Epoxy/PAMAM dendrimer-modified graphene oxide nanocomposite coatings: Nonisothermal cure kinetics study

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ABSTRACT

Highly curable nanocomposite coatings based on epoxy, graphene oxide (GO), and amine-terminated poly-amidoamine (PAMAM) dendrimer-modified GO (GO-PAMAM) are prepared and their cure behavior and kinetics are discussed. The surface of the GO platelets is chemically functionalized by PAMAM and characterized by Fourier transform infrared spectroscopy and thermogravimetric analyses. