

# Multifunctional UV-Cured Epoxy Coatings

By Marco Sangermano

The UV-induced polymerization of multifunctional monomers has found a large number of applications in various industrial fields, mainly in the production of films, inks and coatings.<sup>1</sup> The cationic photopolymerization process of epoxy systems present some advantages compared to the radical one<sup>2</sup>—lack of inhibition by oxygen, low shrinkage, good adhesion and mechanical properties of cured films. In particular, epoxy resins are widely used in industry—especially in the aerospace and electronic applications—due to their excellent thermal and dimensional stability, high modulus and excellent solvent resistance. However, epoxy polymers based on bisphenol-A structure are inherently brittle and toughening additives are needed for specific applications.

There are many approaches to enhance the toughness of epoxy resins involving the modification of

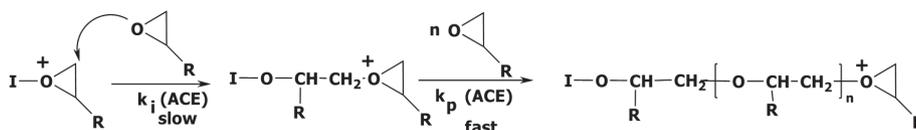
these systems with polymers such as thermoplastics, block-copolymers, liquid rubber or core-shell particles.

In our approach,<sup>3</sup> a new pegylated hyperbranched polymer (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 per hundred resin (phr). The covalent linkage of the HBP additive is possible through the residual hydroxyl (OH) groups present in each macromolecule that can undergo chain transfer reactions. This behavior has already been observed when using this type of polymer and it has been explained on the basis of the activated monomer mechanism described by Penczek and Kubisa.<sup>4</sup> In this mechanism, OH groups can react with epoxides leading to a different propagation mechanism that competes with the well-known

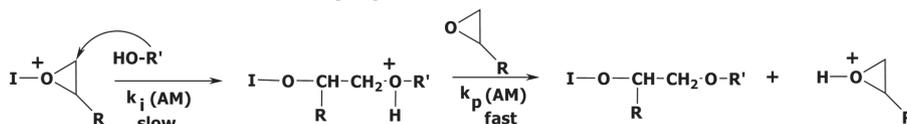
FIGURE 1

## Propagation mechanisms of epoxide cationic ring opening polymerization

### Activated chain end mechanism (ACE)

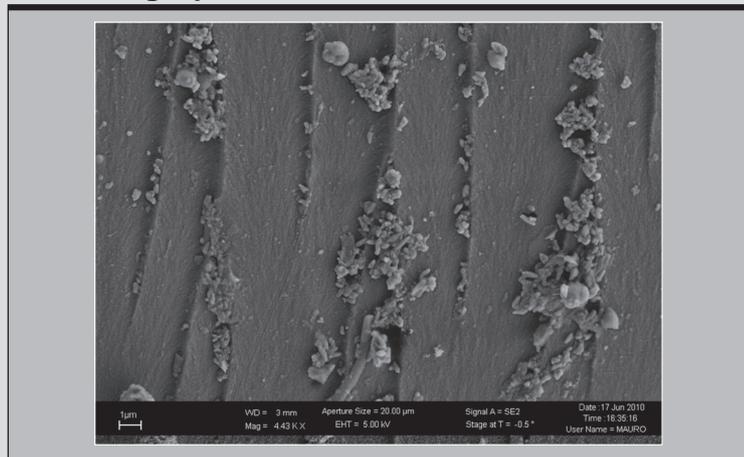


### Activated monomer mechanism (AM)



## FIGURE 2

### FESEM pictures of the surface fracture of a specimen containing 5 phr of HBP/PEG



active chain-end mechanism. Both mechanisms are depicted in Figure 1.

Dynamic Mechanical Thermal Analyses (DMTA) performed on UV-cured films of about 100 µm thickness showed that the  $T_g$  of the materials did not change significantly in the presence of the pegylated HBP, while both the thermal stability and surface hardness were improved on the modified HBP/polyethylene glycol (PEG) thermosets. By Field Emission Scanning Electronic Microscope (FESEM) observation, a phase separation in the materials was observed (Figure 2). The presence of a second phase in the micro/nanometric

scale can lead to improvements in material's toughness.

A further step was the achievement of scratch-resistant tough epoxy coatings. For this reason, partially ethoxysilyl-modified hyperbranched aliphatic-aromatic polyesters (HBPs) were effectively used as toughening (the synthesis is schematized in Figure 3), as well as multisite coupling agents in the preparation of organic-inorganic, UV-thermal, dual-cured epoxy/tetraethyl orthosilicate (TEOS) coatings.<sup>5</sup>

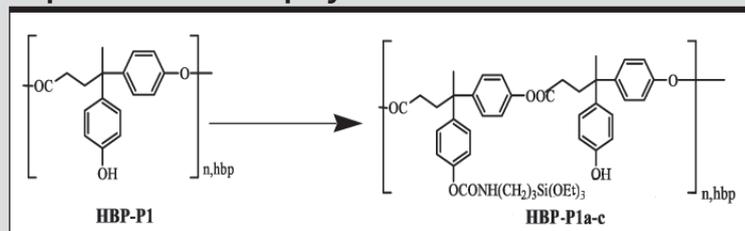
Through chain transfer reaction of the phenolic terminal units of the HBPs, effective incorporation in

the epoxy resin is achieved in the photoinitiated cationic polymerization, whereas the ethoxysilane groups allow effective formation of a strongly interconnected inorganic-organic 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 were the result of using partially ethoxysilyl modified HBPs as multifunctional coupling agents. Epoxy-based nanocomposites with advanced and outstanding properties were also obtained by multiwalled carbon nanotubes (MWCNTs) or functionalized graphene sheets dispersion (FGS).<sup>6-8</sup>

An important increase in electrical surface conductivity was obtained in the cured materials. We observed how the geometry of the filler played a dominant role in the formation of conductive pathways. When MWCNTs were dispersed in the photocurable precursor, drastic enhancements in conductivity and permittivity were already achieved with a very low content (around 0.1 wt%), evidencing the formation of an effective conductive MWCNT percolative network in the epoxy matrix. This was confirmed by the morphology investigation. On the other hand, when the resin was loaded with sheet-like nanofiller (FGS), the increase of these two properties was much lower than for the MWCNT and the thresholds appeared at higher concentrations, but in all cases the antistatic limit of  $10^{-8}$  S/cm, is reached.

