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Hybrid Strategies for the Improvement of the Flame Retardancy of in-situ Silica-Epoxy Nanocomposites cured with Aliphatic Hardener

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Abstract
The aerospace industry requires materials showing good mechanical performance, durability, and thermal stability to satisfy very stringent requirements in several applications. Epoxy-based composites can be a suitable solution, due to the peculiar characteristics of the polymer matrix. Epoxy resins can be cured by aliphatic or aromatic hardeners. The use of aliphatic amines is preferable because of their lower toxicity, though these curing agents are easily flammable. Recently, hybrid systems conjugating in-situ modified epoxy matrix with organic and inorganic additives have been developed to flame retard aliphatic epoxy composites. This short review summarizes some applications of such strategies, which are based on the use of the sol-gel technique, DOPO-based flame retardants, bio-waste compounds and other synergists. The review describes the main concept of this approach and the preparation of no-dripping self-extinguishing silica-epoxy hybrid composites showing low phosphorus loadings, tailored interphases and good mechanical properties.

1. Introduction

Epoxy resins are used in a wide range of industrial applications. These polymers have many advantages, mainly chemical resistance, thermal stability and easy processing [1]. The manufacturing of epoxy-based composites can involve the use of aliphatic, cycloaliphatic or aromatic curing agents. Aliphatic epoxy resins allow for the production of more flexible and sustainable materials, though their easy flammability represents a significant limitation for their use in the aerospace industry, where stringent requirements must be satisfied in terms of fire behavior. For this reason, in the past, halogen-based flame retardants have been incorporated into aliphatic epoxy resins to achieve very good standards [2]. From an environmental point of view, the decomposition of composites containing such halogen-based compounds releases a huge amount of toxic species, which are normally very effective in terminating the oxygen radicals in the flame. Conversely, the use of phosphorous-based flame retardants can represent a greener alternative to halogen ones, as they inhibit flame propagation mainly through

phosphorus-based radicals. The depletion of natural sources, such as phosphorus, is moving the scientific community towards the development of strategies allowing excellent fire performances, keeping low amounts (i.e., 1, 2 wt.%) of phosphorous in the aliphatic epoxy composites. Recently, some methodologies have been proposed in the literature, in which the in-situ generation of silica crystalline domains coupled with the use of phosphorous-based flame retardants, particularly derivatives of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) resulted in no-dripping self-extinguishing (V-0 rating in UL-94 vertical burning tests) epoxy materials, even with a very low phosphorus loading (2 wt.%) and an aliphatic amine as a hardener (i.e., isophorone diamine) [3, 4]. This hybrid flame retardant approach, involving the combined presence of an in-situ inorganic phase and phosphorous-based compounds, has been further explored through the use of a bio-waste derived material as a flame retardant [5]. In particular, humic acid has been very well dispersed into a modified aliphatic epoxy system, together with ammonium polyphosphate (APP) and urea, to prepare sustainable composites showing no dripping phenomena during their combustion and UL-94 V-0 class with only 1 wt.% of phosphorus content [6]. This short review aims to describe the application of hybrid strategies for the preparation of flame retarded DGEBA (Bisphenol A diglycidyl ether)-based epoxy composites cured with aliphatic hardener. The concept of these strategies will be elucidated and the main outcomes resulting from some case studies in terms of flame retardance and sustainability, with a special focus on the perspectives for the preparation of new advanced materials will be summarized.

