DOPO DECORATED MXENE NANOSHEETS FOR FLAME RETARDANT AND REINFORCED PLA COMPOSITE

Y. Zhou [1]*, Y.C. Lin [2], B. Fei [3]

[1] College of Textile and Clothing Engineering, Soochow University, Suzhou, 215123, China;

[2] School of Safety Engineering, China University of Mining and Technology, Xuzhou, 221116, China;

[3] The Hong Kong Polytechnic University, Hong Kong, 999077, China;

* Corresponding author: yuyangzhou@suda.edu.cn (E.mail); +86 18896500651 (Wechat)

Abstract

This study presents a novel and facile strategy for fabricating fire-resistant and tensile enhanced PLA composites using 2D MXene (Ti_3C_2) flakes chemically modified with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). The thermal and burning performances of PLA composites were demonstrated by the limiting oxygen index, UL-94 test, and cone calorimetry. The tensile performances were examined and analysed.

Keywords: PLA; MXene; DOPO; Modification; Flame retardant; reinforcement

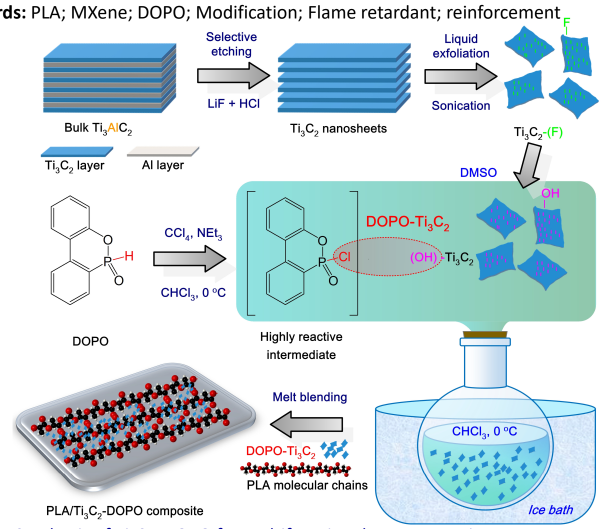


Figure 1 Synthesis of Ti_3C_2–DOPO for multifunctional PLA composites.

Experimental

Functionalization of Ti_3C_2 Nanosheets

The Al of MAX was removed by an etching process. Single or few-layered Ti_3C_2 nanosheets were dispersed in DMSO solution under ultrasound. DOPO was dissolved into the mixture of $CHCl_3$, CCl_4, and NEt_3 (a). Ti_3C_2–(OH) were dispersed in the mixture of $CHCl_3$ and NEt_3 (b). All the mixture (a) was added dropwise to mixture (b) under a nitrogen atmosphere in ice bath. Finally, the sample was purified and subjected to vacuum drying.

Fabrication of PLA/Ti_3C_2–DOPO Composites

PLA composite was fabricated through a melt-blending process. Blends were prepared by mixing granule and Ti_3C_2–DOPO powder on a twin-screw extruder.

