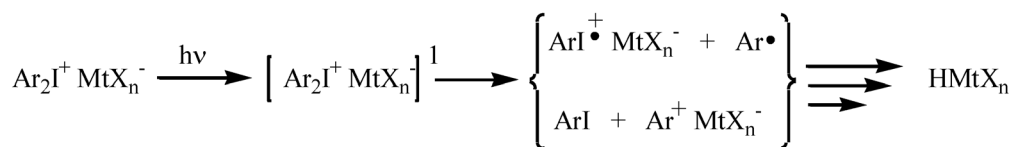
Cationic photoinitiator onium salts (iodonium I or sulfonium II) represent the most widely used classes of photoinitiators [5]. Properties such as thermal stability and inactivity toward polymerizable monomers at ambient temperature render these salts particularly suitable for photocurable formulations [6].



The cationic portion of the salt is the light-absorbing component. For this reason the structure of the cation controls the UV-absorption characteristics: the photosensitivity, quantum yield, whether the compound can be photosensitized, and the ultimate thermal stability of the salt. However, it is the nature of the anion that determines the strength of the acid formed during photolysis and its corresponding initiation efficiency. The nature of the anion also determines the character of the propagating ion pair. This has a direct impact on the kinetics of polymerization and whether terminations can occur [7].

Thus, onium salts may be viewed as photoacid generators. Anions such as BF_4^- , PF_6^- , AsF_6^- , and SbF_6^- are most useful and, under UV radiation, generate “superacids” with Hammett acidities ranging respectively from -15 to -30 [8]. The larger the negatively charged anion, the more loosely it is bound and the more active the propagating cationic species is in the polymerization. The order of reactivity is as follows: $\text{SbF}_6^- > \text{AsF}_6^- > \text{PF}_6^- > \text{BF}_4^-$.

The mechanism of photodecomposition is quite complex, and a simplified schematic representation is depicted for a diaryliodonium salt (Scheme 1).



Scheme 1 Representation of UV-decomposition of a diaryliodonium salt.

The mechanism involves first photoexcitation of the diaryliodonium salt and then the decay of the resulting excited singlet state with both heterolytic and homolytic cleavages; cation and radical fragments are formed simultaneously. The aryl cations and aryl iodine cation radicals generated are very reactive species and can react further with monomers to give the protonic acid, which is the actual initiator of cationic polymerization [9,10].

Light-induced cationic polymerization is one of the most efficient methods to rapidly cure monomers that are inactive toward radical species; different types of monomers and oligomers have been proposed and reported in the literature for cationic process, mainly: epoxides [10–13], vinyl ethers [14–16], and propenyl ethers [17–19]. Actually, the range of monomers polymerizable by a cationic

mechanism is virtually any type of known cationically polymerizable monomers and can allow the synthesis of a wide range of polymers with heteroatoms in the backbone.

In this work, an overview on the research studies accomplished by our group, in the field of cationic photopolymerization, is reported for the different classes of monomers investigated.

CATIONIC UV-CURING OF VINYL ETHER AND PROPENYL ETHER

It was demonstrated that cationic photopolymerization of multifunctional vinyl ethers is rather fast and photocuring rates are in many cases faster than the corresponding free-radical photopolymerization of acrylic monomers [20,21]. These findings made the use of vinyl ether monomers attractive in academia research as well as in industrial applications.

Nevertheless, vinyl ether availability is limited because the synthesis is inconvenient and expensive to carry out. A good alternative is the use of propenyl ethers, obtained by isomerization of the allyl ethers, which show good reactivity [22,23]. These monomers differ structurally from vinyl ethers only by the presence of a methyl group on the β -carbon, which further activates the double bond toward cationic polymerization by increasing the electron density of the double bond, while at the same time slightly retarding its reactivity by steric hindrance.

The effect of the presence of hydrogen donor additives [24] on the curing kinetics and on the properties of the cured vinyl ether systems was investigated.

The kinetics curve of vinyl ethers such as diethyleneglycol divinyl ether (DVE2) and triethyleneglycol divinyl ether (DVE3) showed that the rate of propagation of the photopolymerization changes significantly in the presence of alcohols (e.g., see the curve reported in Fig. 1 for DVE3 in the presence of 2-phenyl-2-propanol). The final conversion of double bonds increases, reaching even completeness in some cases, as reported in Table 1. These results indicate that the alcohol affects the propagation step, probably through a chain-transfer mechanism, known as *activated monomer mechanism*.