2. Growing of silica crystalline domains in the flame retardation of aliphatic epoxy systems

DGEBA-based epoxy resins can be modified through reaction with APTES (3-aminopropyltriethoxysilane) to obtain hybrid organic-inorganic epoxy moieties (i.e., silanized epoxy), where the primary amino group of the coupling agent opens the oxirane rings. This sol-gel modification allows for conferring some polar characteristics to the DGEBA epoxy chain, as the APTES bears three ethoxy groups in its chemical structure. These three ethoxy groups can condensate with TEOS (tetraethyl orthosilicate), a well-known silica precursor, to start the formation of an in-situ SiO_2 phase by sol-gel reactions (Figure 1).
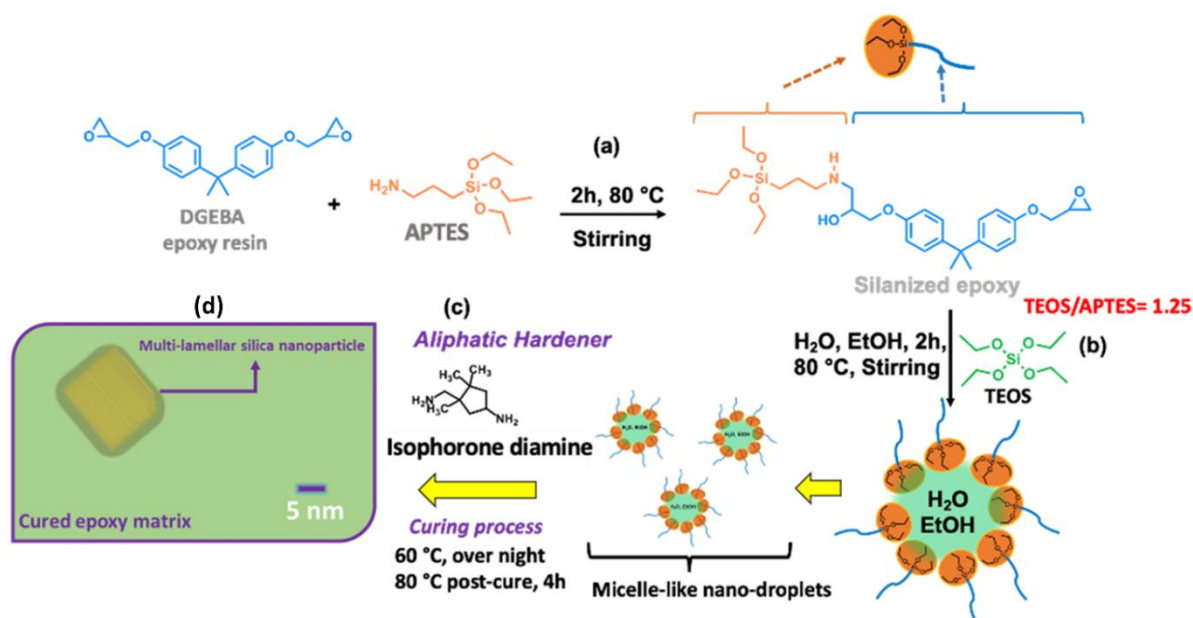

Figure 1. Overall synthesis procedure for the generation of silica crystalline domains in epoxy matrix: (a) generation of the silanized epoxy; (b) addition of the silica precursor; (c) curing process; (d) representation of multi-lamellar silica nanoparticle from morphological investigation.

