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Synthesis of new flame-retardants by radical chain transfer copolymerization of glycidyl methacrylate and dimethoxy-phosphorylmethyl methacrylate

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ABSTRACT

We present a new and original approach to prepare flame retardants (FR) compounds. The strategy adopted consists first in synthesizing new reactive phosphorus-containing oligomers and then to chemically graft them to an epoxy network. These reactive FR compounds are synthesized by radical chain transfer copolymerization of dimethoxy-phosphorylmethyl methacrylate (MAPC1) with glycidyl methacrylate (MAGLY). Reactivity ratios were determined $r_{\mathrm{MAPC1}} = 0.78$ and $r_{\mathrm{MAGLY}} = 1.28$ at 80 °C. The molecular weight of all the (co)oligomers was calculated by steric exclusion chromatography between 1000 and 3000 g mol^{-1}. The synthesized FR were incorporated into an epoxy matrix as reactive binders. Then these formulations were cured at high temperature and the cross-linking densities were determined by DSC. The thermal properties and burning behaviors of cured epoxy resins were investigated. Thermogravimetric analysis showed a small decrease in thermal stability accompanied by a 50% increase in char yield. Pyrolysis combustion flow calorimetry (PCFC) was also used to evaluate the flammability of the modified epoxy resin. A significant decrease in peak of heat release rate (pHRR) and total heat release (THR) was observed. Indeed, with 3‰$_{w}$P, the THR was reduced by 25% and the maximal heat release rate by 60% compared to the reference. These results demonstrate the good flame retardant properties of reactive oligomers in epoxy matrix.

1. Introduction

Epoxy resins are an important part of the thermosets market. They are widely used for their characteristics, such as excellent mechanical properties, adhesion or thermal resistance and have many applications in adhesives industry, coatings, and electronic components. Epoxy resins in combination with fibers are also used as a matrix to form composites used in sports and aeronautic industries. In order to expand their applications and to respect new standards, it is required to adjust their properties by introducing additives. Thus, plasticizers, compatibilizers, crosslinking agents or fillers can be used to tailor mechanical, adhesion or rheological properties. Flammability is directly dependent on the chemical structure of the polymeric matrix and can be modified by adding flame retardants. Phosphorus compounds are currently the most studied FR because of use restrictions of halogenated products imposed by REACH or RoHS regulations [1,2].

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They can act in condensed phase and/or gas phase where they release low toxic compounds [3,4]. The modes of action of phosphorus FR depends on their molecular weight and oxidation state of the phosphorus atoms [5]. For these reasons, our study will be conducted on phosphorus compounds. Flame retardancy can be reached according to two approaches. The first one is the additive approach which consists of physically incorporating an additive in the material during its implementation. The main drawback of this approach is the mobility of the FR in the matrix. This mobility could induce migration of the FR, resulting in leaching and heterogeneous FR concentration in the material resulting in nonpermanent flame retardancy. The release of the additive in the gas phase can also be expected during thermal degradation, and thus the charring effect is reduced. Finally, such a leaching leads to health and environmental risks [6].

To ensure a permanent thermal behavior, FR migration has to be reduced. Wang and Tan [7] showed by mathematic modeling that compounds migration is inversely proportional to their molecular weight. An increase in the molar weight leads to a reduced mobility in the material and a better action in condensed phase [8,9]. Hence, FR oligomers synthesized by radical polymerization of halogenated styrene monomers are commercially available and used in some epoxy resins [10]. Mobility of FR is also dependent on its interactions with the matrix. Oligomers incorporation could be problematic in the case of poor compatibility between oligomers and matrix. Phase segregation can occur and can be detrimental to the properties of the prepared material.