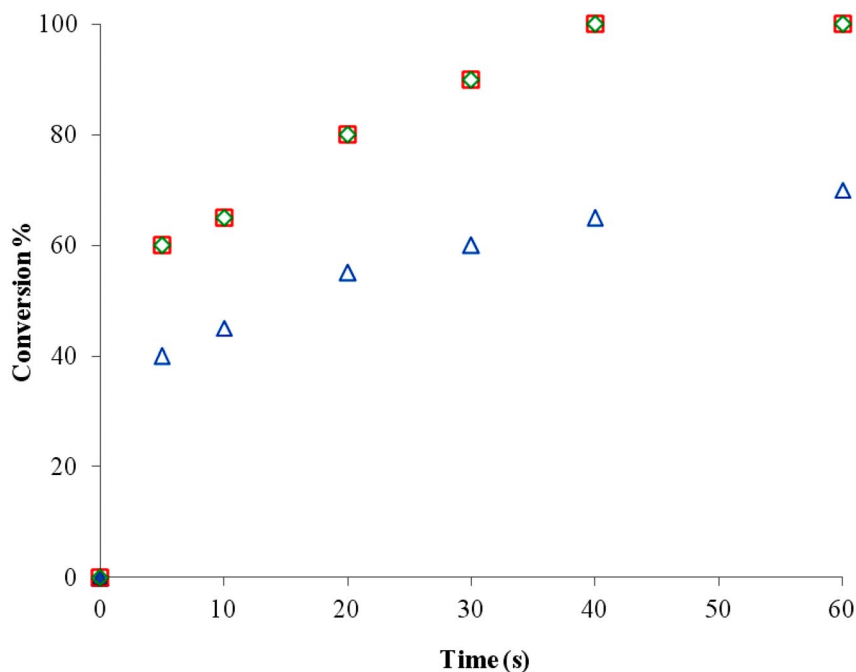
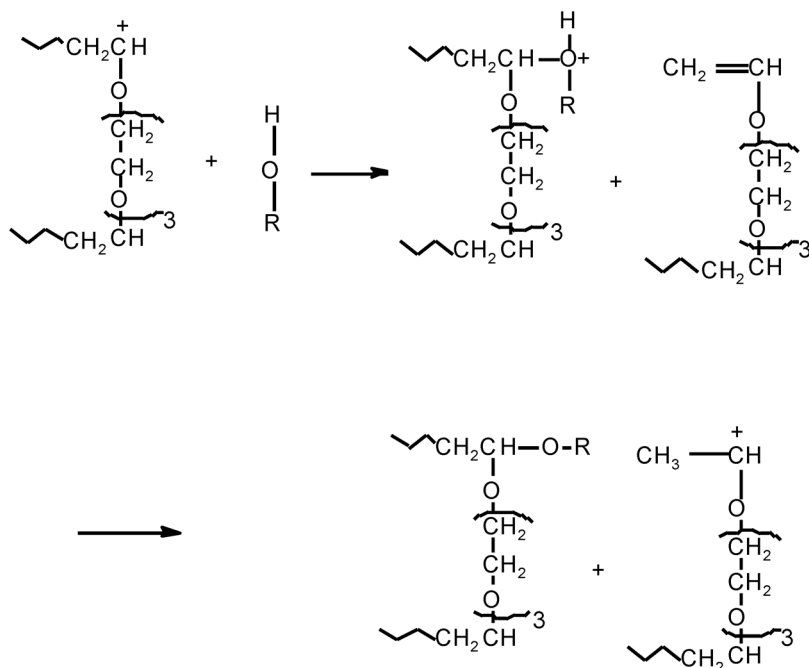


Fig. 1 FTIR kinetic curve of the pure DVE3 monomer (Δ) and in the presence of 5 wt % of HDVE2 (\square) and 2-phenyl-2-propanol (\diamond).

Table 1 Effect of alcohols and hydroxylic monomers on the conversion and properties of vinylether systems (DVE3).

Type of additive	% mol	Conversion (%)	Gel content (%)	T_g (°C)
DVE3	–	93	98	58
1-butanol	15.2	98	93	14
2-phenyl-2-propanol	8.3	100	92	15
HDVE2	14.2	100	96	30
	27.0	96	90	13
	49.5	96	71	–10

As a consequence of the chain-transfer reaction, the polyvinyl ether chain length decreases and free dangling-ends are introduced in the network (see Scheme 2). Therefore, more flexible structures are obtained and an increase of the double bonds conversion can be expected, which can reach complete polymerization.

**Scheme 2** Representation of the chain-transfer mechanism.

When considering photocuring of DVE3 monomer containing the diethyleneglycol monovinyl ether (HDVE2) monomer, we can assume that the same chain-transfer reaction can take place together with the copolymerization of the vinyl ether group present in the monomer. From the kinetic curves of Fig. 1, it is evident that 5 % of HDVE2 allows the polymerization rate to be increased and the complete conversion of the double bonds to obtain after 1 min of irradiation.