More in detail, silica-epoxy nanocomposites were prepared by using APTES and TEOS in a molar ratio of 1.5 to generate 6 wt.% of silica nanoparticles in the epoxy matrix. Interestingly, the morphological investigation revealed that the nanoparticles showed a well-ordered multi-lamellar shape, with an intersheet size of about 0.34 nm, and were finely dispersed throughout the matrix in a hybrid co-continuous network (Figures 1 and 2) [7]. The addition of water and ethanol led to the generation of inverse micelle-like nano-droplets (composed of the epoxophilic hybrid organic-inorganic epoxy moieties) acting as nuclei for the formation of nanocrystalline domains. These latter are suitable nanoenvironments for hydrolysis and condensation reactions of silica precursors. Through a mechanism of nucleation and subsequent aggregation, the nanocrystalline domains can arrange in multisheet lamellar silica-based nanoparticles. It is reported in the literature that the generation of crystalline phases in amorphous epoxy resin usually requires surfactants and high temperatures [8, 9]. On the contrary, the developed sol-gel approach does not involve the use of surfactants and allows for keeping mild operative conditions. The addition of isophorone diamine stops the growing of multisheet silica-based nanoparticles and starts the curing process of the silica-epoxy nanocomposite (Figure 1). Bifulco et al. also prepared aliphatic silica-epoxy nanocomposites on the bases of the same sol-gel approach. The nanocomposites showed high transparency and the presence of a hybrid co-continuous network embedding silica nanoparticles (~1.25 nm in size) in a fully condensed system. Also, the silica-epoxy nanocomposites exhibited no dripping during the UL-94 vertical flame spread tests and a ~40% decrease in the heat release rate (HRR) in cone calorimetry tests with only 2 wt.% of silica loading [10].
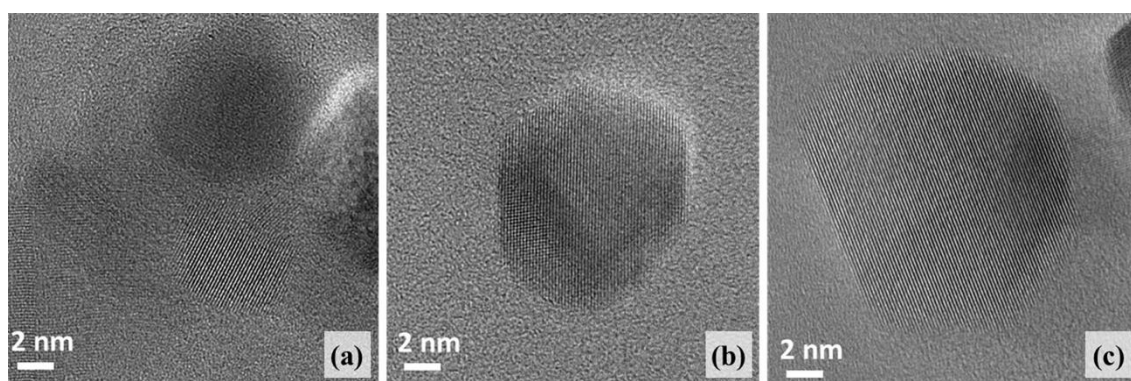

Figure 2. High-resolution transmission electron microscopy (HRTEM) images. (a), (b) and (c) report HRTEM images of multisheet lamellar silica-based nanoparticles in the silica-epoxy nanocomposite.

