UV-Led curable coatings containing porcupine-like carbon structures: thermal, dynamic-mechanical and electrical properties

UV-LED CURABLE COATINGS CONTAINING PORCUPINE-LIKE CARBON STRUCTURES: THERMAL, DYNAMIC-MECHANICAL AND ELECTRICAL PROPERTIES

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Introduction

From the last 10 years onwards, the industrial applications of UV curing processes exhibited a steadily growing trend, due to their high curing rate, reduced toxicity and lower environmental impact as compared to thermally-induced processes [1]. In fact, the use of a UV source to trigger the polymerization reactions allows minimizing the emissions of volatile organic compounds during the process; furthermore, UV curing operations involve short reaction times and low energy consumptions, because of the possibility to complete the polymerization at room temperature by using proper UV sources [2]. Recent researches demonstrated that lower energy consumption and higher curing efficiencies can be achieved through the utilization of light emitting diodes (LEDs) as light sources for UV curing systems. Compared to traditional UV lamps, UV-LED systems show longer full-intensity lifetime and improved electrical-to-optical conversion efficiency [3]. Additionally, due to the absence of emission in the infrared region, UV-LEDs deliver a cool radiation with respect to arc lamps, making the application of this technology suitable for heat-sensitive substrates.

Currently, researches concerning the utilization of UV-LED curing systems are mainly focused on the preparation of inks or photo-curable coatings, while a limited number of studies regarding the exploitation of this technique for the formulation of functional composite systems is reported in the literature [4].

In this work, we propose an innovative approach to modify the morphology of biochar-based particles derived from cellulose nanocrystals through the growth of carbon nanofibers onto their outer surface. This leads to the formation of porcupine-like arrangements that, thanks to their peculiar morphology, may combine the effects provided by either globular or high aspect ratio carbon structures in a single filler. For this purpose, the porcupine (PuP)-like structures were dispersed in a UV-LED curable epoxy-acrylate resin (Ebecryl 150, Bisphenol-A-ethoxylate-diacrylate, EB) at different loadings (ranging from 1 to 10 wt.%). The obtained mixtures (containing also 6 wt.% of TPO) were coated on glass plates using proper wire-wound applicators for obtaining about 200 µm thick coatings suitable for the successive characterizations. The coated glass plates were then subjected to the UV-LED curing process, using a Heraeus Noblelight UV-LED NC1 unit, working in dynamic conditions (belt speed: 1 m/min), at 395 nm. Then, the structure-property relationships of the formulated films were assessed, also considering the effect of the embedded particles on the thermal and electrical features of the cured system.

Results and discussion

The preliminary characterization of the carbonaceous structures (performed through Raman, thermogravimetric and morphological characterizations) documented the achievement of a highly carbonized material involving spherical biochar particles having an average diameter ranging from 15 to 20 µm, covered by fibers displaying length up to 100 µm, as shown in the SEM micrographs reported in Figure 1.

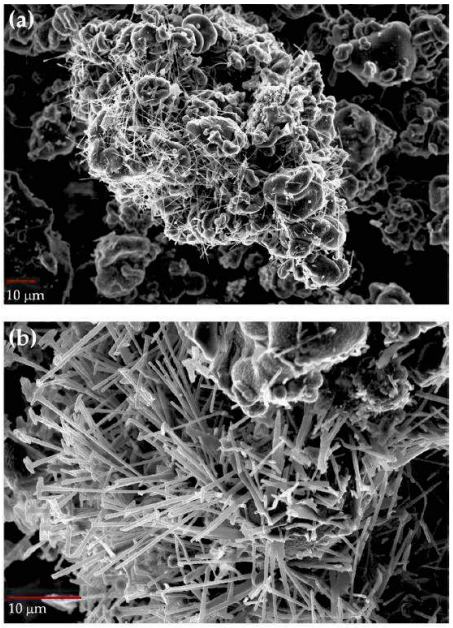

Figure 1: SEM pictures of PuP structures at different magnifications.