Characterizations

XRD; SEM-EDX; TGA; DSC; FTIR; Tensile assessment

LOI; Cone calorimetry; Vertical burning test

Results and Discussion

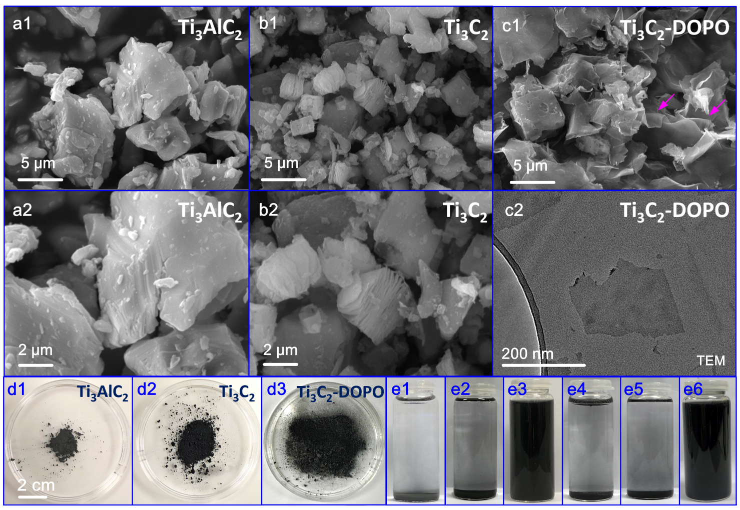


Figure 2 (a1,2; b1,2; c1) SEM images; (c2) TEM image; (d1-3) photos of powders; Dispersions in various solvents: (e1,3,5) Ti_3AlC_2, Ti_3C_2, and Ti_3C_2–DOPO in water, (e2,4,6) Ti_3AlC_2, Ti_3C_2 and Ti_3C_2–DOPO in chloroform.

A special accordion-like morphology with a cross-sectional shear slip of stacked multilayer MXene nanosheets is observed, indicating the removal of Al layer from Ti_3AlC_2. The increased interlayer distance between the individual nanosheets reveals that Al layers are removed leaving multiple thin layers of Ti_3C_2 nanosheets shown in the SEM images.

When exfoliated Ti_3C_2 was dispersed in water and chloroform, the later agglomerated and settled at the bottom of the container, whereas the sample dispersed in DI water remained stable. The dispersive stability of the exfoliated Ti_3C_2 in water is attributed to the electrostatic equilibrium and the interactions of the polar solvent with the –F, –O, and –OH terminations on the Ti_3C_2 nanosheet surfaces, induced by the etching process. After covalent modification of the Ti_3C_2 nanosheets with DOPO, it became highly unstable in water resulting from the existence of the hydrophobic benzene moieties in DOPO.

Results and Discussion

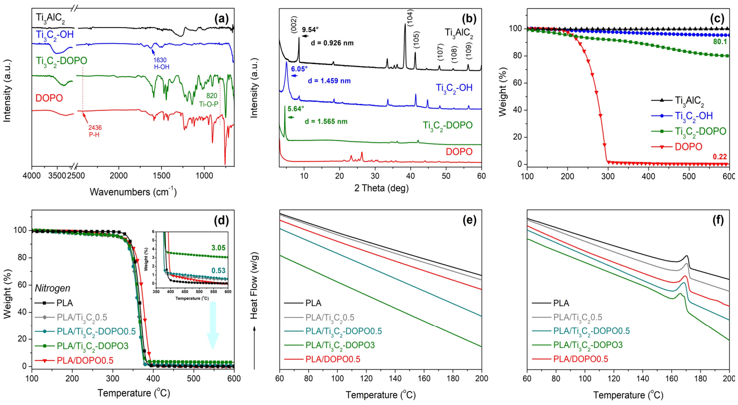


Figure 3 (a) FTIR, (b) XRD, and (c) TGA of Ti_3AlC_2, Ti_3C_2–(OH), Ti_3C_2–DOPO, and DOPO; (d) TGA and (e) cooling and (f) second heating phases of DSC of PLA composites.

The thermal property of pristine PLA and PLA/Ti_3C_2–DOPO composites was evaluated. Pristine PLA showed typical one-stage degradation within a narrow temperature range (307–377℃) with a maximum degradation occurring at 358 ℃. The composite containing 0.5wt % Ti_3C_2 and DOPO, respectively; however, the amount of char residue is quite noticeable. With the introduction of 0.5wt % Ti_3C_2–DOPO in PLA, the composites degraded quite early compared to PLA, however, with a higher char residue.

