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An attempt to mechanistically explain the viscoelastic behavior of transparent epoxy/starch-modified ZnO nanocomposite coatings

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ABSTRACT

The effects of bare and starch-modified ZnO (ZnO-St) nanoparticles on viscoelastic and mechanical properties are studied by dynamic mechanical and tensile analyses. Transparent epoxy-based nanocomposite films are prepared by incorporating bare or starch-modified ZnO particles into the epoxy matrix. The results demonstrated that ZnO particles hindered the curing reactions and hence the final properties of the cured epoxy. As a result, glass-transition temperature (T_g) and crosslinking density demoted. However, starch as a surface modifier compensated for the undesired effects of ZnO in a way that by enhancing the curing reactions through autocatalytic mechanism, T_g and crosslinking density increased. The storage moduli for epoxy, epoxy/ZnO and epoxy/ZnO-St are accordingly as 13.84, 3.95 and 19.54 MPa. Therefore, the molecular weight between the entanglements is calculated as 0.2878, 1.0089 and 0.2039 in the same order. Moreover, considering the peaks of the tanδ diagrams, T_gs for epoxy, epoxy/ZnO and epoxy/ZnO-St are obtained as 95.95, 100.16 and 101.24 °C, respectively. Comparing epoxy/ZnO-St nanocomposite to epoxy, it can be inferred that the network becomes tougher in the elastic region and then becomes softer passing this region. Mechanistic sketches of epoxy network formation in the presence of bare and surface-treated nanoparticles are discussed.

1. Introduction

When it comes up with the familiar term of “Organic Coating”, epoxy is positioned almost as the first bringing up in the mind thanks to its outstanding specifications [1–3]. Nonetheless, its favorable properties are always accompanied with some undesirable drawbacks. Epoxies are suffering from some mechanical weaknesses, e.g. high brittleness and very low elongation, and weathering faintness, e.g. very low ultra violet resistivity – what confines its versatility [4,5]. To triumph over these unwanted disadvantages, various approaches were examined among which nanotechnology looks one the most promising ones [6–8]. Multitudes of researches have already focused on nanocomposite coatings based on epoxy and various nanoparticles and their influences on the curing behavior and final properties have been investigated [9–11].

In a previous study, two kinds of layered double hydroxides (LDH), i.e. Mg-Al and Zn-Al LDH nanofillers were added to epoxy and the interplay between curing kinetics and viscoelastic behavior was discussed [12]. Incorporation of Mg-Al LDH into the epoxy increased the heat of reaction and consequently changed the viscoelastic behavior in a way that T_g shifted towards higher temperatures and crosslinking density increased as well. On the other hand, addition of Zn-Al LDH to epoxy increased its fracture energy. In another study, graphene oxide was chemically modified by amine aliphatic molecules and introduced into an epoxy matrix [13]. It was observed that activation energy in amine-functionalized reduced compared to the pure epoxy, mostly due to the high reactivity of the —N—H functional groups that facilitated curing at higher conversions. Elsewhere modification of graphene oxide by polyamidoamine dendrimers and incorporating it into the epoxy led to a fall in activation energy corroborating unhindered network formation [14]. Ganjaee et al. modified clay nanoplatelets by polyester amide hyperbranched polymer and used the modified clay as nanofiller to

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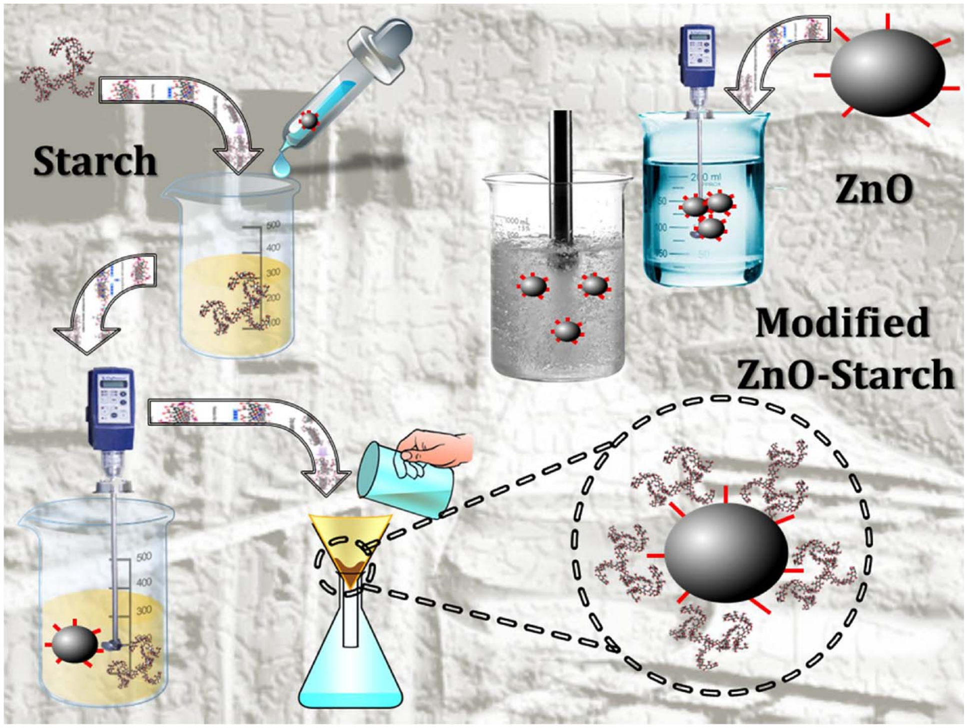

