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Tuning the properties for the self-extinguishing epoxy-amine composites containing copper-coordinated curing agent: Flame tests and physical–mechanical measurements

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ABSTRACT

An uncomplicated mode of preparing the fire retardant-hardener labeled *DETA*-$CuSO_4$ (*DETA* – diethylenetriamine) with its subsequent incorporation into framework of epoxy resin to obtain self-extinguishing epoxy-amine composites possessing the balanced physical-mechanical properties and fire retardancy has been elaborated. The influence of the *DETA*-$CuSO_4$ complex formation onto the epoxy resin curing processes has been studied by means of data of the rheological, IR spectroscopic and quantum-chemical analyses of the *DGEBA–DETA*–$CuSO_4$ system (*DGEBA* – bisphenol A diglycidyl ether). The flammability of the epoxy-amine composites with different content of the fire retardant (0, 5, 16, and 80 mass parts) has been studied. The rate of burning of the epoxy-amine composites (*DGEBA/DETA*-$CuSO_4$) containing 16 and 80 mass parts of the fire retardant is intensely depressed (their samples do not propagate flame generally), while $r_{burn.}$ values for samples of *DGEBA/DETA* and *DGEBA/DETA*-$CuSO_4$(5) are equal 25.2 and 24.0 mm·min^{-1}, respectively. The flammability was evaluated by means of UL94 test method and according to all-Union State Standard 12.1.044-89. The smoke-formation is maximal suppressed by fire retardant ($CuSO_4$) in the largest quantities. Physical-mechanical properties were studied by means of the measurements of surface hardness, tensile strength, water absorption, and chemical resistance.

1. Introduction

The wide use of polymer composites in an industry and daily life results in a violent increase of number of fires initiated by ignition of the materials made of polymers [1]. Among a lot of the prevalent polymer materials, the polymers on the base of epoxy resins play a significant role in the technics, as these find wide application in many fields, that is, from electronics to public transport *etc.* [2]. That is why the most rigid conditions concerning fire safety should be put forward to such composites. Unfortunately, epoxy polymers by the nature are combustible substances and at burning they are able to release a great deal of a smoke and toxic products of combustion [3].

Currently, the varied types of the fire retardants are widely used for the effective combustibility lowering of epoxy resins [4]. In this regard, the best fire retardants are the reactive fire retardants. There are several different kinds of reactive fire retardant materials obtained by incorporation of Si, N, B, and P atoms in the monomers [5–9]. Such monomers can easily undergo various reactions at polymers synthesis. In the latter time, the fire retardants containing *d*-metal complexes (mainly, on the basis of Mn, Co, Ni, Cu, Zn *etc.* salts of organic acids) [10–12] find a wide application. These complexes play a part of both modifiers and curing agents of epoxy resins at the composite materials obtaining. But, the major merits of the using the metal complexes consist in avoidance of the complicated monomer synthesis and the wide variety of choice of the metals and the ligands. Nevertheless, despite ability of these metal complexes to decrease combustibility of the polymer composites, their use results frequently in change of physical-mechanical properties of polymer materials. Therefore, at choosing a fire retardant apart from accessibility, cheapness and desire to attain to the substantial decrease of combustibility for the polymer composites it is necessary to take into consideration fire retardant's influence on the operating characteristics of the materials and to monitor the process-dependent parameters of obtaining and processing the products [13].

In our previous researches [14–16] the [Cu(*DETA*)(H_2O)]SO_4·H_2O chelate complex made out of the copper vitriol and diethylenetriamine (*DETA*) has been structurally characterized. The effectiveness of bonding a combustible *DETA* (curing agent) with an incombustible

