PREPARATION AND CHARACTERIZATION OF UV-LED CURABLE BIO-BASED COATINGS CONTAINING POLYMERIC CARBON DOTS

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Introduction

The development of sustainable coatings based on renewable resources is becoming increasingly important due to growing environmental concerns and stricter regulations regarding fossil-derived materials. Among the available alternatives, UV-curable bio-based resins have attracted considerable attention because of their rapid processing, low energy consumption, solvent-free formulations, and tunable chemical architectures [1]. However, the mechanical and thermal performances of many bio-derived resins still require improvement to meet the demands of advanced applications.

Nanofillers offer an effective strategy for enhancing the properties of photocurable systems. In particular, polymeric carbon dots (PCDs) have emerged as versatile nanomaterials owing to their fluorescence emission, low toxicity, tunable surface chemistry, and potential production from sustainable precursors [2,3]. Despite their extensive use in biomedical fields, their application in UV-curable bio-based coatings remains largely unexplored.

In this work, PCDs synthesized from citric acid and 1,4-phenylenediamine were incorporated into an acrylated epoxidized soybean oil (ESBOA) resin and subsequently cured through UV-LED irradiation. The objective was to investigate the influence of PCDs on the optical, thermal, and physicochemical properties of the resulting coatings while maintaining a high bio-based content.

Results and discussion

PCDs were synthesized through an ultrasound-assisted route using citric acid and 1,4-phenylenediamine as precursors. Structural characterization through FTIR, Raman spectroscopy, XPS, and XRD confirmed the formation of nitrogen-containing polymeric carbon structures characterized by aromatic domains interconnected through amide-based linkages.

Optical characterization demonstrated that the synthesized PCDs exhibited intense blue fluorescence emission together with UV-visible absorption bands associated with nitrogen-containing aromatic domains (Figure 1).

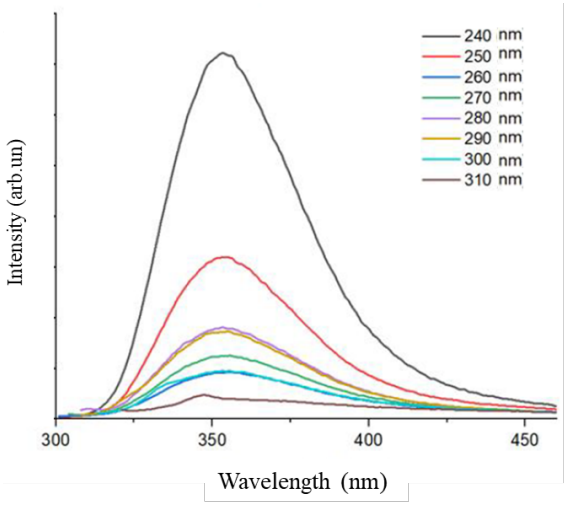

Figure 1. Fluorescence spectra of PCDs in the range between 300 and 470 nm.

Composite coatings were prepared by dispersing different amounts of PCDs (0.5, 1, and 2 wt.%) within the ESBOA resin followed by UV-LED curing at 395 nm. FTIR analyses confirmed the complete conversion of the acrylic double bonds under the adopted irradiation conditions, demonstrating that the presence of the nanofiller did not interfere with the photopolymerization process.

Morphological investigations revealed that low filler loadings generated homogeneous coatings, whereas increasing the PCD loading promoted the formation of nanoscale aggregates that progressively modified the surface topology. Nevertheless, these aggregates did not compromise the curing process or the integrity of the polymer network.

The optical response of the coatings strongly depended on filler concentration. Significant fluorescence emission was observed only for

coatings containing 2 wt.% PCDs, indicating that a threshold concentration is required to achieve detectable luminescent behavior in the cured network. The emission spectra displayed broad bands attributable to the coexistence of differently sized emissive domains and filler–matrix interactions (Figure 2).

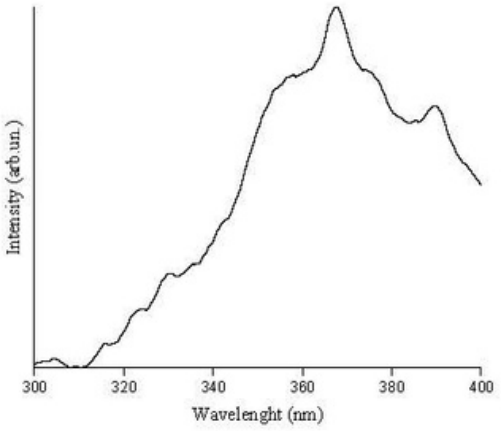

Figure 2. Fluorescence emission of 2 wt.% PCDs-containing film excited at 240 nm.

Differential scanning calorimetry showed that the incorporation of PCDs did not significantly affect the glass transition temperature of the coatings. All systems exhibited Tg values close to 10 °C, indicating that the nanofiller did not alter the crosslinking density or the segmental mobility of the polymer network.
Thermogravimetric analyses revealed a beneficial effect of the nanofiller on thermal stability. Under nitrogen atmosphere, the degradation onset increased from 265 °C for the unfilled coating to 282 °C for the formulation containing 2 wt.% PCDs (Figure 3). Similar improvements were observed under oxidative conditions, where both degradation temperatures and residual char increased with filler loading. These results suggest that the aromatic carbonaceous domains of the PCDs exert a protective effect on the degrading polymer matrix and promote char formation during thermal decomposition.

Conclusions

Polymeric carbon dots synthesized through a sustainable ultrasound-assisted process were successfully incorporated into UV-LED curable coatings based on acrylated epoxidized soybean oil. The obtained composites retained the fluorescence properties of the nanofiller while maintaining complete curing and unchanged crosslinking density.
The incorporation of PCDs enhanced the thermal stability of the coatings and promoted char formation during degradation, while significant fluorescence emission was achieved at the highest filler loading (i.e., 2 wt.%). These findings demonstrate that polymeric carbon dots are promising multifunctional bio-derived nanofillers for the development of sustainable fluorescent coatings suitable for advanced optical and protective applications.

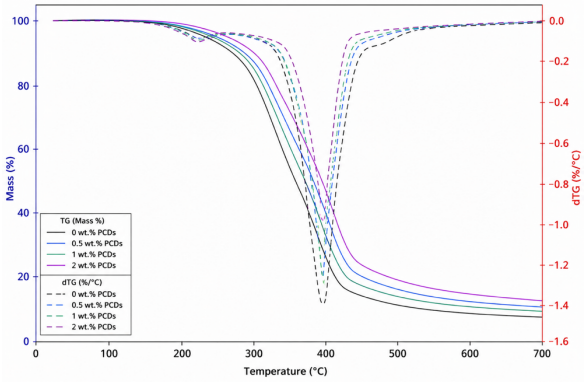

Figure 3. TG and dTG curves of the UV-LED cured coatings (atmosphere: nitrogen).

References

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