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Synthesis of biobased phosphorus-containing flame retardants for epoxy thermosets comparison of additive and reactive approaches

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ABSTRACT

This study presents a two-steps synthesis of novel additive or reactive phosphorus-and-sulfur-containing flame retardants (P-FR) for epoxy thermosets. The first step consists in totally epoxydizing the phloroglucinol. Then, the epoxy functions grafted are partially or totally open by a thiol bearing a phosphonate group to obtain a reactive P-FR and an additive P-FR respectively. The two synthesized P-FR are then incorporated into a DGEBA-IPDA matrix according to an appropriate approach. The impact of these P-FR on glass transition temperature (Tg) is assessed by DSC. Tg values exhibit the plasticizing effect of the additive P-FR and the loss of epoxy functionality due to the incorporation of the reactive P-FR. The thermal properties of the prepared thermosets are characterized by TGA, showing the more efficient action of the reactive P-FR in condensed phase (charring). TGA-FTIR coupling show the presence of phosphorus-containing gases released during the thermal degradation but these P-containing gases have no radical scavenging action in the gas phase. PCFC analyses prove the similar flame retardant properties of the two P-FR by reducing significantly the pHRR, the THR and the EHC. The cone calorimeter tests exhibit a strong intumescent effect of the residue brought by the two P-FR, leading to insulating expanded residue.

1. Introduction

Epoxy resins are an important part of the thermosets market and are widely used for their characteristics, such as excellent mechanical properties, adhesion or thermal resistance and they have many applications as adhesives, coatings, electronic components and materials for energy. Epoxy resins in combination with fibers are also used as matrix of composites used in sports and aeronautic industries. However, the flammability of these resins is one of their main drawbacks and requires the systematic introduction of flame retardant compounds (FR) in their formulation, allowing them to meet the fire standard.

Until recently, most of the organic flame retardants used in epoxy materials were halogenated additive systems, which present several disadvantages mainly due to the presence of halogen atoms. Indeed, beyond their intrinsically toxicity, the combustion of halogenated FR produces toxics and corrosive smokes. Since 2008, new restrictions of halogenated products were imposed by REACH [1] or RoHS [2] regulations. Organophosphorus compounds are a good alternative to halogenated FR due to their combined modes-of-action (charring of the condensed phase/radical scavenging in the gas phase). Moreover, their chemical structure (degree of oxidation, aliphatic/aromatic nature of the substituent groups, molecular weight …) can be varied to fit with the polymer matrix in which they are incorporated. It is important to note that phosphorus FR release much less toxic compounds than halogenated ones.3 Currently, phosphorus-containing FR (P-FR) represent an important part of flame retardant market [4] and are currently the most studied FR systems. Our team reported [5] the synthesis of some biobased phosphorus-containing additive flame retardants by grafting phosphate functions onto hydroxyl groups of phloroglucinol. This study highlighted the potential of these compounds to improve the thermal behavior of epoxy thermosets. However, it also showed that some incompatibility issues between the additive FR and the flame-retarded matrix may be encountered, leading to

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phase segregation [5] and opacity of the material.

Moreover, the additive character of these low molecular weight FR gives them mobility in the thermoset network, that may lead to their migration to the material surface and forward to a decrease of the fire performance. A plasticizing effect of the thermoset network is also often observed [5], leading to a decrease of its mechanical properties.

In opposition to this additive approach, the reactive approach consists in covalently bonding the matrix and the FR. These bondings avoid the mobility of the FR and allow a permanent fire behavior of the epoxy thermoset. Moreover, we showed [6] that the covalent bonding prevents the phase segregation and probably the leaching. To provide this covalent bonding, different functions can be used. Indeed, the literature shows that phosphorus moieties can be brought either from epoxy monomers or from the curing agents, i.e. compounds bearing functions which are able to react with oxirane cycle, carboxylic acid, anhydride, alcohol, thiol [7] or amine. For instance, Ren et al. [8] synthesized a diepoxy phosphorus-containing aromatic FR, Braun et al. [9] focused their study on the synthesis of phosphorus-containing diamine and used it as curing agent in epoxy resin. Xie et al. [10] carried out a two step synthesis of novel reactive phosphorus-containing curing agent, bearing a hydroxyl group and a secondary amine.

To the best of our knowledge, no biobased reactive P-FR commercially used in epoxy matrix [11,12] has been reported so far. Recently, some studies of the literature have reported the synthesis of biobased cross-linkers and epoxy monomers containing phosphorus moieties for epoxy thermosets. Gu et al. [13] synthesized phosphorus-and-nitrogen containing diol from vanillin functionalized with DOPO (9,10-dihydro-9-oxy-10-phosphaphenanthrene-10-oxide). Ma et al. [14] grafted DOPO on the C=C double bond of glycidylated itaconic acid to afford both aromaticity and phosphorus content. Lligadas et al. [15] also grafted DOPO onto glycidylated fatty acid derivatives. To favor the stability and charring of the polymer, it should be noted that the phosphorus moieties and the aromaticity are mainly brought by the DOPO, i.e. a synthetic chemical.