Similarly, the effect of alcoholic additive or monofunctional hydroxyl-containing monomer was investigated for propenyl ether photopolymerization [25]. For this purpose, trimethylolpropane tripropenyl ether (TPE) was synthesized following a previous method reported in the literature from

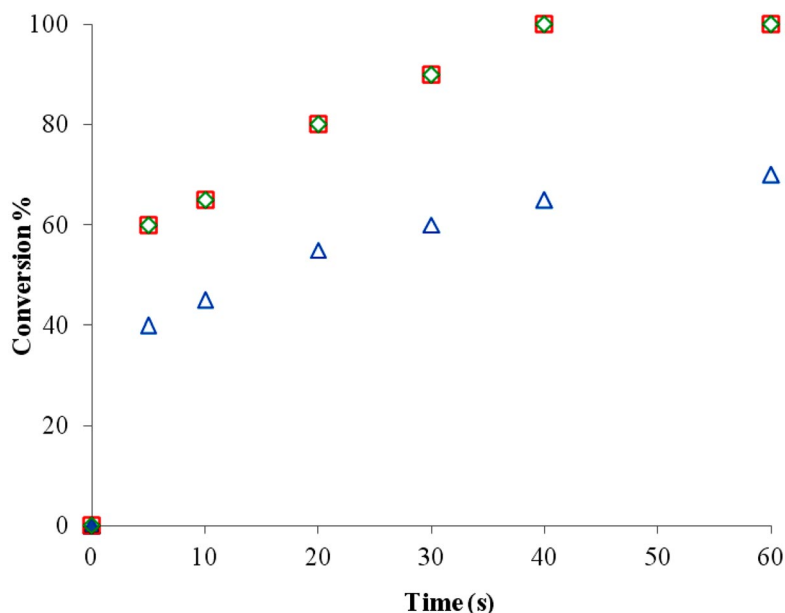


Fig. 2 FTIR kinetic curve of the pure TPE monomer (Δ) and in the presence of 5 wt % of DPE (\square) and 2-phenyl-2-propanol (\diamond).

Crivello [26,27]. The kinetics of the curing of TPE with and without alcohols or trimethylolpropane dipropenyl ether (DPE) are shown in Fig. 2.

The kinetic rates are higher in the presence of 2-phenyl-2-propanol or DPE, and the final conversions can reach 100 %: for the TPE alone the yield never overcomes 80 %. These results can be interpreted on the basis of a chain-transfer reaction involving the OH groups, as evidenced in the case of vinyl ethers systems.

CATIONIC UV-CURING OF EPOXY MONOMERS

Epoxy resins are the most widely used thermoset precursors in technological applications such as coatings, adhesives, structural materials, or electronics. This is due to their high mechanical properties, relatively low shrinkage, and chemical and thermal resistance [28]. Nevertheless, epoxy matrix suffers from fragility and low toughness; besides, for specific applications, shrinkages should be highly decreased: these are important goals to be reached in epoxy UV-curing.

Toughness enhancement

Despite high thermal and chemical resistance, epoxy high cross-link density during curing leads to a low-impact resistance material that shows poor resistance to crack propagation, hence their brittleness is the major drawback.

Toughening properties of epoxy thermosets have attracted widespread attention over the last decade; they remain a major topic in the development of these materials [29–31] and need to be addressed. These studies have established that the incorporation of a second phase such as rubber particles, thermoplastic particles, or mineral fillers can improve both stiffness and impact resistance in polymer composites [32,33].

The main research efforts are in the direction to develop toughening agents that do not affect thermomechanical properties. In fact, most often, toughening of a polymeric matrix is accompanied by

a reduction in modulus, due to a modification of the network structure, thus the challenge will be to increase the toughness of high-performance thermosets without affecting their thermomechanical properties.

Since commercial tougheners such as rubber, thermoplastic, or glass particles can affect the glass-transition temperature (T_g) of the cured material, compromising the thermomechanical behavior, various approaches based on polymeric additives like block copolymers (BCPs) [34,35] or polymer particles [36] were explored to further improve toughening of cross-linked epoxy resins.

With this regards hyperbranched polymers (HBPs) have also been recently suggested as organic toughening additive of UV-curable epoxy resins [37–39]. In all these papers, the effects of the presence of HBP on toughening properties of UV-cured films have been investigated.

In a recent approach [40], a new pegylated HBP was synthesized by esterification of phenol-terminated HBP. The synthesized molecule was added to 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexyl carboxylate (CE) in the range between 5 and 10 phr (per hundred resin). The covalent linkage of the HBP additive is possible because there were still some OH groups present in each macromolecule that can undergo chain-transfer reactions. This behavior has already been observed when using this type of polymers, and it has been explained on the basis of the activated monomer mechanism. The dynamic mechanical thermal analysis (DMTA) performed on UV-cured films of about 100 μm thickness showed that the T_g of the materials did not changed significantly in the presence of the pegylated HBP, while both the thermal stability and surface hardness were improved on the modified HBPpeg thermosets. A phase separation in the materials was observed (Fig. 3) by field emission scanning electron microscopy (FESEM) observation.

