



Flame retardant epoxy/halloysite nanotubes nanocomposite coatings: Exploring low-concentration threshold for flammability compared to expandable graphite as superior fire retardant



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ARTICLE INFO

Keywords:

Epoxy
Flame retardancy
Nanocomposites
Halloysite nanotubes
Expandable graphite

ABSTRACT

Epoxy nanocomposites containing halloysite nanotubes (HNTs) were developed and their low-concentration thresholds for thermal stability and flame retardancy were compared with that of epoxy system containing expandable graphite (EG), as a reference with superior flame retardancy. The effects of HNTs and EG on the peak of Heat Release Rate (pHRR), Total Heat Release (THR), and Time-To-Ignition (TTI) of the prepared samples were subsequently discussed. At low loading level of 3 wt.%, HNTs appeared more effective, as signaled by an enhanced thermal stability compared to the EG-incorporated composite at an identical loading, because of hindered mobility of epoxy chains in a well-cured epoxy network. At higher loadings (6 and 9 wt.%), however, exfoliation of EG because of heat build-up in the system was dominantly hindered the crosslinking of epoxy in the presence of HNTs, which consequently deteriorated thermal stability of epoxy. This was featured by the formation of intumescent flake on the surface of the epoxy that played the role of a physical barrier, and assisted in reduction of the value of pHRR, while it doubled the TTI value. Different functions of HNTs and EG in regard with thermal stability and flame retardancy of epoxy/amine systems were discussed experimentally and mechanistically.

1. Introduction

Epoxy resins are known as the most versatile thermosetting polymers with appropriate chemical and corrosion resistance, adhesion properties, curability, low shrinkage and mechanical properties [1–6]. Epoxy resins can be crosslinked together with a wide variety of curing agents under different curing circumstances [4,5,7]. Noticeably, however, they suffer from poor thermal stability, high flammability and poor fracture toughness, which limit their use in engineering applications [1,8]. In this sense, different kinds of fillers/additives have been examined to gain high-performance epoxy systems. Epoxy composites are receiving much more attention every day because of the properties of epoxy-based composites being manipulatable for desired applications.

When used as coating materials, epoxy suffers from inadequate potential for protecting the underlying substrate against fire [9–11]. However, in electronic devices such as printed wiring boards and cable industry, fire retardancy of epoxy resins is of premier importance [12].

For such purposes, the coating should be designed so as to minimize heat transfer across the coating thickness during the combustion process [13]. Moreover, one would be wise to develop eco-friendly flame retardants for epoxy prior to the time a coating is expected to retard burning. The fire retardancy of epoxy can be enhanced by the incorporation of flame retardant additives or chemical reactive flame retardants into the resin [14,15]. Combustion is a complex process through which physical and chemical mechanisms take place simultaneously. This hardens prospective identification of the combustion process and determination of the main mechanism that dominantly controls over flame retardancy of composites [16–18]. Classically saying, four important zones have been identified in the combustion process: flame zone, char layer, molten polymer and underlying polymer. Char layer is known as the most critical zone which mainly controls over the heat and mass transfer phenomena. Typically, char decelerates the release of heat by formation of a protective layer against heat flux source [16,19]. This layer with its low thermal conductivity hardens heat transfer leading to polymer degradation rate reduction

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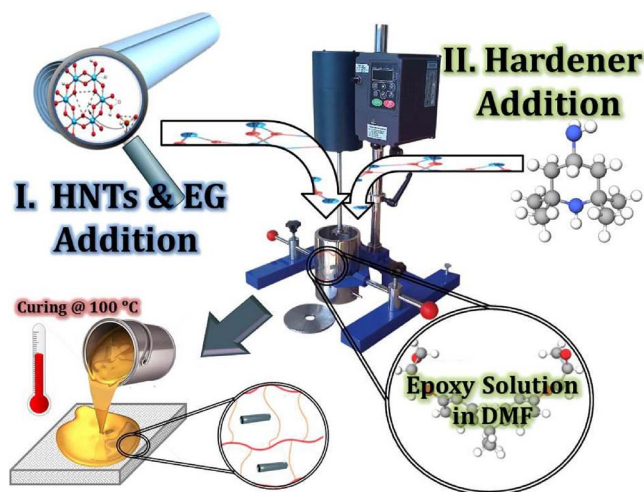


Fig. 1. Schematic of procedure applied in sample preparation.

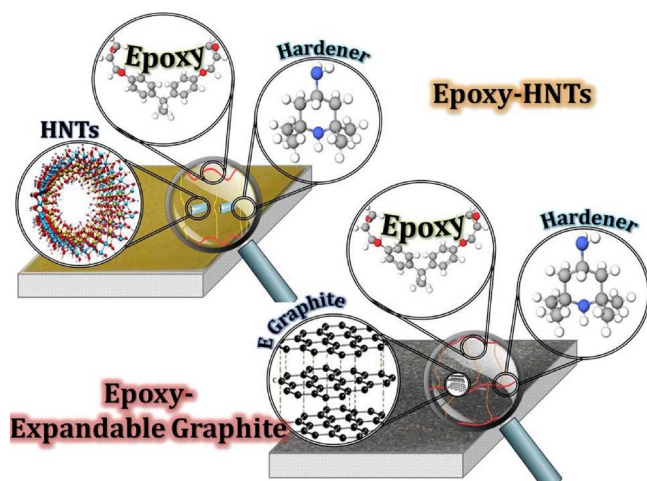


Fig. 2. Schematic of chemical structure of EG/epoxy and HNTs/epoxy composites.