Fig. 1. Descriptive sketch of the modification process of nano ZnO by starch.

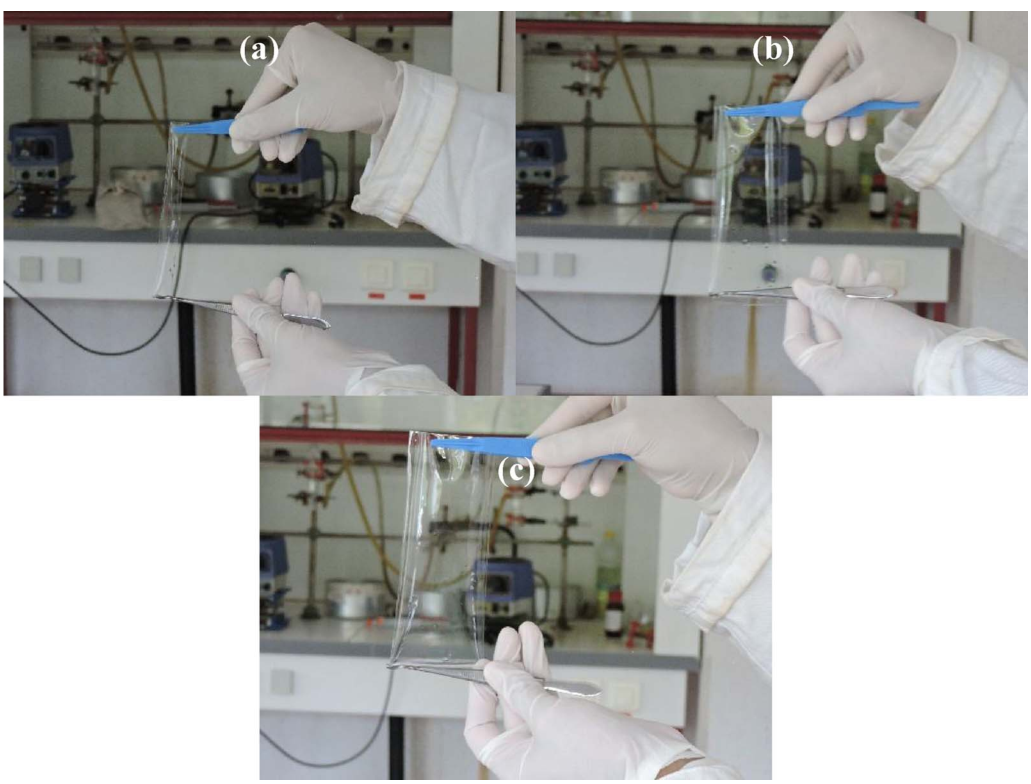

Fig. 2. Transparent films of neat epoxy (a); epoxy/ZnO (b) and epoxy/ZnO-St (c) films for the sake of transparency comparison.

develop an epoxy-based nanocomposite coatings [15]. The viscoelastic and mechanical properties of nanocomposite coatings have been significantly improved by addition of this nanofiller, similar to their excellent corrosion resistance enhancement [16]. Graphene oxide and clay nanoplatelets were simultaneously modified and added to epoxy coating formulation [17]. The results showed that incorporating the modified particles into the epoxy resin significantly increased the corrosion resistance of the nanocomposite coating, possibly due to the network evolution in the presence of the modified nanofillers. It was also demonstrated that using the modified graphene oxide-*co*-clay nanoplatelets at an optimum ratio leads to epoxy toughening and enhances the mechanical properties [18]. In various studies carried out by the current team, it was recognized that epoxy-based nanocomposite coatings with improved network characteristics are fortunately