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inorganic salt – $CuSO_4$ (fire retardant) in many respects predetermines behavior of the obtained diethylenetriamine copper(II) chelate complex as a fire retardant-hardener of epoxy resins. Exceptional ability of the inorganic cupric salts to complexation has let us foreknow the potentiality of utilizing the dehydrated chelate complex – *DETA*-$CuSO_4$ to make the epoxy-amine composite materials with suppressed combustibility. Eventually, we have attained the aim and obtained the polymeric samples of the epoxy-amine composites modified by $CuSO_4$ as well as investigated their thermal behavior and determined combustibility parameters [16]. The thermic stability and anti-flammability of the elaborated *DGEBA/DETA*-$CuSO_4$ composites (*DGEBA* – bisphenol A diglycidyl ether) were appreciably improved by comparison with unmodified *DGEBA/DETA* polymer; the maximal combustion temperature of gaseous products for *DGEBA/DETA* compared to *DGEBA/DETA*-$CuSO_4$ has gone down from 867 °C to 640 °C and weight loss has also decreased from 89.0 wt% to 78.6 wt%.

Taking into account the aforesaid, we undertook an attempt to elaborate an uncomplicated mode of the *DETA*-$CuSO_4$ fire retardant-hardener preparing and to incorporate this compound into framework of epoxy resin for obtaining several samples of the epoxy-amine composites having the different molar ratio of *DGEBA*: *DETA*: $CuSO_4$ (see Table 1). Thus, begun researches have allowed making the samples of the self-extinguishing epoxy-amine polymers belonging to a new generation of the composite materials. The synthesis and structural characterization (XRPD and FTIR), rheological and quantum-chemical analyses as well as an influence studying of the fire retardant-hardener onto change of the fire hazard indices (flame propagation rate and smoke formation factor) and the tuning the requisite physical-mechanical properties of the epoxy-amine composite materials are reported in the present article.

2. Experimental

2.1. Materials

For synthesis of the fire retardant-hardener (*DETA*-$CuSO_4$) and the self-extinguishing epoxy-amine composites (*DGEBA/DETA*-$CuSO_4$), the following chemicals were used: the fire retardant – copper(II) sulfate pentahydrate ($Cu_2SO_4{\cdot}5H_2O$) (light blue crystals, M_r = 249.5, $\Delta t_{dehydration}$ = 90–280 °C [17,18]); the curing agent of epoxy resins – diethylenetriamine, $NH_2C_2H_4NHC_2H_4NH_2$ (*DETA*) (colorless liquid, M_r = 103.17, d^{20} = 0.955 g·cm^{-1}, n_D = 1.484, $t_{boiling}$ = 204.1 °C, $t_{ignition}$ = 97 °C, $t_{self\text{-}ignition}$ = 350 °C [19], IR (KBr cuvette, cm^{-1}): 3372, 3254 and 3210 (ν_{NH}); 2934, 2908 and 2790 (ν_{CH}); 1600 (δ_{NH}); 1460 (δ_{CH})); the binder – bisphenol A diglycidyl ether (*DGEBA*) (colorless resin, ED-20 grade with almost 22% epoxy groups content, value of viscosity from 12 to 18 Pa·s (at 25 °C), M_r = 390–430 ($\overline{M}_r$ = 410)). All reagents have been purchased through commercial sources and used as-received without further purification.

2.2. Characterization

The X-ray powder diffraction (XRPD) pattern (Fig. S1, Supp. Info) of the polycrystalline sample of the [Cu(*DETA*)(H_2O)]$SO_4{\cdot}H_2O$ chelate complex – the precursor of the *DETA*-$CuSO_4$ fire retardant-hardener was carried out at room temperature on the HZG-4A diffractometer (Cu K_α-radiation, Bragg-Brentano geometry, angular range $8 \le 2\theta \le 50^\circ$ with a step size of 0.02° and exposition time per point 20 s). The profile and structural parameters were refined by the Rietveld method using the package of program FullProf Suite [20]. Indexing of XRPD pattern was fulfilled automatically by means of the method described in [21], using DICVOL91 software package [22]. The structure model was taken from single crystal data [14].