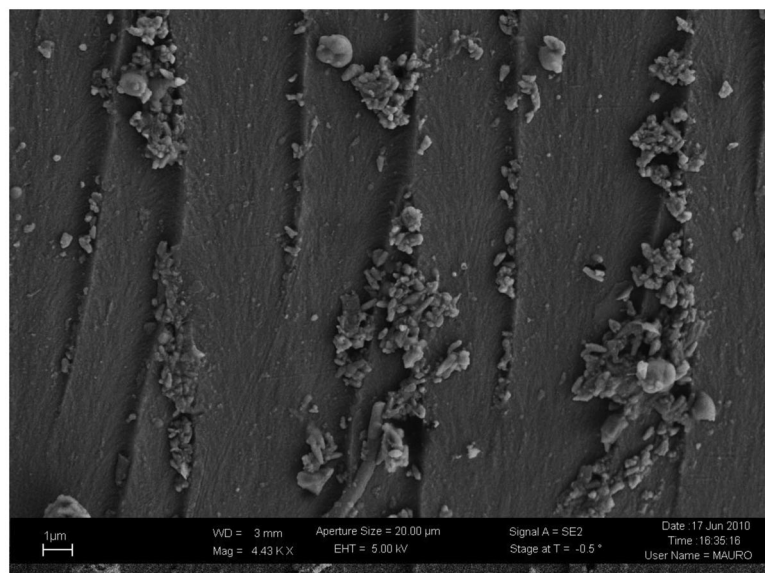
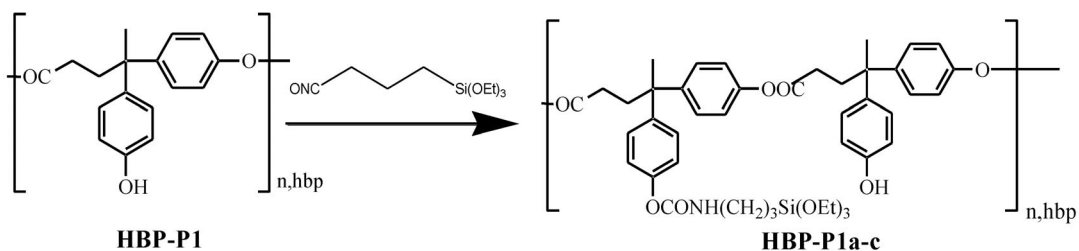


Fig. 3 FESEM pictures of the surface fracture of a specimen containing 5 phr of HBPpeg.

A further step [41] was the achievement of scratch-resistant tough epoxy coatings. For this reason, partially ethoxysilyl-modified HBPs were effectively used as toughening as well as multi-site coupling agents in the preparation of organic–inorganic UV-thermal dual-cured epoxy/tetraethoxy-orthosilicate (TEOS) coatings. Their synthesis is schematized in Scheme 3.

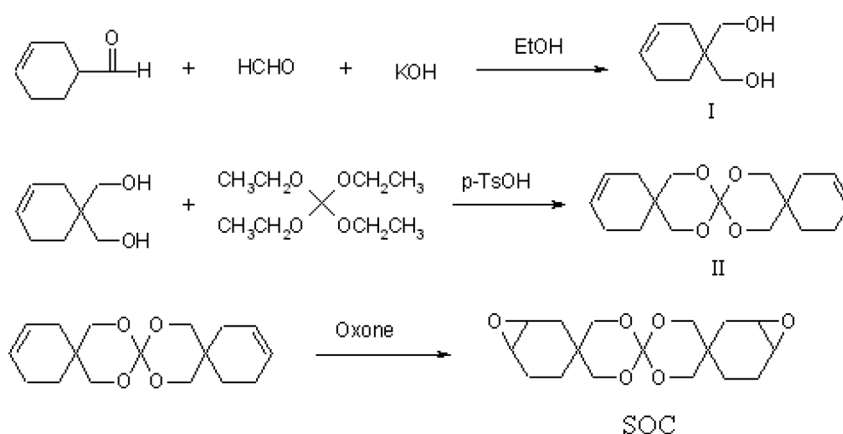


Scheme 3 Ethoxysilyl modification of HBPs.

Through chain-transfer reaction of the phenolic terminal units of the HBPs, effective incorporation in the epoxy resin is achieved in the photo-initiated cationic polymerization, whereas the ethoxysilane groups allow effective formation of a strongly interconnected organic–inorganic network during the in situ sol gel process with TEOS by binding the organic to the inorganic phase. Under those conditions, the addition of the inorganic precursor to the epoxy/HPB (20 wt %) system induced an increase of the storage modulus and more important, an improvement of the viscoelastic properties by extending the performance of the elastic modulus to higher temperatures. Thus, highly transparent hybrid coatings with enhanced thermal-mechanical and surface hardness properties resulted by the use of the partially ethoxysilyl-modified HBPs as multifunctional coupling agents.

Lowering the shrinkage upon curing

Most epoxy thermoset resins shrink about 2–6 % in volume during polymerization. Volume shrinkage often causes a large build-up of internal stress in the resin as well as the volumetric and dimensional changes. The suppression or control of the volume shrinkage during polymerization is of great importance in the design of materials requiring precise dimensions or for the preparation of composites. One way to achieve low-shrinkage/low-stress materials has been the incorporation of spiroorthocarbonates (SOCs), spiroortho esters, and other strained bicyclic monomers in the polymer network. In our study [42], an epoxy functionalized SOC was synthesized. The synthetic pathway for the preparation of SOC is reported in Scheme 4.



Scheme 4 Synthetic pathway for the preparation of SOC.

