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Study on the effect of hexamethylene diamine functionalized graphene oxide on the curing kinetics of epoxy nanocomposites

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ABSTRACT

The curing kinetics of epoxy nanocomposites prepared by incorporating pristine graphene oxide (GO) and hexamethylene diamine functionalized graphene oxide (AGO) was studied using non-isothermal differential scanning calorimetry (DSC) experiments. Loading of AGO in epoxy matrix resulted in the decrease of peak exotherm temperature (T_P) at all heating rates corroborating the enhanced curing reactions, when compared to the pristine GO filled epoxy system. The kinetic parameters of the curing processes of the neat, pristine and functionalized GO filled epoxy were determined using isoconversional methods viz. Kissinger and Friedman methods. In comparison to pristine GO filled epoxy system, epoxy nanocomposites loaded with AGO showed lower activation energy (E_α) over the range of conversion (α) revealing the enhanced curing reactions in these system. The predicted curves determined using the kinetic parameters fit well with the non-isothermal DSC thermograms revealing the proposed kinetic equation clearly explain the curing kinetics of the prepared epoxy nanocomposites.

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1. Introduction

Graphene, a single-atom-thick sheet of sp^2 bonded carbon atoms, has generated much interest due to its high specific area and novel mechanical, electrical, and thermal properties [1–3]. The discovery of graphene with its unique combination of extraordinary physical properties has motivated the researchers to use it as nanofillers in polymer system leading to the development of a new class of polymer nanocomposites. Reported methods for fabricating graphene, such as micromechanical exfoliation [4], epitaxial growth [5] and [6] and chemical vapor deposition [7] and [8] are difficult to scale up for the fabrication of polymer nanocomposites. Alternatively, chemical methodologies such as harsh oxidation of graphite leading to the formation of graphene oxide (GO) [9] and its modified derivatives [10] is an effective technique to produce graphene based nanofillers in bulk quantities, which can be subsequently used in the preparation of polymer nanocomposites. However, loading of GO in the polymer matrix resulted in the formation of composites materials with little or no conductivity and highly reduced strength due to the presence of irreversible defects and disorderness in the GO [11]. To overcome this critical issue, reduction techniques such as chemical [12] or thermal reduction [13] are often employed to reduce the surface defects in the GO. However, employing reduction techniques resulted in the formation of graphene agglomerates or restacking of graphene sheets due to the strong van der Waals interaction between the graphene sheets restricts the performance of nanocomposites, when loaded in polymer matrix [11,14]. Alternatively, surface functionalization techniques such as reactions with alkyl amines [14–18], isocyanate [19] and polyethylene glycol [20] were employed by various research groups to modify the GO surfaces. It is expected that these modified GO could significantly improve the physical properties, when loaded in the polymer matrix due to the improvement in polymer–filler interactions.

Epoxy as one of the most important engineered polymers has drawn attention due to its wide applications

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including structural materials, tissue substitutes [21], anti-corrosion coatings [22] and flame retardant additives [23]. Epoxy nanocomposites reinforced with nanofillers have attracted much interest because of their cost effective processability and tunable physical properties, such as mechanical, magnetic, optical, electrical and electronic properties [24–26]. Wide range of nanofillers including inorganic nanoparticles such as silica (SiO_2) [24], titania (TiO_2) [27], alumina (Al_2O_3) [28] and layered silicate nanoplatelets [29] and hard nanocarbon fillers such as carbon nanotubes [30–33] and fullerenes [34] have been studied. Recently, graphene nanofiller loaded epoxy nanocomposites have received significant research importance due to the significant improvement in physical, mechanical, fatigue and fracture properties [35–42].

Generally, improvement in the properties of the epoxy nanocomposites filled with pristine or modified graphene oxide depends on the formation of the crosslinked molecular network, which is often influenced by the mechanism and kinetics of the epoxy resin curing that involves various chemical reactions. Understanding the cure process in the epoxy system is the essential part in order to get better control of the cure reactions and in consequence to optimize the physical properties of the final product. One of the most widely used techniques for studying the kinetics of the cure reaction of epoxy system is thermal analysis by differential scanning calorimetry (DSC) in isothermal or dynamic modes followed by kinetic analysis using phenomenological models [43]. Among these models, Borchardt–Daniels [44], Ozawa and/or Flynn and Wall [45], Kissinger [46], isoconversional [43–47] and autocatalytic cure rate methods [48–50] are widely applied to understand the curing mechanism of thermosetting resins. Significant studies have been conducted on the curing reaction kinetics of the thermosetting epoxy resins and its nanocomposites by employing various techniques, experimental procedures and data analysis methods [51–55]. Recently, we have fabricated epoxy nanocomposites filled with hexamethylene diamine modified graphene oxide and observed significant improvement in the mechanical, electrical and flexural properties in comparison to its counterpart. However, to the best of our knowledge no research report has been published that depicts the curing mechanism and kinetics of these epoxy nanocomposites filled with hexamethylene diamine modified graphene oxide nanofillers.

