



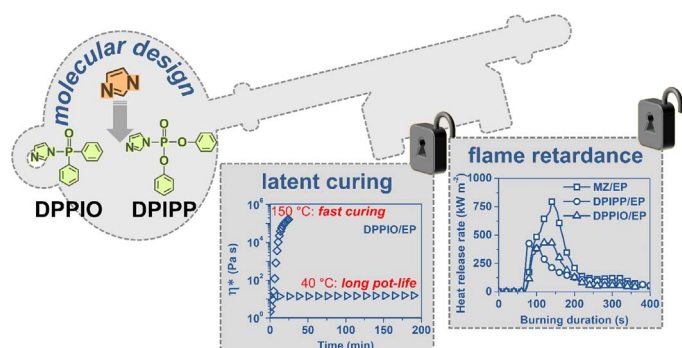
A novel and feasible approach for one-pack flame-retardant epoxy resin with long pot life and fast curing



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GRAPHICAL ABSTRACT



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ABSTRACT

Liquid epoxy resins (EP), curing agents, as well as other additives such as flame retardants are preferred to be formulated as one-pack materials rather than being mixed just prior to their applications. Therefore, they suffer premature curing with increasing of viscosity during storing and operating. To address the above challenging problem, we designed and synthesized a novel latent flame-retardant curing agent named 1-(diphenylphosphinyl)-1H-imidazole oxide (DPPIO) for EP, which was proved exhibiting not only long pot life during storing and fast curing as operating, but also excellent flame retardance after curing. It was observed from dynamic rheometry that, DPPIO/EP kept stable near room temperature for a long time but quickly gelled within only 6.5 min at 150 °C. With only 15 wt% addition of DPPIO, the limiting oxygen index (LOI) of the cured sample increased to 38.0% from 21.0% of the contrast sample, and UL-94 V-0 rating at 1.6 mm thickness was successfully achieved. Peak of heat release rate (PHRR) and total heat release (THR) obtained from cone calorimetry further certified excellent flame retardance of DPPIO/EP. Another typical flame-retardant group with different chemical environment was designed for modifying imidazole to obtain a derivative named diphenyl 1H-imidazol-1-ylphosphonate (DPIPP) in the same way. It was verified that DPIPP/EP showed acceptable latent curing efficiency and satisfactory flame retardance as DPPIO/EP did. Therefore, it's a generally effective and facile approach to develop latent flame-retardant curing agents for EP by modifying imidazole with appropriate flame-retardant groups. Taking advantage of the features, these one-pack flame-retardant epoxy materials can bring more chances for widespread applications.

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1. Introduction

Epoxy resins (EP) have long been widely used in electronic devices (as excellent electrical insulators), laminates, encapsulations (covering the integrated circuitry from environment), coatings, adhesives and advanced composite matrices for decades [1–4], owing to their excellent moisture, heat and chemical resistance, low shrinkage on curing, fine toughness, strong adhesion to diverse substrates, as well as satisfactory mechanical and dielectric properties [5–8]. Nonetheless, the flammable nature seriously restricts their widespread applications, especially in the areas requiring high flame retardance such as construction, transportation, aerospace and electrical/electronic fields [9–12].

Under this consideration, several approaches have been proposed to overcome such predicament by introducing different flame retardants [13–16]. In fact, the incorporation of halogen-based flame retardants into epoxy matrices has long been proved to be an efficient way to achieve expected flame retardance. Unfortunately, taking into account the recycling requirement and environmental impact, the use of such halogen-containing substances like tris(dibromopropyl) phosphate (TDBPP) needs to be forbidden [17,18]. For decades, halogen-free flame retardants, particularly phosphorus-containing ones have received more attention for substitute due to the flame-retardant activity both in gaseous and condensed phases [19,20]. Phosphorus-containing flame retardants, or flame-retardant groups, can be expediently introduced into EP by physically mixing or chemically bonding. Comparably, chemically bonding flame-retardant groups, or so-called intrinsically flame retarding endows the resulting materials with long lasting flame-retardant performance and environment tolerance. In our group's previous works [21–23], Wang et al. successfully modified ammonium polyphosphate (APP) as organic-inorganic hybrid flame-retardant curing agents via the cation exchange reaction between APP and different organic amines including diethylenetriamine, piperazine and branched polyethyleneimine. Among them, the piperazine-modified one (PAz-APP) gave excellent flame resistance and smoke suppression efficiency to EP matrices. Furthermore, the incorporation of the hybrid didn't worsen the mechanical properties instead of improving the impact strength of the resulting flame-retardant sample.