The SOC and the dicycloaliphatic epoxy resin (CE) are compatible in the range between 5–10 wt % of SOC. The formulations, under UV irradiation, give rise to transparent cured copolymeric networks. A flexibilization increase was evidenced by increasing the SOC content in the photocurable formulation. The copolymerization reaction has been confirmed by the presence of a single $\tan\delta$ peak in the DMTA thermogram, and further investigations are in progress in order to better elucidate the copolymerization mechanism. Shrinkage during photopolymerization was calculated by measuring the density of the starting formulations and of the corresponding cured films; it has been demonstrated that SOC acts as shrinkage reduction additive or even as an expanding monomer in the epoxy UV-induced polymerization.

Nanostructured UV-cured epoxy films

The combination of small-sized nanoparticles with those of the epoxy matrix yields hybrid materials with unique and versatile properties. The aim of the research in this field is to obtain polymeric coatings with functions like low abrasion and/or low wear, high chemical stability, easy to clean behavior, long-term stability, high impact resistance, easy processability, and low or at least reasonable costs.

The strategy for the preparation of organic–inorganic nanostructured epoxy coatings concerns the incorporation of inorganic nanoscale materials, either by dispersion of the inorganic nanoobject in the polymeric matrix [43] or via an in situ generation through a sol-gel process [44–46].

In both cases, the key point is the achievement of a full deagglomeration of the nanoparticles within the epoxy matrix. Even though the particles might be well dispersed in the prepolymer solution, aggregation might occur in the matrix, especially during the thermal curing process.

In this respect, it is particularly attractive that the very rapid nature of the photopolymerization process may allow a polymer network formation much more rapidly than phase separation or macroscopic aggregation can occur [47].

In order to achieve a molecular dispersion and avoid macroscopic phase separation, the interactions between the organic and inorganic domains need to be stronger than the agglomeration tendency of the inorganic component. As a consequence, the nature of the interface between the organic and inorganic components has been used to classify these hybrids into two main classes.

When only weak interactions are present between organic and inorganic domains (such as van der Waals contacts, or other weak bonds) the hybrids are classified as *Class I*. When at least a fraction of the organic and inorganic components are linked through strong chemical bonds, the hybrids are classified as *Class II*.

Inorganic nanoparticles can be either dispersed into the epoxy monomer or generated in situ during the polymerization, via a sol-gel process. In the following paragraphs, both systems are taken into consideration.

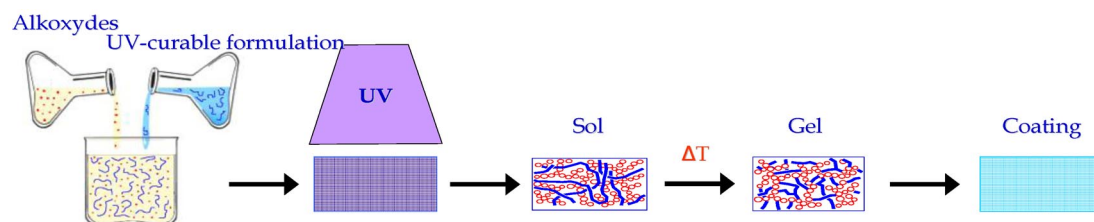
The incorporation of inorganic nanoscale materials into an epoxy matrix provides access to higher hardness and improved scratch resistance to an epoxy coating. Surface functionalization of the nanofiller is often necessary in order to increase their compatibility, optimize their dispersion, and to achieve higher property improvements.

Silica nanoparticles were employed in the range between 5–15 wt % in order to obtain organic–inorganic hybrid coatings via UV curing of an epoxy-based system [48]. The influence of the presence of SiO₂ on the rate of polymerization was investigated by real-time Fourier transform infrared (RT-FTIR). The silica nanofiller induced both a bulk and a surface modification of UV-cured coatings with an increase on T_g values, modulus values, and surface hardness by increasing the amount of silica into the photocurable monomer. Transmission electron microscopy (TEM) investigations confirmed that silica filler keeps a size distribution ranging between 5–20 nm, without macroscopic agglomeration.

Antistatic epoxy coatings were obtained, for the first time, by cationic UV curing of an epoxy monomer in the presence of a very low content of carbon nanotubes (CNTs). It was shown that the addi-

tion of only 0.025 wt % of CNTs into the epoxy monomer was sufficient to obtain a nanocomposite suitable for applications requiring electrostatic discharge [49]. An extended percolative structure forming a conductive CNT network was clearly evidenced, by TEM analysis, within the polymeric matrix. The use of such UV-cured epoxy material system for antistatic coatings is quite realistic and promising.

An interesting method to obtain hybrid organic–inorganic materials as alternative to nanoparticle dispersion, is the in situ sol-gel process, which allows one to synthesize inorganic domains within the polymeric network [50]: it involves a series of hydrolysis and condensation reactions starting from a hydrolyzable multifunctional metal-alkoxide as precursor of the inorganic domain formation [51]. The polymeric matrix is formed by UV-curing, then the sol-gel process is triggered and the inorganic phase is formed. Preferably, method B is applied when the polymer matrix is rubbery so that there is enough mobility to permit the inorganic reactions to proceed (see Scheme 5).



