



Transparent nanocomposite coatings based on epoxy and layered double hydroxide: Nonisothermal cure kinetics and viscoelastic behavior assessments



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ABSTRACT

Layered double hydroxide (LDH) has a particular place in clay family because of its flame retardant action. The nanoplatelet-like structure of LDH makes possible development of polymer composites with cationic or anionic nature structures in which macromolecules are positioned in between nanoplatelet galleries. In this work, neat epoxy and its transparent nanocomposite coatings with sodium dodecylbenzene sulfonate (SDBS)-modified LDHs; Mg-Al and Zn-Al LDHs, were prepared and their cure kinetics and viscoelastic behavior were tracked through nonisothermal calorimetric and dynamic mechanical analyses. The higher progression of crosslinking in the epoxy network was observed for epoxy/Zn-Al LDH nanocomposites, while activation energy of cure reaction took a higher value for Mg-Al LDH-incorporated systems. Moreover, epoxy/Mg-Al LDH system revealed higher value of storage modulus and glass transition temperature thanks to larger galleries of Mg-Al nanoplatelets. Network formation in the presence of SDBS-modified Zn-Al LDH nanoplatelets was facilitated due to the action of Zn metal as an adduct with a lone-pair of oxygen atom of epoxy leading to an enhanced epoxy ring-opening. Viscoelastic behavior of transparent coatings containing Zn-Al LDH and Mg-Al LDH was studied through temperature-sweep test at various frequencies to compare the results of calorimetric and thermo-mechanical analyses.

1. Introduction

Polymer composites comprising well-dispersed layered inorganic nanostructures have taken a particular place in academia and the industry alike due to their action on electrical, thermal, rheological, and mechanical properties at low loading levels [1–4]. Among these layered inorganic nanostructure fillers are layered double hydroxides (LDHs) with their unique characteristics such as high aspect ratio, tunable charge density and high value of anion exchange capacity [5,6]. The LDH has been recognized as anionic clay with brucite-like structure in

which anions were found to be positioned in between clay galleries neutralizing the positive charge of cations. Facile synthesis route of LDH with various metal cations, intercalated anions, and desirable surface modification [7,8] makes it a strong candidate for a broad range of application ranging from water treatment [9,10] and hydrothermal reactor [11] to drug and gene delivery [12] and biosensor [13]. Accordingly, coprecipitation, electrogeneration, polyol route and sol-gel techniques were appeared as efficient routes in tailoring the structure of LDH for having diverse chemical compositions, sizes and shapes [5].

The majority of the commonly used polymers from high

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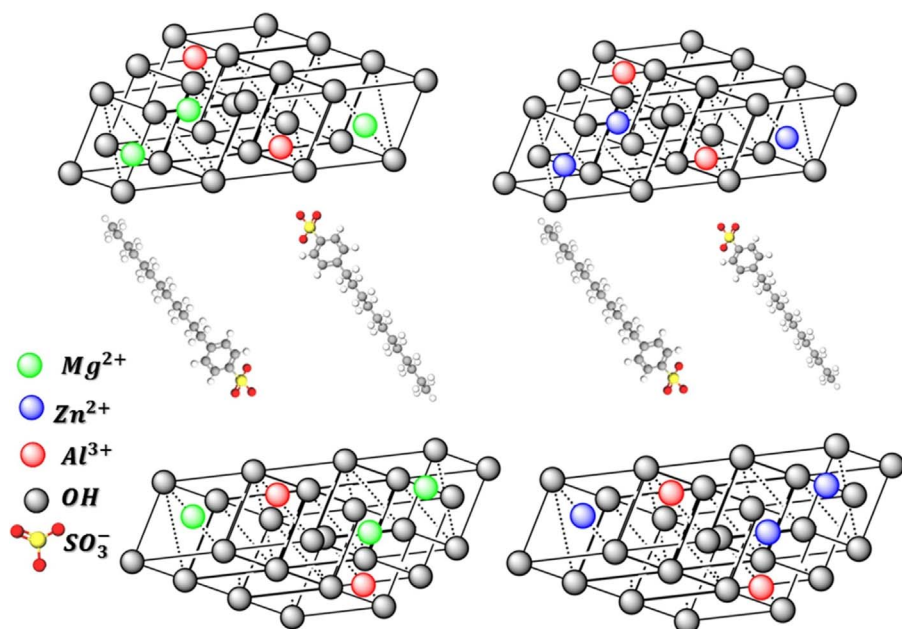


Fig. 1. Schematic of chemical structure of the Mg-Al LDH and Zn-Al LDH clays used in this work.