FR mobility can also be reduced by a second approach (called reactive approach) which consists in creating covalent bonds between matrix and FR. The reactive approach promotes an action in the condensed phase and the formation of a high temperature stable residue. Many studies pointed out the phosphorus FR efficiency in epoxy matrices. Different approaches have been reported. Lligadas et al. [11] have synthesized a derivative form of 9,10-dihydro-9-oxa-phosphaphenanthrene-10-oxide (DOPO) with reactive epoxy which has good reactivity with various aromatic diamines. Ren et al. [12] have also shown the efficiency of the reactive approach through the synthesis and the curing of diepoxy phosphonate compounds. This study also demonstrated the better efficiency in condensed phase of reactive phosphonate compared to reactive halogenated compounds. Schartel et al. [13] have shown the flame retardant action of phosphorylated diamines used as curing agent. All these studies reported an important charring effect during thermal decomposition when a phosphorylated compound is used as matrix or curing agent.

The purpose of the present study is to combine both the above-described approaches to limit the FR mobility and migration in the matrix through the synthesis of reactive phosphorylated oligomers and their chemical incorporation in epoxy resin. This strategy consists in copolymerizing two methacrylic monomers by radical chain transfer polymerization. The two chosen monomers are dimethoxy-phosphorylmethyl methacrylate (MAPC1) and glycidyl methacrylate (MAGLY) for its oxirane reactive ring. Radical copolymerization of these two monomers with methyl methacrylate (MMA) has already been studied but no paper has reported the synthesis of MAPC1/MAGLY copolymers so far.

Neugebauer et al. [14] reported the radical copolymerization of MMA with MAGLY by atom transfer radical copolymerization. The statistical structure was deduced from reactivity ratios ($r_{\mathrm{MAGLY}} = 1.24$, $r_{\mathrm{MMA}} = 0.85$ at 80 °C). Iwakura et al. [15] carried out the synthesis of a MAGLY/MMA copolymers by conventional radical copolymerization and the reactivity ratios also confirmed a statistical structure. The chains formed had good reactivity with secondary amine due to the epoxy functions. Finally, an-other study carried out by Gluckman et al. [16] confirmed the statistical structure from reactivity ratios ($r_{\mathrm{MAGLY}} = 1.05$, $r_{\mathrm{MMA}} = 0.80$ at 80 °C). El-Asri [17] studied the synthesis of the phosphonated methacrylic monomer (MAPC1) and its radical copolymerization with MMA. Results showed close reactivity ratios ($r_{\mathrm{MAPC1}} = 1.08$, $r_{\mathrm{MMA}} = 1.00$) enabling to assume a statistical structure. Thus, according to the literature, the radical copolymerization of MAGLY with MAPC1 should result in statistical copolymers, which would favor a homogeneous repartition of both epoxy and phosphonate groups along the backbone.

In this article, the synthesis of MAGLY/MAPC1 copolymer by radical chain transfer polymerization (RCTP) in the presence of mercaptoethanol as chain transfer agent is reported. RCTP allows a low degree of polymerization (DP_n) of the produced chains. Thiol based chain transfer agent (CTA) is suitable for methacrylic monomers copolymerization, since it exhibits a transfer constant close to 1 with methacrylic monomers. Hence DP_n is limited by the $[\mathrm{thiol}]_0/[\mathrm{monomers}]_0$ ratio. In this study, targeted DP_n was targeted to 15 monomers units to obtain molar weights around 3000 g/mol. Oligomeric chains were then introduced in different amounts in epoxy matrix and a comparative study of material behaviors was carried out by thermogravimetric and PCFC analyses.

2. Experimental part

2.1. Materials

Glycidyl methacrylate, 2-mercaptoethanol, diethylether, acetonitrile, diglycidyl ether of bisphenol A (DGEBA) resin and curing agent isophorone diamine (IPDA) were purchased from Sigma–Aldrich. 2,2-Azobisisobutyronitrile (AIBN) was purchased from Sigma–Aldrich and have been purified by recrystallization in methanol (10 g/200 ml). Dimethoxy-phosphorylmethyl methacrylate (MAPC1) was purchased from Specific Polymers.

2.2. Synthesis of copolymers

The following experimental conditions enabled to optimize the monomer conversions.

The comonomer mixture (0.20 mol, used ratios are detailed in Table 1) was transferred with 20 mL of acetonitrile in a 100 mL two-necked round-bottomed flask equipped with a stirrer, a rubber septum and a condenser