Scheme 5 Cartoon of dual UV-thermal curing for achieving organic–inorganic hybrid films.

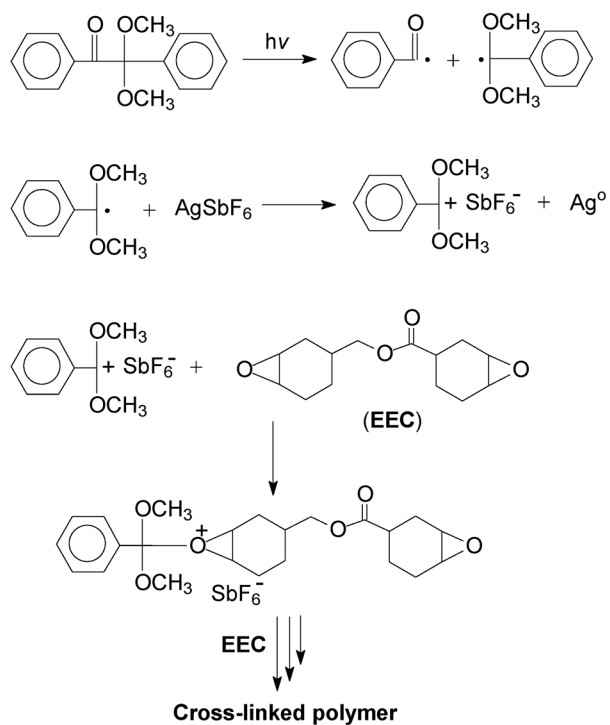
The use of a suitable coupling agent permits one to obtain a strictly interconnected network preventing macroscopic phase separation. The coupling agent provides bonding between the organic and the inorganic phases, therefore, well-dispersed nanostructured phases may result [52].

Organic–inorganic hybrid coatings containing silica domains were prepared by using TEOS as inorganic precursor for the silica network and glycidoxypropyl-trimethoxysilane (GPTS) as coupling agent. The organic epoxy matrix was obtained by cationic ring-opening polymerization initiated by a photogenerated Brønsted acid [53,54]. Under this acidic condition, siloxane groups react with moisture and generate silanol groups that can condense to form siloxane cross-links [55]. Therefore, both the epoxy ring-opening polymerization and the sol-gel reaction of TEOS can be acid-catalyzed by the UV degradation of an onium salt. GPTS can act as a coupling agent inducing a strong chemical interaction between the organic and inorganic domains, which is crucial for the formation of the nanocomposite films.

Titania [56] and zirconia [57] inorganic domains were achieved within the epoxy matrix using the same technique with different inorganic precursors: optical properties were deeply modified achieving the formation of transparent coatings with high refractive index. These new materials could find advanced applications as antireflective coatings or in the optical industry.

An efficient synthetic methodology [58] for in situ generation of silver nanoparticles during photoinduced cationic curing of bisepoxides was also reported. The approach toward the preparation of silver nanocomposites is unique in the way that silver nanoparticles and initiating cations are formed in a single redox process. The CE epoxy resin was used to serve as the cationically polymerizable monomer. Photoinduced cleavage of 2,2-dimethoxy-2-phenyl acetophenone (DMPA) is a good source of electron donor radicals, namely, alkoxy benzyl radicals. Thus, irradiation of DMPA in the system in the presence of AgSbF_6 leads to its reduction with rapid generation of both metallic silver and initiating cations without any undesirable side reactions. The overall process is represented in Scheme 6.

All of the cured samples were transparent, indicating the formation of metallic particles in nanometer range size, which was also confirmed by TEM analysis. Figure 4 shows the bright-field TEM micrographs for the cured films containing 5 wt % of silver salt in the epoxy resin. Metallic particles



Scheme 6 Photoinduced synthesis of silver-epoxy nanocomposites.

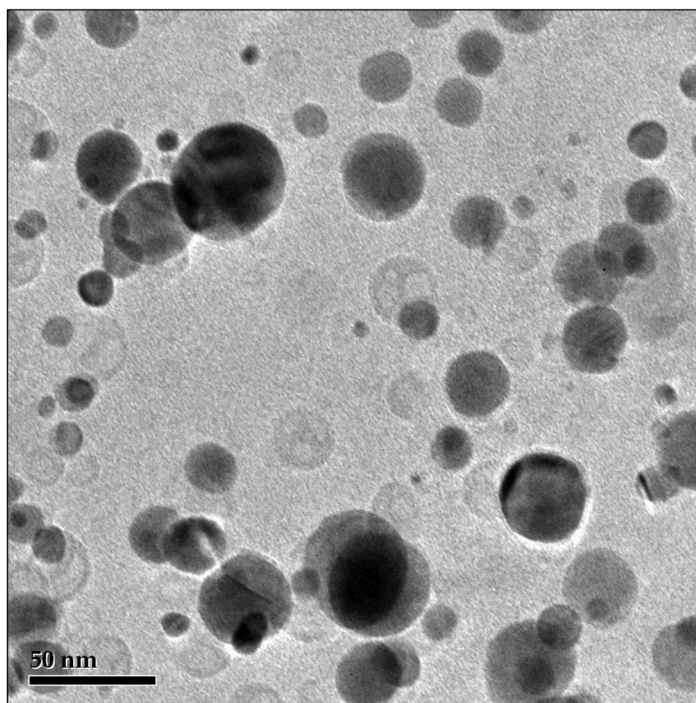


Fig. 4 Bright-field TEM micrograph of the epoxy UV-cured films containing 5 wt % AgSbF_6 .