flammability because of their petroleum-based nature. Incorporation of flame retardant agents into the polymeric matrices could to a large extent make them suitable for applications where heat generation was significant. Recent studies suggest that LDH can be employed as a halogen-free flame retardant in polymers [14–18]. A series of LDH/polymer nanocomposites have accordingly been developed in view of flame retardant action of LDH [19–21]. However, hydrophilic nature of such nanoplatelet-like structures necessitates modification of LDH to enhance the degree of compatibility of LDH with hydrophobic polymeric matrices [22,23]. The presence of voluminous organic anions embedded in between interlayer spaces could to an acceptable extent solve this challenge by exfoliation of LDH nanosheets [15,24]. For instance, Wang et al. [25] reported an improved flame resistance properties for polypropylene upon introduction of organomodified magnesium–aluminum (Mg–Al) LDH, as evidenced by drop in specific heat release rate, heat release capacity and total heat release.

Epoxy thermosetting resins are well-known for their superior young modulus, low shrinkage after curing and excellent corrosion resistance [26]. Therefore, they have been widely exploited in adhesives, coatings and composites applications [27–29]. On the other hand, high flammability and brittleness to some extent narrowed application of epoxy in engineering fields [30]. Zammarano et al. [31] reported an improved flame resistance performance for epoxy composites comprising LDH compared to counterparts having montmorillonite clay because of intrinsic properties of LDH. Becker et al. [32] revealed an improved performance of epoxy-based nanocomposites containing various loadings of LDH comparing their burning rate with neat epoxy. They reported that the highest mechanical properties was with composites containing 1 wt.% LDH. It can be concluded that though LDH enhanced flame resistance of epoxy, it could deteriorate the mechanical and crosslinking reactions, which necessitates careful formulation of epoxy with LDH.

There is no need to emphasize for experts in the field of thermosetting coatings that almost all properties of epoxy-based composite coatings are pertinent to promotion of network formation in the course of curing reaction [33–35]. Analysis of the cure kinetics offers worthwhile evidence about chemical reactions taking place during cure process towards understanding of structure-property relationship [36]. In a previous study, the role of graphene oxide (GO) nanoplatelets modified with aliphatic amines on cure kinetics and fracture behavior of epoxy resin was discussed [37]. It was observed that modification of

GO increases the crosslinking density by association of amine functional groups attached to the GO platelet surface to epoxy ring opening reactions. Similar trends were observed when using nanofillers having different geometrical shapes in epoxy like multi-walled carbon nanotubes modified with amine precursor [38,39] and Fe₃O₄ magnetic nanoparticles modified with β -cyclodextrin [40].

Two kinds of LDH, i.e. Mg–Al and zinc–aluminum (Zn–Al) LDH were employed here to prepare epoxy-based transparent nanocomposite coatings. It was known that both kinds of LDH can improve thermal stability and flame retardancy of polymers [21,41–43]. The cure kinetics and viscoelastic behavior of transparent epoxy films containing Mg–Al and Zn–Al nanoplatelets modified with sodium dodecylbenzene sulfonate (SDBS) was comprehensively discussed in this work. Cure kinetics was studied by nonisothermal calorimetric analyses under different heating rates using an in-house code that finds parameters of model-free and model-fitting equations. Analyses were interpreted based on activation energy as a function of the extent of cure in the presence and absence of Mg–Al and Zn–Al LDHs. Viscoelastic properties of transparent coatings were analyzed through mechanical and thermo-mechanical tests to find glass transition, heat of cure, and activation energies of neat and LDH-incorporated epoxy coatings. The role of Mg–Al and Zn–Al LDH on the aforementioned properties was uncovered through a comparative view of results as well as mechanistic description of network formation in the presence of nanoplatelets.

2. Experimental

2.1. Materials

Epoxy resin with commercial name D3415 was purchased from Sigma-Aldrich Co. (USA). Cycloaliphatic polyamine resin with a viscosity of 55,000 mPa.s (Epikure F205) was provided by Hexion Chemical Co. (USA) and used as amino curing agent. The curing agent was mixed with epoxy with weight ratio of 2:3 with respect to epoxy resin. To synthesize Mg–Al LDH and Zn–Al LDH, all ingredients including magnesium nitrate, zinc nitrate, aluminum nitrate, sodium hydroxide, sodium dodecylbenzene sulfonate (SDBS) were provided by Merck Co. (USA). The tetrahydrofuran (THF) used for dissolving epoxy and hardener in film formation was provided by Merck (USA) and used as received.

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