The above reported sol-gel methodology can be also applied by using a magnesium-based precursor (i.e. magnesium ethoxide) to generate a different inorganic phase embedded in a hybrid epoxy network. It is well known that metal hydroxides are suitable flame retardant compounds. These latter decompose during the combustion releasing metal oxides and water molecules, which cause a thermal shielding effect and a dilution of the flammable species in the gas phase, respectively. By performing a similar procedure reported in Figure 1, epoxy systems containing in situ synthesized $Mg(OH)_2$ nanoparticles were prepared [11]. The synthesis route is a solvent-free one pot procedure (Figure 3) and allows for the generation of $Mg(OH)_2$ nanocrystals showing nanometric structures with an intersheet size of about 0.43 nm, which is approximately the lattice spacing of $Mg(OH)_2$ (001) planes. Thermal analysis revealed that the in-situ formed $Mg(OH)_2$ nanofiller at 5 wt.% loading in the epoxy nanocomposites was responsible for an anticipation of the degradation onset, though it allowed producing a quite stable char, hence greatly increasing the residues at the end of the tests performed in inert atmosphere [11].
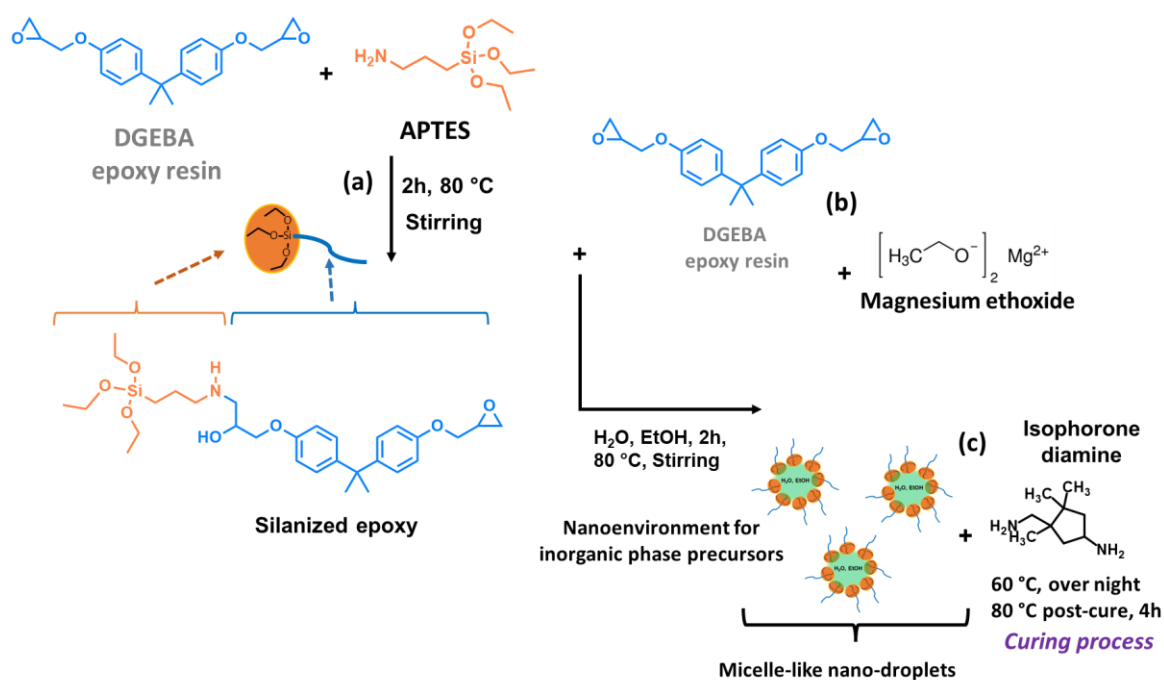
Figure 3. Overall synthesis procedure for the preparation of epoxy nanocomposites containing Mg(OH)$_2$ nanocrystals: (a) generation of the silanized epoxy; (b) addition of magnesium-based precursor (i.e. magnesium ethoxide) in the polymer matrix for its dispersion; (c) curing process.

3. Flame retardation of silica-epoxy nanocomposites cured with aliphatic hardener and containing DOPO-derivative flame retardants