are well dispersed with no significant macroscopic agglomerations. The observed features have a size distribution ranging between 10–50 nm.

CONCLUSIONS

This review, which is not to be considered exhaustive, reports the work performed in the last 13 years by my group at Politecnico di Torino in Italy, in the field of cationic UV-curing. The cationic UV-curing process is a powerful tool in the field of coatings in order to achieve specific properties for high-tech applications.

Vinyl ether, propenyl ether, and epoxy systems were investigated. It has been shown that by simply acting on the photocurable formulation component it is possible to tune the final properties of UV-cured films, getting specific properties for functional applications.

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REFERENCES

1. P. Dufour. In *Radiation Curing in Polymer Science and Technology*, Vol. I, J. P. Fouassier, J. F. Rabek (Eds.), p. 1, Elsevier, London (1993).
2. C. Decker. *Prog. Polym. Sci.* **21**, 593 (1996).
3. L. Schlegel, W. Schabel, P. Dufour. In *Radiation Curing in Polymer Science and Technology*, Vol. I, J. P. Fouassier, J. F. Rabek (Eds.), p. 119, Elsevier, London (1993).
4. J. V. Crivello, J. H. W. Lam. *J. Polym. Sci., Polym. Chem.* **16**, 2441 (1978).
5. J. V. Crivello. In *Photoinitiators for Free-radicals Cationic and Anionic Photopolymerization*, G. Bradley (Ed.), p. 329, John Wiley, New York (1998).
6. J. V. Crivello. *J. Polym. Sci., Polym. Chem.* **37**, 4241 (1999).
7. J. V. Crivello. *Makromol. Chem. Macromol. Symp.* **188**, 145 (1987).
8. G. A. Olah, G. K. Surya Prakash, J. Sommer. In *Superacid*, pp. 7–8, John Wiley, New York (1985).
9. J. P. Fouassier, D. Burr, J. V. Crivello. *J. Macromol. Sci. A* **31**, 677 (1994).
10. Y. Takimoto. In *Radiation Curing in Polymer Science and Technology*, Vol. III, J. P. Fouassier, J. F. Rabek (Eds.), p. 269, Elsevier, London (1993).
11. C. Decker, T. N. Thi Viet, H. P. Thi. *Polym. Int.* **50**, 986 (2001).
12. J. V. Crivello, R. A. Ortiz. *J. Polym. Sci., Polym. Chem.* **39**, 2385 (2001).
13. M. Sangermano. "UV cured nanostructured epoxy coatings", in *Epoxy Polymers: New Materials and Innovations*, J. P. Pascault, R. J. J. Williams (Eds.), Wiley-VCH, Weinheim (2010).
14. C. G. Roffey. In *Photopolymerization of Surface Coatings*, p. 74, John Wiley, New York (1982).
15. C. Decker, F. Morel. *Polym. Mater. Sci. Eng.* **76**, 10 (1997).
16. M. Sangermano, G. Malucelli, R. Bongiovanni, A. Priola, U. Annby, N. Rehnberg. *Eur. Polym. J.* **38**, 655 (2002).
17. J. V. Crivello, K. Di Jo. *J. Polym. Sci., Polym. Chem.* **31**, 1437 (1993).
18. J. V. Crivello, K. Di Jo. *J. Polym. Sci., Polym. Chem.* **31**, 1483 (1993).