Prior to the UV-LED curing process, the EB/PuP mixtures were characterized through rheological analyses. The obtained results indicated that the incorporation of increasing loadings of PuP particles causes a progressive rise of the EB complex viscosity values, especially in the very low frequency region, and the appearance of an apparent yield stress behavior, due to a restriction of the

macromolecular dynamics resulting from the the formation of a highly entangled structure that hinders the complete relaxation of EB oligomeric chains.
Then, UV-LED cured EB-PuP films were subjected to DSC analyses that demonstrated the completeness of the curing reactions also in presence of high PuP loadings, thus indicating the effectiveness of the experimental conditions adopted for the UV-LED curing process.
Figure 2 reports the results from dynamic-mechanical analyses, in terms of storage modulus as a function of temperature for all the investigated UV-LED cured films. A progressive increase of the storage modulus values with increasing the loading of PuP particles can be noticed, especially in the glassy region. Tanδ curves were also recorded, indicating a slightly higher glass transition temperature values for the composite films as compared to the unfilled counterpart; besides, a progressive decrease of the peak intensity was noticed with increasing the particle loading. These findings can be related to the strong level of interfacial interactions taking place between the oligomeric chains and the introduced PuP particles; in fact, the embedded particles are able to restrict the segmental dynamics of the polymeric phase located in the interfacial region, causing a progressive shift of the glass transition temperature values towards higher temperatures as a function of particle loading. Furthermore, the restriction of the segmental chain motion induces an increased elasticity; as a result, a lower extent of energy is dissipated during the mechanical test and this phenomenon causes the lowering of the peak intensity [5].

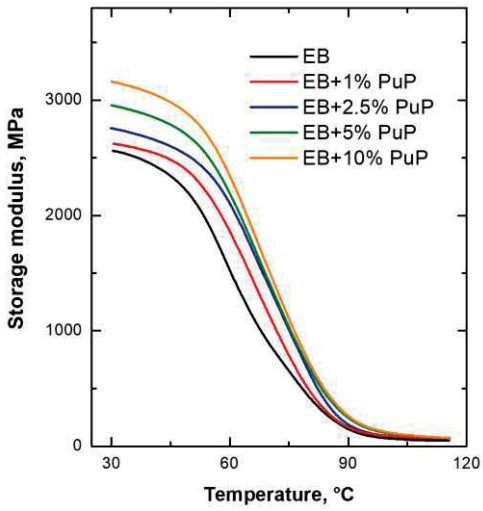

Figure 2: Storage modulus as a function of temperature for UV-LED cured EB-PuP films.

Figure 3 presents the thermal conductivity data of unfilled EB cured film and of all investigated composites as a function of the amount of PuP particles. From an overall point of view, the introduction of increasing amounts of PuPs induces a progressive increase of the material thermal conductivity. The observed trend seems to indicate a homogeneous dispersion of the particles within the polymer network, as also confirmed by morphological observations.

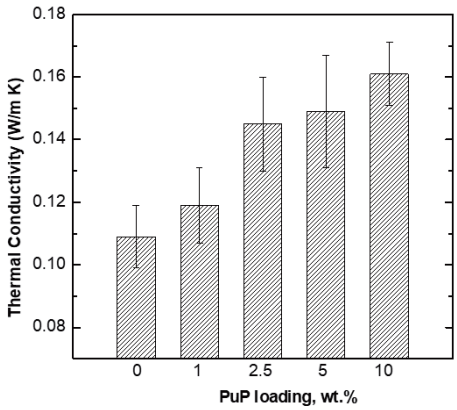

Figure 3: Thermal conductivity of UV-LED cured EB and its composite films as a function of filler loading.

Besides, a progressive increase of the electrical conductivity was observed for the composites containing increasing PuP particle loadings.

Conclusions

Biochar-based particles derived from cellulose nanocrystals were successfully modified by growing carbon nanofibers onto their outer surface; the obtained porcupine-like structures were introduced in a UV-LED curable epoxy-acrylate resin, aiming at achieving composite films with enhanced properties. Preliminary rheological analyses performed on the UV-LED curable dispersions showed a significant effect of the embedded carbonaceous structures on the material low-frequency behavior, suggesting the occurrence of strong interactions between the oligomeric chains and the carbon nanofibers of the PuP structures. Furthermore, the DSC characterization of the cured films demonstrated the completeness of the curing reactions also in presence of high PuP loadings. Dynamic-mechanical analyses demonstrated the achievement of progressively higher values of the storage modulus for the composite films containing increasing loadings of particles as compared to the unfilled counterpart. Finally, a monotonic increase of the thermal and electrical conductivity was observed as a function of the PuP content.

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