9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) is a phosphorus-based flame retardant that is largely used in the flame retardation of epoxy systems. DOPO can react with oxirane rings modifying the epoxy chain through the introduction of phosphorus species along the structure. Such modification results in a detrimental effect on the glass transition temperature of the epoxy material, as it limits the crosslinking degree. Therefore, the scientific community has developed several DOPO derivatives, which are unable to react with epoxy resin but can still confer improved fire behavior to the final product [12]. Zhang et al. prepared self-extinguishing (UL-94 V-0 flammability class) DGEBA-based composites cured with diamino diphenyl methane (i.e., an aromatic curing agent) through the addition of 9.1 wt.% 6H-dibenz[c,e][1,2]oxaphosphorin,6-[(1-oxido-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-yl)methoxy]-,6-oxide (DP) to the epoxy matrix [13]. The research group also observed a remarkable increase in the limiting oxygen index and a significant decrease in the peak of the heat release rate. Differently, Bifulco et al. modified the DGEBA epoxy resin by following a similar procedure reported in Section 2 and synthesized no dripping self-extinguishing systems cured with isophorone diamine (cycloaliphatic amine), exploiting the incorporation of 17.3 wt.% of DP (which means 2 wt.% of P loading) and the in-situ generation of 2 wt.% of silica nanoparticles (Figure 4). This hybrid flame retardant strategy also involved the use of a nitrogen source (i.e., melamine) to obtain a combined effect of silica and P-N synergism on the fire behavior of the final composites. Despite the use of a more flammable hardener, silica-epoxy nanocomposites showing not only a UL-94 V-0 rating but also a strong reduction (up to 80% with respect to pristine resin) in the HRR measured by cone calorimeter tests were successfully obtained [3, 14].
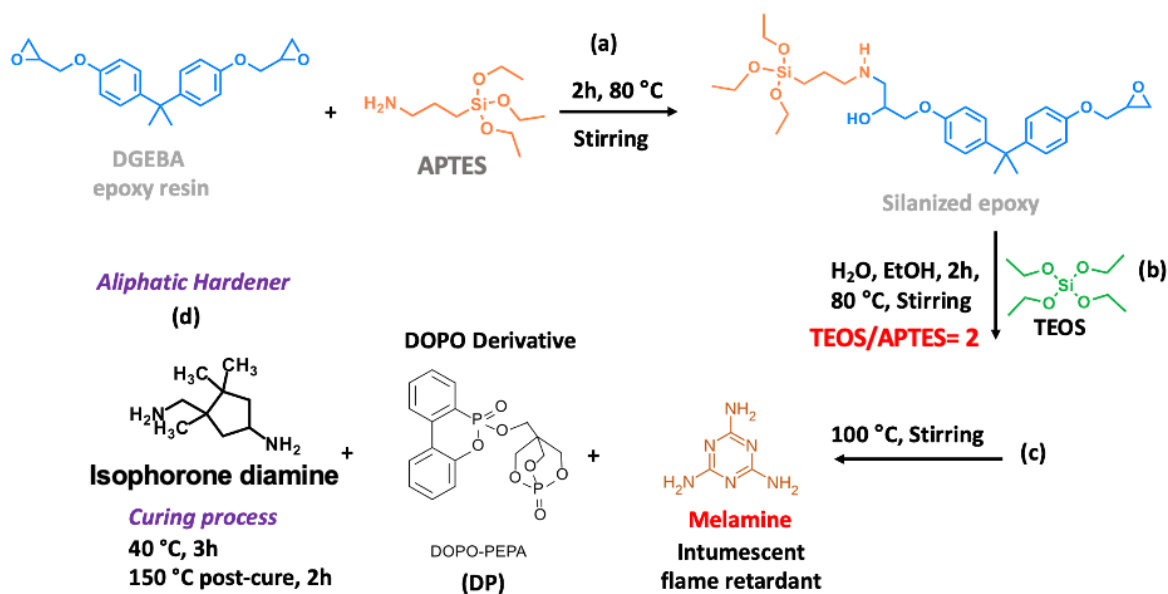
Figure 4. Overall synthesis procedure for the preparation of silica-epoxy nanocomposites containing DP and melamine: (a) generation of the silanized epoxy; (b) addition of the silica precursor; (c) incorporation of intumescent and phosphorus-based flame retardants; (d) curing process.