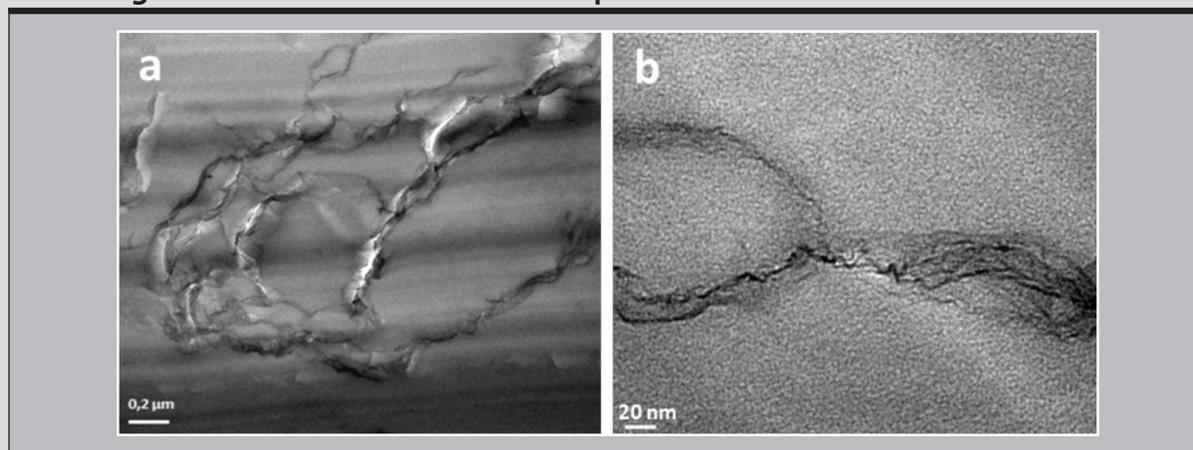
## FIGURE 3

### Ethoxysilyl modification of hyperbranched aliphatic-aromatic polyesters



## FIGURE 4

### TEM images of the 1.5 wt.% FGS nanocomposite



The differences in the percolation thresholds obtained were attributed to the geometry of the fillers. First of all, it would be easier for polymer chains to intercalate between the MWCNT than between sheets facilitating the disentanglement of the MWCNT. Moreover sheet-like nanofiller would be more likely to form aggregates due to their in-plane interactions. The rod-like geometry of the MWCNT could generate a huge number of overlapping

contacts among them, causing an effective electronic transport, while sheet-like nanofillers are connected through a shorter number of connections, such as plane-to-plane, edge-to-plane and edge-to-edge, which are not equally efficient from the electrical point of view.

We investigated the dispersion states of the different nanofillers in the epoxy resin by SEM and Transmission Electron Microscopy (TEM) inspections

on cured materials in order to get some conclusions of the morphology effect of the nanocomposites on their electric properties. We chose the highest loading fraction for each set of samples. Figure 4 a and b are images at different magnifications of the nanocomposite with 1.5 wt.% of FGS obtained by transmission electron microscopy. The achieved morphology showed a random and homogeneous distribution of single graphene sheet or stacks of a few nanometers adopting a wrinkled configuration.

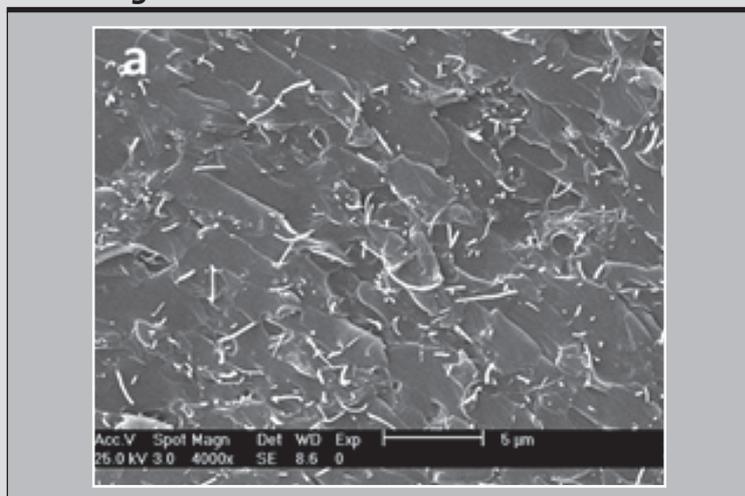
The SEM images shown in Figure 5 correspond to the analysis of the cryofractured surface of the nanocomposites containing 1 wt.% MWCNT. The nanotubes were very well dispersed and spread out in the epoxy matrix without forming agglomerates.

### Conclusion

We have shown some of the potential applications of the UV-cationic induced polymerization. Advanced multifunctional coatings were prepared by UV curing the epoxy-based formulations containing HBPs and an epoxy-functionalized alkoxysilane additive. Advanced scratch-resistant and tough nanocomposite epoxy

## FIGURE 5

### SEM images of the 1 wt.%



coatings were obtained by properly selecting the formulation components. Epoxy-based nanocomposites with advanced and outstanding properties were also obtained by carbon nanotubes or graphene-oxide dispersion. An important increase of electrical surface conductivity was obtained in the cured materials.

Multifunctional epoxy coatings were achieved, which could find interesting applications in different fields. ▀

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