IR absorption spectra (Fig.1) of *DETA*, [Cu(*DETA*)(H_2O)]$SO_4{\cdot}H_2O$, *DETA*-$CuSO_4$, *DGEBA/DETA*-$CuSO_4$ and *DGEBA/DETA* were recorded in the spectral range of 4000–500 cm^{-1} with a resolution of 2 cm^{-1} on a Perkin Elmer SpectrumTwo FTIR spectrometer. The IR measurements were performed with a solid sample pressed in spectroscopically pure KBr pellet, or a liquid sample using a KBr cuvette.

The flammability of *DGEBA/DETA*-$CuSO_4$ and *DGEBA/DETA* was evaluated by means of UL94 test method. The flame propagation rate was determined according to IEC 60695-11-10 [23]. Each test piece was mounted horizontally to its long axis and at an angle of 45° to its short axis. The molded samples by 125 mm length, 10 mm width, and 5 mm thickness were exposed to a 20 mm high blue Bunsen burner flame at an angle of 45°. The polymer samples were tested after conditioning for 48 h, at 25°C and of 50% relative humidity. At a testing result, the time ($\Delta\tau_{burn.}$, s) of the travel of the flame front between two gauge marks was measured and the burning rate ($r_{burn.}$, mm·min^{-1}) of the polymer samples was calculated.

The smoke-formation factor was determined according to all-Union State Standard 12.1.044-89, (the item 4.18). The optical density of the smoke forming at burning or smoldering of the polymers of a certain weight has been measured on the device for the smoke-formation factor determination. The samples assaying were fulfilled at two test mode. At a smoldering mode the sample was exposed solely to a thermal current by density of 35 ± 3.5 kW·m^{-2} whereas at a burning mode it was exposed to both a thermal current and a gas burner flame jointly. Smoke-formation factor (D_m, m^2·kg^{-1}) was calculated by means of ratio:

$$D_m = \frac{V}{L{\cdot}m} \ln \frac{T_0}{T_{min}}$$

where V is a volume of the measuring chamber, 0.343(4) m^3; L is a path length of a light beam in a smoke medium, 0.7000(5) m; m is a mass of the sample, kg; T_0 and T_{min} are values of initial and final transmittance, respectively, %.

The ignition point ($t_{ign.}$) and self-ignition point ($t_{self\text{-}ign.}$) for *DETA*, *DGEBA/DETA*, *DETA*-$CuSO_4$, and *DGEBA/DETA*-$CuSO_4$ have been measured on a TF devise according to all-Union State Standard 12.1.044-89 (the items 4.7 and 4.9).

Physical-mechanical properties of the composite materials were studied by means of measurement of the following parameters: surface hardness, tensile strength, water absorption, and chemical resistance. The surface hardness of the samples was measured on the Höppler's consistometer by indentation of a steel cone having angle of 53°08′ at weighting in 50 N and duration 60 s.

Uniaxial tensile tests were determined on the epoxy-amine composites according to all-Union State Standard 11262-80 at room temperature using a P-0.5 type tensile testing machine. Rectangular samples with dimensions 250 × 10 × 3 mm^3 were used. A displacement rate of 100 mm·min^{-1} was adopted. The tensile properties were averaged from the results obtained from a minimum of three samples.

The water absorption or chemical resistance was studied by gravimetric method; a weight change of the polymer films after their immersion into distilled water or corrosive medium for a certain time was measured.

Table 1
Stoichiometry of the epoxy-amine composites.

Composite	*DGEBA*:*DETA*:$CuSO_4$ (molar ratio)	Ingredients (mass p.)		
		DGEBA	*DETA*	$CuSO_4$
DGEBA/DETA	5:2:0	100	10	–
DGEBA/DETA-$CuSO_4$(5)	5:2:0.625	100	10	5
DGEBA/DETA-$CuSO_4$(16)	5:2:2	100	10	16
DGEBA/DETA-$CuSO_4$(80)	5:2:10	100	10	80

2.3. Preparation of the fire retardant-hardener

The powdery fire retardant-hardener (*DETA*-$CuSO_4$) suitable to the polymerization has been obtained by dehydration of the [Cu(*DETA*)