Bifulco et al. further investigated the beneficial effect resulting from the application of the sol-gel approach illustrated in Section 2. In particular, DP was replaced with 3-(6-oxidodibenzo[c,e][1,2]oxaphosphinin-6-yl)propenamide (DA, 22 wt.% in the DGEBA epoxy resin), which is another DOPO-derivative composed of amide groups (Figure 5). The use of DA also guaranteed no-dripping self-extinguishing capability, though the combined presence of in-situ silica nanoparticles and melamine was crucial to achieve UL-94 V-0 rating [14].
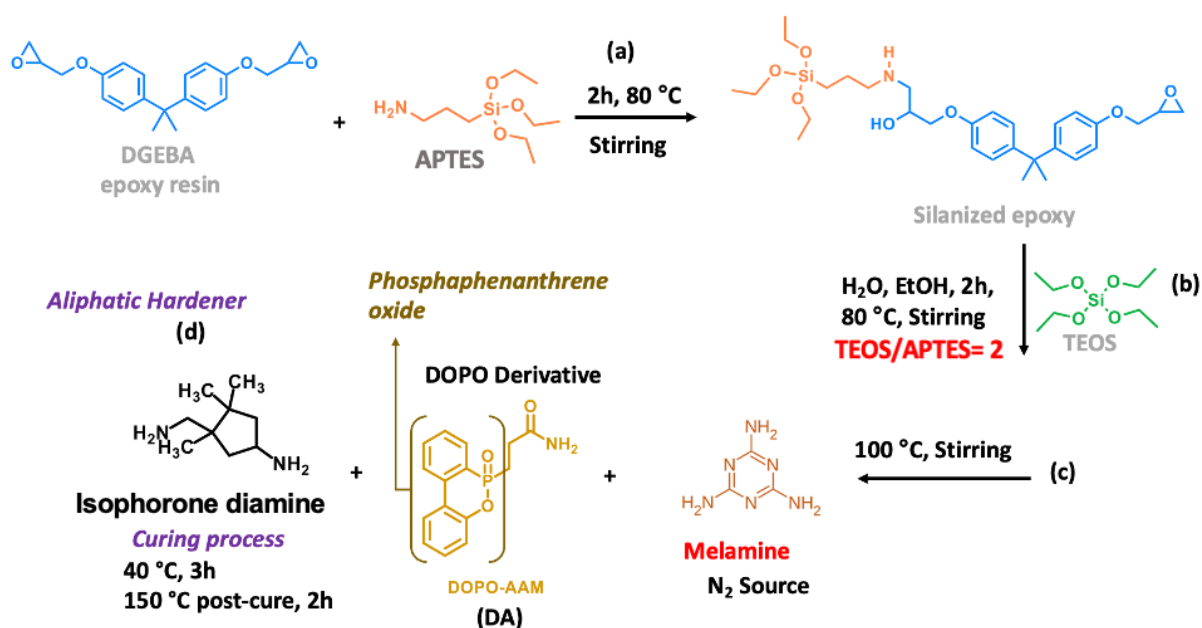

Figure 5. Overall synthesis procedure for the preparation of silica-epoxy nanocomposites containing DA and melamine: (a) generation of the silanized epoxy; (b) addition of the silica precursor; (c) incorporation of intumescent and phosphorus-based flame retardants; (d) curing process.

The incorporation of DA/DP did not affect the curing process, as the differential scanning calorimeter curves did not show any residual exothermic peak. The amide groups in the chemical structure of DA confer some polar characteristics to this flame retardant, which negatively impacted the interactions between cured epoxy chains and thus their arrangement in the matrix [15]. Nuclear magnetic analysis proved that the reduction (~35%) in the glass transition temperature caused by DA was due to a plasticizing effect and did not concern any reaction with oxirane rings. On the other side, the presence of P=O groups in DP allowed for the establishment of hydrogen bonding interactions with OH species formed during crosslinking reactions, resulting in an increase (~9%) of the glass transition temperature compared to the unmodified epoxy systems [14]. The application of the flame retardant hybrid strategy, involving the modification of the epoxy resin with the in-situ generation of silica nanoparticles and the addition of phosphorus-based additive into the matrix, significantly influenced the thermal behavior of the aliphatic epoxy system. In particular, the silica-epoxy nanocomposites containing DA/DP and melamine (as nitrogen source) as co-additive showed an earlier decomposition stage, due to the generation of acidic phosphorus compounds during the decomposition of DOPO-derivatives, the acidity of the sol-gel based silica nanoparticles and the release of nitrogen and phosphorus species able to boost the degradation of the thermosetting resin. The incorporation of DA/DP into the silica-epoxy matrix positively affected the overall thermal stability of the composites, leading to the production of abundant aromatic char at high temperatures. Composites containing DA/DP showed an increase of up to 13% of the char formed as assessed by thermogravimetric measurements, mainly ascribed to the combined effect of sol-gel silica nanoparticles and acidic phosphorus species, promoting the dehydration process of the epoxy resin and thus the char formation [4].