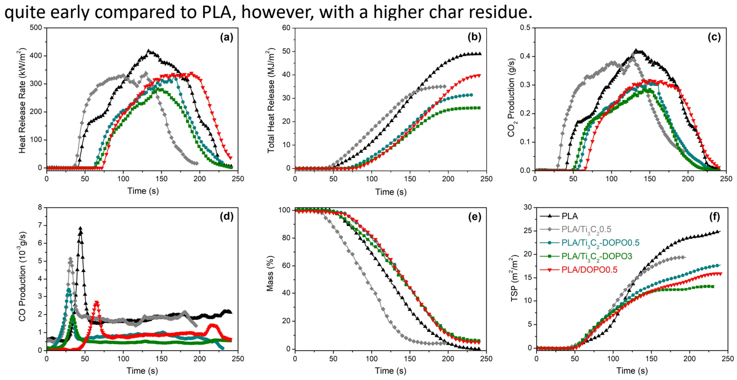
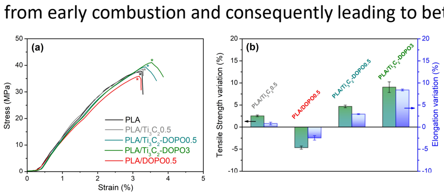


Figure 4 (a) FTIR, (b) XRD, and (c) TGA of Ti_3AlC_2, Ti_3C_2–(OH), Ti_3C_2–DOPO, and DOPO; (d) TGA and (e) cooling and (f) second heating phases of DSC of PLA composites.

Marginal reductions in PHRR are obtained by adding Ti_3C_2 in PLA matrix. PLA/Ti_3C_2 composite exhibited early TTI than PLA due to the catalytic effect of MXene in fire, which is attributable to the oxidation of TiO_2 into its anatase phase under an oxygenated atmosphere resulting in a strong exothermic behavior. PLA/Ti_3C_2 composite had a shorter flame time compared to PLA. Notwithstanding, the PLA/DOPO composite prolonged the burning time than pristine PLA. Ti_3C_2–DOPO composites showed improved FR performance by significantly reducing the PHRR and the THR with the increasing FR content. 3wt % Ti_3C_2–DOPO led to ~34 and ~47% reductions, respectively, in PHRR and THR. PLA/Ti_3C_2 composites had early mass loss compared to PLA due to the catalytic nature of Ti_3C_2 in fire. In contrast, the PLA/DOPO composite remained thermally stable with a gradual mass loss and a higher char residue. The PLA/Ti_3C_2–DOPO composites showed a marginally higher char residue as the content of DOPO-decorated Ti_3C_2 increased in the matrix. The thermally stable char layer served as a barrier that protected the underlying composite from early combustion and consequently leading to better flame retardancy.



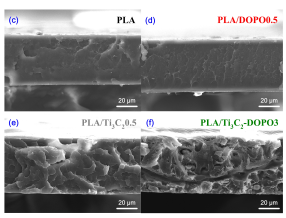


Figure 5 (a) Tensile stress and elongation, (b) variation, (c–f) SEM image of rupture after tensile test.

When Ti_3C_2–DOPO increased to 3 wt %, the tensile properties and the elongation at break of the composites increased, which is due to the strong interfacial adhesions between delaminated MXene decorated by DOPO and their effective dispersion in the PLA matrix.

Conclusion

- 2D MXene (Ti_3C_2) flakes were chemically modified with DOPO to achieve fire-resistant, and tensile-enhanced PLA composites.
- Ti_3C_2–DOPO (3wt %) upgraded PLA to a V-0 rating in the UL-94 test accompanied by slight melt dripping.
- Significant reductions in PHRR (33.7%), THR (47%), peak PCO (58.8%), and TSP (41.7%) were achieved by incorporating 3wt % Ti_3C_2–DOPO into PLA.
- PLA/Ti_3C_2–DOPO (3wt %) showed an increase (~9%) in tensile strength.
- This study presents a novel chemical modification of 2D MXene flakes with DOPO for PLA composites, which is a sustainable way to achieve multifunctional plastics.

Special Issue ''Sustainable Colouration and Functional Finishing of Textiles'' in **Materials** (**IF 3.748**)

Keywords: Sustainable Production; Smart & Functional Textile; Protective Textile; Safety & Ecology of Textile

Welcome for Submission Before 10 February 2023!!!