A SUSTAINABLE SOL-GEL APPROACH FOR THE PREPARATION OF SELF-EXTINGUISHING HYBRID EPOXY NANOCOMPOSITES CONTAINING COFFEE-DERIVED BIOCHAR

A. Bifulco[1], C. Imparato[1], M. Bartoli[2,3,4], I. Climaco[1], M.C. Franchino[1], D. Battegazzore[5], R.A. Mensah[6], O. Das[6], H. Vahabi[7], G. Malucelli[5], A. Aronne[1]

[1] Department of Chemical, Materials and Production Engineering, University of Naples Federico II, 80125 Naples, Italy
e-mail: aurelio.bifulco@unina.it
[2] Center for Sustainable Future Technologies–CSFT@POLITO, 10144 Turin, Italy
[3] Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), 50121 Florence, Italy
[4] Department of Applied Science and Technology, Politecnico di Torino, 10129 Turin, Italy
[5] Department of Applied Science and Technology, Politecnico di Torino, 15121 Alessandria, Italy
[6] Division of Structural and Fire Engineering, Department of Civil, Environmental, and Natural Resources Engineering, Luleå University of Technology, Luleå, 97187 Sweden
[7] CentraleSupélec, LMOPS, Université de Lorraine, F-57000 Metz, France

The improper recycling of polymeric wastes is causing several issues. More waste-to-wealth routes are needed to prepare functional polymer-based products with low contents of flame retardants (FRs). Limiting the concentration of phosphorus (P) in the manufacturing of FR epoxy systems counteracts the rising depletion of natural resources. The use of industrial biowastes (e.g., spent coffee grounds (SCGs)) in combination with other synergists allows for the exploitation of low P loadings (i.e., 1 wt.%) to obtain self-extinguishing epoxy composites, whose matrix undergoes proper sol-gel modification. Herein, we demonstrate that the pyrolysis of SCGs enables the preparation of hybrid epoxy materials showing no dripping V-0 rating in UL 94 tests and a significant decrease (up to ~65%) in the peak heat release rate.

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Introduction

The improper management of polymeric wastes and their recycling is causing serious concerns to both human health and the environment. High-performing polymer-based products can be obtained by waste-to-wealth routes to limit the use of toxic compounds (e.g., flame retardants (FRs)). Epoxy resins show notable chemical resistance and good thermal stability, though most of them are easily flammable [1, 2]. For this reason, to be suitable for aerospace applications, the epoxy resins need to be flame retarded by the addition of halogen- or phosphorus(P)-based FRs. The exploitation of such species results in tougher recycling procedures and the depletion of natural resources. To counter these drawbacks, the scientific community is fostering the use of industrial biowastes as sustainable FRs in epoxy-based composites, where the amounts of P and other functional additives are very low. As spent coffee grounds (SCGs) represent one of the largest produced wastes in the world, herein, we pyrolyzed the SCGs and explored the use of coffee biochar as a FR additive in silicon-modified aliphatic epoxy composites to improve their fireproof performances.

Results and discussion

Following a waste-to-wealth approach, spent coffee grounds can be pyrolyzed into a coffee-derived biochar (CB) and used as a flame retardant additive in epoxy systems. The sol-gel chemistry enables the modification of bisphenol A diglycidyl ether (DGEBA)-based epoxy resins with (3-aminopropyl)-triethoxysilane (APTES) [3]. Through this strategy, silicon-modified epoxy chains are formed and subsequently CB can be uniformly distributed throughout the resin, before curing with a cycloaliphatic amine hardener (Figure 1). The sol-gel methodology also allows for the synthesis of a functional ternary metal oxide (Si-Ti-Mg) with peculiar acidic characteristics. CB can be exploited alone or together with ammonium polyphosphate (APP) and Si-Ti-Mg oxide to improve the thermal, fire, and mechanical performances of the final epoxy composite.

As proved by cone calorimetry (CC) tests, the incorporation of CB into the silicon-modified DGEBA resin results in a notable production of a ceramic char, responsible for a significant decrease in the peak heat release rate (by ~65%, pkHRR) and in the total smoke production (~17%), with respect to the pristine resin.

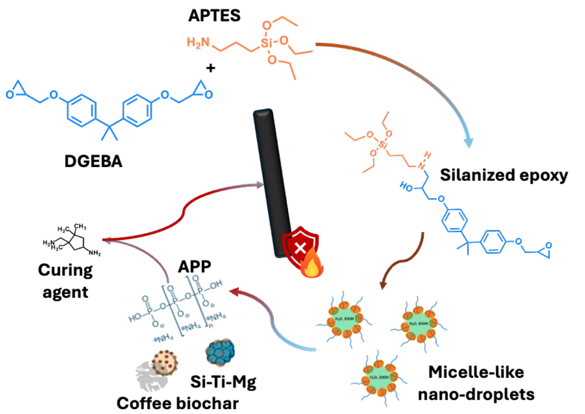

Figure 1: Preparation procedure of the hybrid epoxy material

The hybrid epoxy formulation containing 20 wt.% CB, together with APP and Si-Ti-Mg oxide, allows for the preparation of no dripping self-extinguishing (UL 94-V-0 rating) hybrid epoxy nanocomposites with only 1 wt.% of phosphorus content. However, the flammability tests reveal that CB was crucial in reducing the extinguishing times after flame application. The presence of acidic moieties, CB, APP, and Si-Ti-Mg oxide in the hybrid epoxy system accounts for a strong reduction (up to 42%) in pkHRR values, a slower decomposition rate, and a remarkable increase (up to 35%) in flexural modulus. Raman spectroscopy, microscopy analysis, and the morphological study of the residual chars support a strong flame retardant action in the condensed phase, exerted by all the additives. CB, APP, and Si-Ti-Mg oxide cause the formation of a graphitized continuous char containing N–P–O–Si substructures [3, 4], working as heat and oxygen barrier during the decomposition of the epoxy matrix (Figure 2).

Figure 2: Flame retardant action of additives in the condensed phase during the combustion

The values of CO/CO_2 ratios, measured by CC tests, additionally confirm a predominant flame retardant action in the condensed phase exerted by CB and the other fillers. Their combined mode of action provides an effective synergism in the flame retardation of the hybrid epoxy resin [3, 5].

Conclusions

The synthesis of silicon-modified hybrid epoxy moieties into the polymer matrix enables a good distribution of the biowaste throughout the system. Besides, the combined use of a properly designed ternary metal oxide contributes to limiting the amount of required phosphorus-based flame retardant to obtain epoxy composites with improved fire behavior and good mechanical properties. This strategy may inspire future developments of more flame retardant thermosets, whose self-extinguishing capability is achieved by low concentrations of phosphorus and different types of biowastes.

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