Bifulco et al. found that the minimum loading of phosphorus required to achieve non-dripping UL-94 V-0 rating was 2 wt.%. Particularly, DP alone could already prevent the occurrence of dripping phenomena, whereas the use of DA together with melamine and silica nanoparticles was necessary to obtain a similar result. Melamine acted as an intumescent flame retardant and its dilution effect on flammable gases contributed to lowering the flammability of composites [16]. The silica-epoxy nanocomposite containing DA did not capture the flame, because of the strong gas phase activity exerted by the flame retardant from the first decomposition steps. Conversely, DP needed the combined action of melamine to positively affect the flammability of composites. Concerning the cone calorimetry tests, only the use of DA/DP could guarantee a decrease in HRR up to 70% with respect to the pristine resin, though the presence of silica nanoparticles was crucial to prevent dripping and lower the mass loss rate and total heat release parameters of the systems. The incorporation of DA with melamine into silica-epoxy nanocomposites led to an increase of CO/CO_2 compared to unmodified epoxy, supporting a significant gas phase activity. Unlike DA, the use of DP caused the generation of a notable amount of char and a low value of CO/CO_2, revealing a prevalent condensed phase mechanism. The formulations characterized by DA/DP, in-situ generated silica nanoparticles and melamine showed a strong delay in the time to ignition (up to 50%), as well as in the time to peak of the heat release rate. The presence of melamine was responsible for the production of an intumescent char with multicellular morphology, hence behaving as a very effective thermal insulator. Since DA acted mainly in the gas phase compared to DP, the combustion of silica-epoxy nanocomposites containing DA and melamine gave rise to a high value of total smoke release, also due to the flame inhibitors released in the gas phase. Finally, DA/DP also negatively affected the toughness, the elongation at break and the fracture strength of the final composites, though the flame retardants accounted for a higher (up to +30%) Young modulus with respect to the pristine resin.

4. Flame retardation of sustainable APTES-modified epoxy system containing humic acid as bio-waste flame retardant

Nowadays, a sustainable approach to the development of new functional materials is mandatory. In addition, the depletion of such natural resources as phosphorus is moving the scientific community to look for alternatives to phosphorus-based flame retardants. To face this challenge, the use of bio-wastes as flame retardants seems to be a promising methodology. This approach allows for low-cost