[16]. The effectiveness of a flame retardant system is highly pertinent to its capacity to form a protective layer during the combustion. Overall, a dense and compact layer of char residue is required for a proper heat barrierity [9,20,21].

The use of nano-scale additives has been practiced as a profound solution for the poor flame retardancy of polymers. Nanoparticles not only can improve the fire performance, but they can also improve to a desired level mechanical properties of polymer matrix [19]. Formation of nanoparticle-rich char layer could effectively reinforce its cohesiveness. As a result, the rate of mass loss decreases, which is reflected in a fall in the peak of heat release rate (pHRR), while nanoparticles could limitedly improve the total heat release (THR). Moreover, the broadness of the heat release rate (HRR) curve could be a signature of appropriateness of nano-scale additives when used as flame retardant in polymers. Graphite in both micro- and nano-scale size is known as a superior flame retardant because of its covalently bonded hexagonal structure [22]. Pristine graphite can hardly be used as a flame retardant for polymers due to the compactness of carbon flakes in the natural graphite structure, which prevent penetration of polymers into the galleries of graphite sheets [16]. The chemically modified graphite (expandable graphite, EG), however, appears as a superior flame retardant benefiting from its exfoliation potential [16]. There are numerous examples demonstrating the excellence of EG as a commercially available flame retardant for various polymeric matrices [16,21–27]. It has been mechanistically explained that in the course of combustion EG expands hundred times leading to formation of a worm-like char layer

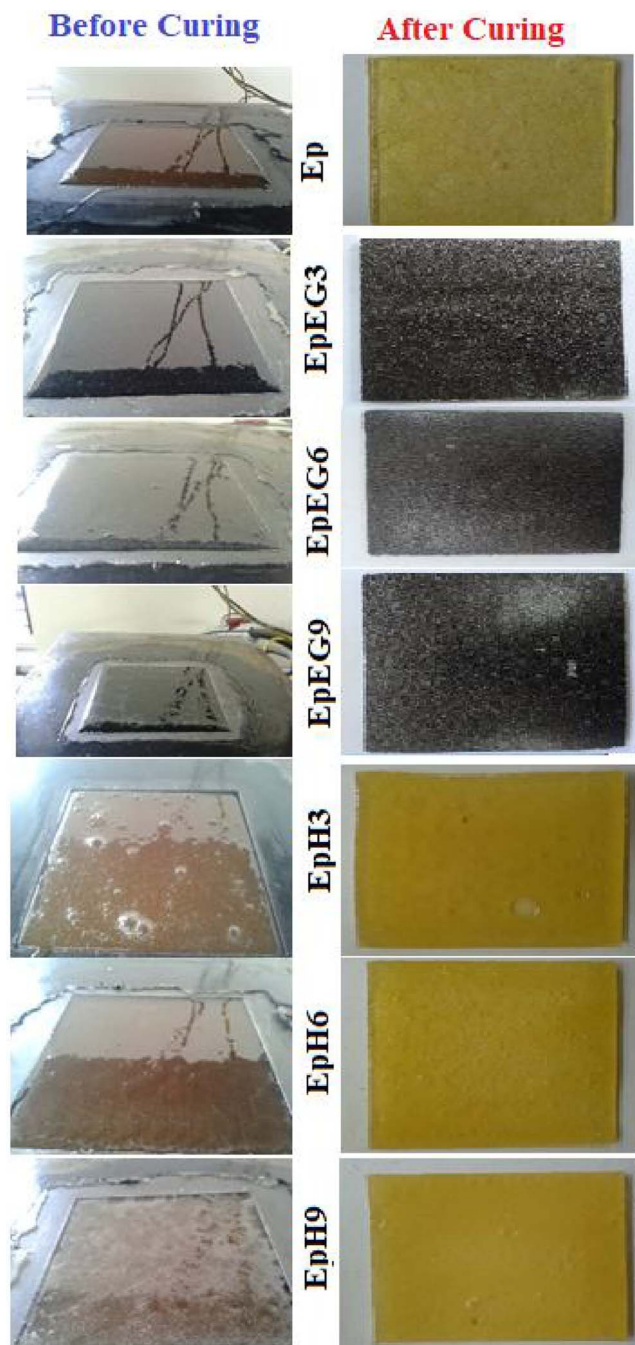


Fig. 3. Samples' appearance right before and after curing process.

on the surface of polymer, which acts as a barrier against heat and mass transfer [28,29]. There is a general agreement that flame retardancy of epoxy can significantly be improved by incorporation of such carbonous materials [30–32].

The use of inexpensive, one-dimensional nano-scale additives such as halloysite nanotubes (HNTs) has received a particular attention in recent years [33–37]. Thanks to its tubular nanostructure and high aspect ratio in addition to its natural availability, HNTs resembles carbon nanotube (CNTs) – the reason why HNTs exhibit unique properties such as good biocompatibility and acceptable mechanical strength – and can be considered as an alternative to CNTs for high-performance applications [38–40]. HNTs with molecular formula $(Al_2Si_2O_5(OH)_4 \cdot nH_2O)$ are similar to kaolin, but their hollow structure gives reason to hope that it can be considered as a flame retardant additive [39,41]. Previous studies have uncovered the fact that addition

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