In practice, EP, curing agents, as well as other functional and filling additives would like to be formulated as one-pack materials for large batch production rather than being mixed prior to applying. In this case, gradual increasing of viscosity and premature curing of the materials as being stored should be solved, which is of special relevance as amines being used as curing agents [24–26]. Thus, latent curing systems need to be developed to solve the tough problem. The phrase latent curing denotes the curing activity inert at room temperature while promoting a rapid cure at higher temperature. Therefore, at the presence of latent curing agents, EP can be stored under the form of one-pack curing systems over a very long period in the liquid state and fast curing can be triggered at the exact time and place desired by the operator. This approach combines both storing and processing advantages, particularly in the process for electronics such as encapsulation or coatings. Kudo et al. synthesized a kind of imidazole derivative [27] as thermal latent curing agents. Ascribed to the intramolecular hydrogen bond between the phenolic hydroxyl group and the nitrogen atom in the imidazole ring, latent curing reactivity was tailored via the breakage of intramolecular hydrogen bonds at 150 °C; whereas the epoxy composition showed long-term storing stability at room temperature. Except such reversible hydrogen bonds, thermo-labile covalent bonds [28], microencapsulation types [29] and metal-imidazole complexes [30] were also widely reported in order to achieve one-pack epoxy materials containing both epoxy resins and curing agents with long-time storing stability and on-site operating reactivity.

In the present work, two typical phosphorus-containing flame-retardant groups were designed for modifying imidazole to obtain functional derivatives as flame-retardant latent curing agents for EP. As a

way to kill two birds with one stone, appropriate latency with long pot life and acceptable curing activity, as well as satisfactory flame retardance were endowed to EP simultaneously. Storage stability and curing behaviour were investigated by differential scanning calorimetry (DSC) and dynamic rheological analysis; and the corresponding curing procedure was explored by X-ray photoelectron spectroscopy (XPS). Thermal properties were studied by thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). At last, flame retardance and burning behaviour were evaluated by the limiting oxygen index (LOI), UL-94 vertical burning test (UL-94 V) and cone calorimetry.

2. Experimental section

2.1. Materials

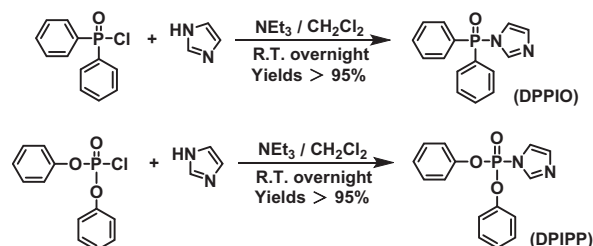
Diphenoxychlorophosphine oxide (98%), diphenylphosphinyl chloride (98%) and 1-methyl imidazole (99%) were purchased from Energy Chemical Co., Ltd. (Shanghai, China); imidazole (99%), anhydrous magnesium sulfate (99%), triethylamine (AR, 99%) and dichloromethane (99.5%) was provided by Kelong Chemical Reagent Co., Ltd. (Sichuan, China); diglycidyl ether of bisphenol A type EP (E-44, EEW = 210–240 g·eq⁻¹, viscosity = 15–23 Pa·s (25 °C)) was obtained from Xingchen Synthetic Materials Co., Ltd. (Nantong, China). Triethylamine and dichloromethane were utilized after being dried, and other materials were used as received.

2.2. Preparation of DPPIO and DPPIP

In N₂ atmosphere, imidazole and the equivalent triethylamine were dissolved in 250 ml dichloromethane at ambient temperature. And then the equivalent diphenylphosphinyl chloride was dropwise added into the solution. After stirring overnight, triethylamine hydrochloride was filtered off, and then the filtrate was washed with excessive water and dried over anhydrous magnesium sulfate. After evaporation of the solvent in vacuum, the product 1-(diphenylphosphinyl)-1H-imidazole (DPPIO) was obtained as a white solid product. The diphenyl 1H-imidazol-1-ylphosphonate (DPPIP) was prepared in a similar way. The corresponding synthesis routes of DPPIO and DPPIP were shown as Scheme 1. (Yield > 95%) ¹H NMR (400 MHz, DMSO-*d*₆), DPPIP: δ 8.97 (s, 1H, CH), 7.61 (d, 2H, CH), 7.23 (t, 4H, CH), 7.14 (d, 4H, CH), 6.97 (t, 2H, CH); DPPIO: δ 8.14 (s, 1H, CH), 7.71 (t, 4H, CH), 7.40 (d, 6H, CH), 7.21 (s, 2H, CH). ³¹P NMR (400 MHz, DMSO-*d*₆), DPPIP: δ 11.55; DPPIO: δ 18.75. The melting point, DPPIP: 82–83 °C; DPPIO: 101–102 °C.

2.3. Curing

Different amount of DPPIP or DPPIO (as mass fraction) was dispersed with EP under stirring prior to curing. The composition was removed bubbles in a vacuum oven and poured into a Teflon mold; then cured at 120 °C for 2 h and 180 °C for another 2 h. For comparison, a reference sample cured by 1-methyl imidazole (MZ/EP) was cured following the similar procedure but heated at different temperatures: 70 °C and 140 °C for every 2 h, respectively. Apparently, no sedimentation of the curing agent occurred in all cured samples.



Scheme 1. Synthesis routes of DPPIO and DPPIP.

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