manufacturing processes and promotes the spreading of circular economy. In this context, due to its highly polar chemical structure, humic acid has been selected as a suitable additive to enhance the flame retardancy of epoxy-based composites. Humic substances are fully decomposed remains of organic life, mainly consisting of three components: humic acids, fulvic acids and humin. To investigate the fire response of epoxy composites containing humic acid, Liu et al. prepared complexes of the bio-waste material with four metal ions and added them to a DGEBA epoxy system [17]. The combined use of the metal ions together with the humic acid boosted the charring formation during the combustion, resulting in a strong decrease of the limiting oxygen index as well as of the peak of the heat release rate compared to the pristine resin. Despite the good fire behavior, Liu et al. could not achieve UL-94 V-0 rating. To obtain self-extinguishing epoxy composites cured with isophorone diamine and containing humic acid, Venezia et al. modified DGEBA by reaction with APTES, to improve the dispersion of the bio-waste throughout the whole polymer matrix, and applied a hybrid flame retardant strategy (Figure 6), similar to the one reported in Section 2 [6].
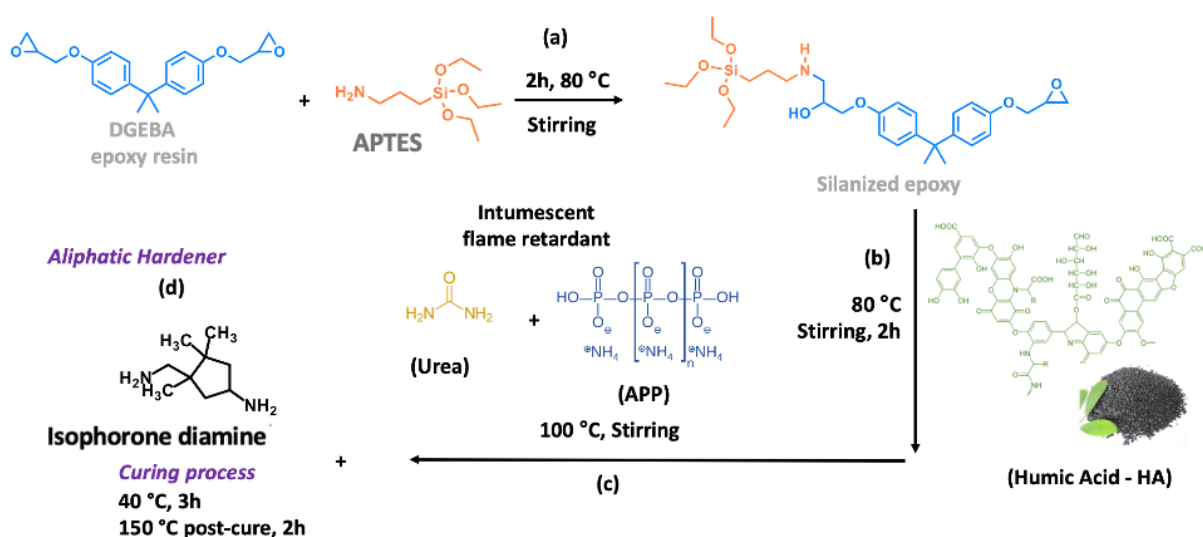

Figure 6. Overall synthesis procedure for the preparation of APTES-modified epoxy nanocomposites containing humic acid, ammonium polyphosphate and urea: (a) generation of the silanized epoxy; (b) addition of the bio-waste flame retardant; (c) incorporation of intumescent and phosphorus-based flame retardants; (d) curing process.

Venezia et al. achieved UL-94 V-0 rating by the addition of 6 wt.% of humic acid and 1 wt.% of phosphorus content into APTES-modified epoxy nanocomposites. Samples with humic acid only burned without any dripping during the flammability tests. The cone calorimetry tests allowed for assessing the influence of APP and urea on the fire behavior of final composites. The combined use of APP and humic acid promoted the dehydration of the epoxy resin, which led to an abundant production of char during the combustion. Conversely, urea acted as an intumescent flame retardant affecting the flammability limits through a strong dilution of the gas phase. The combined effect of APP, humic acid and urea resulted in a significant decrease in the peak of the heat release rate (up to 52%) and a notable delay of the time to ignition (up to 21%), accounting for a higher glass transition temperature compared to pristine resin and unchanged mechanical performances [6].

5. Conclusions
This short review has summarized some of the main applications of hybrid flame retardant strategies, which allow for flame retarding aliphatic epoxy systems through a combination of in-situ generation of silica nanostructures and the incorporation of phosphorus-based additives. The presence of silica nanoparticles, finely and widely distributed throughout the polymer matrix, allows for preventing

dripping phenomena and generates an effective thermal insulating char. Also, these strategies lead to a significant delay in the time to ignition through a P-N synergism, rising from the addition of an intumescent flame retardant into the epoxy system. Harnessing the sol-gel technique with an accurate choice of precursors and operating conditions offers the possibility of controlled and flexible chemical modifications of the epoxy matrix. Its modification by coupling agents guarantees a better dispersion of polar additives, paving the way for the use of bio-waste compounds as flame retardants. The application of these hybrid flame retardant strategies makes possible the preparation of aliphatic epoxy composites exhibiting self-extinction without dripping, low phosphorus loadings and enhanced sustainability.

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