It is also possible to use an aromatic biobased raw material. Phenolic products coming from lignin depolymerization exhibit the required aromatic structure and are easily available. Indeed, lignins are the second most abundant raw polymer in nature and the most abundant aromatic polymer.

The action of the P-FR depends upon several parameters as the oxidation state of the phosphorus atoms [9] and in most cases the action in the condensed phase is preferred. Indeed, the amount of carbon stored in the char does not feed the combustion and reduces the heat released during the combustion, slowing the propagation of the fire. Moreover, the char formed can protect the material acting as a barrier to the heat flux and gas flow. Thus, the charring effect of the epoxy thermosets during their thermal decomposition appears as the key parameter of their flame-retardancy. The covalent bonding brought by the reactive approach could favor the charring effect. Recently, Szolnoki et al. [16] reported a study which compares the additive approach to the reactive one in epoxy thermoset using a phosphorus-containing diamine (curing agent) as reactive P-FR and the ammonium polyphosphate as additive P-FR, showing that a lower phosphorus content is required to reach the V-0 grade at UL-94 test by the reactive approach. However, the P-FR systems used possess different chemical structures which can influence the results. Schartel et al. [17] reported a comparison between the two approaches with P-FR systems based on DOPO. The authors showed that additive P-FR volatilizes at the beginning of decomposition even if interactions between the additive and epoxy resins were also observed. On the contrary, most of the phosphorus remained in the condensed phase when it was covalently linked to the network. However, the used additive and reactive P-FR present different phosphorus-containing groups. Indeed, the synthesis of the reactive P-FR transforms the P–H bond of the DOPO in a P–C bond which is more thermally stable.

The present study aims to assess the influence of the covalent bonding between the FR and the matrix, comparing the additive approach to the reactive one with two biobased P-FR of comparable chemical structures, with the same phosphorus-containing groups.

Concerning the syntheses of the P-FR, both are obtained from the same biophenol, which is totally functionalized with reactive groups. Then, the reactive functions are partially or totally functionalized by a phosphorus-containing moiety, leading both to a reactive P-FR and to an additive P-FR respectively. These two P-FR are then incorporated in epoxy matrix according to the appropriate approach, i.e. additive or reactive. The flame retardant properties of the obtained thermosets are then characterized from small scale (TGA and PCFC) to bench scale test (cone calorimeter).

2. Experimental part

2.1. Reagents

Phloroglucinol, epichlorhydrin, benzyltriethylammonium chloride (TEBAC), diethylallyl phosphonate, thioacetic acid, triethylamine and acetonitrile were purchased from Sigma–Aldrich. Potassium cyanide and benzophenone were purchased from Alfa Aesar. For epoxy resins components, diglycidylether of bisphenol A (DGEBA) resin and isophorone diamine (IPDA) as curing agent were purchased from Sigma–Aldrich.

2.2. Characterizations

Chemical structures of the prepared compounds were determined by ^{31}P NMR, ^{13}C NMR (IG) and ^{1}H NMR spectroscopy in a Bruker Avance 400 MHz spectrometer at room temperature in DMSO-d_6 solutions. External references were tetramethylsilane (TMS) for ^{1}H NMR and ^{13}C NMR and phosphoric acid (H_3PO_4) for ^{31}P NMR. Shifts are given in ppm.

UV irradiation was performed in a Rayonet RPR-200 UV reactor equipped with a cooling fan and 16 lamps of 35 W each with $\lambda_{max} = 254$ nm. Thermogravimetric analyses (TGA) were performed using a Pyris 1 TGA Perkin Elmer at a heating rate of 10 °C/min under nitrogen atmosphere. TGA-FTIR (Fourier Transformed Infrared spectroscopy) coupling was carried out using a Setaram Setsys Evolution TGA (heating rate 10 °C/min, nitrogen flow 100 ml/min) and an FTIR apparatus ThermoScientific Nicolet Is10 (resolution 0.5 cm^{-1}, wavenumber range 400–4000 cm^{-1}).

Differential Scanning Calorimetry (DSC) analyses were carried out using an NETZSCH DSC200F3 calorimeter. Constant calibration was performed using Indium, n-Octadecane and n-Octane standards. Nitrogen was used as the purge gas. The thermal properties were analyzed at 15 °C/min between 20 and 200 °C to observe the glass transition temperature determined as the inflexion value in the heat capacity jump and the residual curing.

Samples were observed using an FEI Quanta 200 scanning electron microscope with the Energy Dispersive X-Ray spectroscopy (EDX) using Oxford INCA Energy 300 system and a detector of 133 eV (at Mn). Samples were characterized after metallization in high vacuum sputtering metallizer Bal-Tec CED 030 Blatzer.

Flammability was assessed using a Pyrolysis-Combustion Flow Calorimeter (PCFC) from Fire Testing Technology (FTT UK). About 3 mg was placed in the pyrolyzer, undergoing an increase of temperature from 20 °C to 750 °C at 1 °C/s under a nitrogen flow. Decomposition gases were sent to a combustor heated at 900 °C under air flow ($N_2/O_2 = 80/20$). At this temperature and with 20% of