The aim of the present work is to study the effect of hexamethylene diamine grafted graphene oxide on the cure mechanism and kinetics of the epoxy resin (diglycidyl ether of bis-phenol A, DGEBA) cured with polyamidoamine (G-A0533) so as to understand the structure–property relationship. For this purpose, non-isothermal DSC measurements has been carried out to reveal the cure behavior of these epoxy systems and the empirical approaches are used to model the kinetics of the curing reactions.

2. Experimental

2.1. Materials

The epoxy resin used in this study, YD-115, was provided by Kukdo Chemical Co., Korea. Kukdo YD-115 consists of diglycidyl ether of bisphenol-A (DGEBA) with a epoxide equivalent weight of 180–190 g equiv^{-1}. The resin was cured with G-A0533, supplied by Kukdo Company, Korea. G-A0533 is a liquid polyamidoamine resin with an amine hardener equivalent of 95–115 g equiv^{-1}. Natural graphite flakes used for the synthesis of graphene oxide was purchased from Sigma Aldrich Chemical Company Inc., USA. Sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$), 30 wt.% hydrogen peroxide (H_2O_2) solution, thionyl chloride ($SOCl_2$) and hexamethylene diamine (HMDA) were also procured from Aldrich Chemical Company Inc., Korea.

2.2. Preparation of graphene oxide (GO)

GO was synthesized from purified natural graphite by modified Hummer's method [56,57]. In brief, 1 g of graphite flakes was added to 100 mL of concentrated sulfuric acid and subjected to sonication for 30 min using a Branson digital sonicator (S450D, 500 W, 30% amplitude) followed by the addition of 1 g of sodium nitrate ($NaNO_3$) in an ice bath. To this mixture, 6 g of potassium permanganate was slowly added under ice-cold conditions. The mixture was stirred for 2 h, and the temperature was raised and maintained at 35 °C in a water bath for another 0.5 h. Next, 46 mL of 70 °C water was added dropwise to the solution and the temperature of the system was increased to 98 °C. Finally, 140 mL of 70 °C water was added, followed by 20 mL of 30 wt.% hydrogen peroxide (H_2O_2) solution to terminate the reaction [58]. The synthesized graphite oxide was suspended in water and purified by dialysis to completely remove residual salts and acids. The resulting GO was dried overnight at 55 °C under vacuum (40 mmHg) to produce GO powder.

2.3. Synthesis of hexamethylene diamine grafted graphene oxide (A-GO)

GO (2 g) was dispersed in 500 mL of thionyl chloride and heated at 70 °C for 24 h in the presence of 5 mL dimethyl formamide to generate GO–COCl. After purification, 1 g of GO–COCl was dispersed in ethanol containing 4 g of hexamethylene diamine (HMDA), and the suspension was sonicated for 2 h at 60 °C. After cooling to room temperature, excess HMDA was removed by washing with ethanol several times. The remaining solid was separated by filtration using a 0.2-μm membrane filter. The collected solid was again washed with ethanol several times and dried at 60 °C under vacuum to generate HMDA-GO powders (A-GO).

2.4. Nanocomposite preparation

Pristine graphene oxide (GO) and hexamethylene diamine grafted graphene oxide (AGO) was incorporated at concentrations (1 wt.%) relative to the epoxy resin. Acetone was used as a solvent to facilitate the mixing. Weight ratio of epoxy (DGEBA)/hardener (PAA) was 2:1. DGEBA and PGO with solvent were mixed for 3 min at 25 °C using a high speed mechanical stirrer at 2500 rpm. Then hardener was added and mixed for 5 min. Mixture was dried for 30 min at 25 °C under vacuum to remove the solvent. Pre-

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