19. M. Sangermano, G. Malucelli, R. Bongiovanni, A. Priola, U. Annby, N. Rehnberg. *Polym. Int.* **50**, 998 (2001).
20. J. V. Crivello, J. L. Lee, D. A. Conlon. *J. Rad. Cur.* **1**, 6 (1983).
21. J. V. Crivello, D. A. Conlon. *J. Polym. Sci., Polym. Chem.* **22**, 2105 (1984).
22. J. V. Crivello, G. Lohden. *J. Polym. Sci., Polym. Chem.* **34**, 2051 (1996).
23. M. Sangermano, G. Malucelli, R. Bongiovanni, A. Priola, U. Annby, N. Rehnberg. *Polym. Int.* **50**, 998 (2001).
24. M. Sangermano, G. Malucelli, F. Morel, C. Decker, A. Priola. *Eur. Polym. J.* **35**, 639 (1999).
25. M. Sangermano, G. Malucelli, R. Bongiovanni, A. Priola, U. Annby, N. Rehnberg. *Polym. Int.* **50**, 998 (2001).
26. J. V. Crivello, S. Liu. *J. Polym. Sci., Polym. Chem.* **38**, 389 (2000).
27. J. V. Crivello, K. D. Jo. *J. Polym. Sci., Polym. Chem.* **31**, 1473 (1993).
28. C. A. May. In *Epoxy Resins: Chemistry and Technology*, C. A. May, Y. Tanaka (Eds.), Marcel Dekker, New York (1973).
29. S. Kar, A. K. Banthia. *J. Appl. Polym. Sci.* **96**, 2446 (2005).
30. K. P. Unnikrishnan, E. T. Tachil. *Design. Monom. Polym.* **9**, 129 (2006).
31. M. Messori, M. Toselli, F. Pilati, C. Tonelli. *Polymer* **42**, 9877 (2001).
32. B. B. Johnsen, A. J. Kinloch, R. D. Mohammed, A. C. Taylor, S. Sprenger. *Polymer* **48**, 530 (2007).
33. J. Jordan, K. I. Jacob, R. Tannenbaum, M. A. Sharaf, I. Jasiuk. *Mater. Sci. Eng.* **393**, 1 (2005).
34. S. Ritzenthaler, F. Court, L. David, E. Girard-Meydet, L. Leibler, J. P. Pascault. *Macromolecules* **35**, 6245 (2002).
35. S. Ritzenthaler, F. Court, E. Girard-Reydet, L. Leibler, J. P. Pascault. *Macromolecules* **36**, 118 (2003).
36. M. Sangermano, M. Messori, A. Rizzoli, S. Grassini. *Prog. Org. Coat.* **68**, 323 (2010).
37. M. Sangermano, M. Messori, M. M. Gallego, G. Rizza, B. Voit. *Polymer* **50**, 5647 (2009).
38. D. Foix, X. Ramis, A. Serra, M. Sangermano. *Polymer* **52**, 3269 (2011).
39. F. Dabritz, B. Voit, M. Naguib, M. Sangermano. *Polymer* **52**, 5723 (2011).
40. D. Foix, X. Fernandez-Francos, X. Ramis, A. Serra, M. Sangermano. *React. Funct. Polym.* **71**, 417 (2011).
41. F. Dabritz, B. Voit, M. Naguib, M. Sangermano. *Polymer* **52**, 5723 (2011).
42. M. Sangermano, R. Acosta Ortiz, B. A. Puente Urbina, L. Berlanga Duarte, A. E. Garcia Valdez, R. Guerrero Santos. *Eur. Polym. J.* **44**, 1046 (2008).
43. C. Sanchez. *J. Mater. Chem.* **15**, 3559 (2005).
44. S. Mann, S. L. Burket, S. A. Davis, C. E. Fowler, N. H. Mendelson, S. D. Sims. *Chem. Mater.* **9**, 2300 (1997).
45. M. Antonietti, B. Berton, C. Gottner, H. P. Hentze. *Adv. Mater.* **10**, 154 (1998).
46. S. A. Bagshaw, E. Pronzet, T. Pinnavaia. *Science* **269**, 1242 (1995).
47. J. D. Clapper, L. Sievens-Figueroa, C. Allan Guymon. *Chem. Mater.* **20**, 768 (2008).
48. M. Sangermano, G. Malucelli, E. Amerio, A. Priola, E. Billi, G. Rizza. *Prog. Org. Coat.* **54**, 134 (2005).
49. M. Sangermano, S. Pegel, P. Pötschke, B. Voit. *Macromol. Rapid Commun.* **5**, 396 (2008).
50. J. E. Mark, C. Lee, P. A. Bianconi. *Hybrid Organic-Inorganic Composites*, ACS Symposium Series No. 585, American Chemical Society, Washington, DC (1995).
51. A. Bandyopadhyay, A. R. Bhowmick, M. De Sarkar. *J. Appl. Polym. Sci.* **93**, 2579 (2004).
52. P. M. Ajayan, L. S. Schadler, P. V. Braun. *Nanocomposite Science and Technology*, p. 112, John Wiley, New York (2003).
53. E. Amerio, M. Sangermano, G. Malucelli, A. Priola, B. Voit. *Polymer* **46**, 11241 (2005).
54. E. Amerio, M. Sangermano, G. Malucelli, A. Priola, G. Rizza. *Macromol. Mater. Eng.* **291**, 1287 (2006).

55. K. Zou, M. D. Soucek. *Macromol. Chem. Phys.* **205**, 2032 (2004).
56. M. Sangermano, G. Malucelli, E. Amerio, R. Bongiovanni, A. Priola, A. Di Gianni, B. Voit, G. Rizza. *Macromol. Mater. Eng.* **291**, 517 (2006).
57. M. Sangermano, B. Voit, F. Sordo, K. J. Eichhorn, G. Rizza. *Polymer* **49**, 2018 (2008).
58. M. Sangermano, Y. Yagci, G. Rizza. *Macromolecules* **40**, 8827 (2007).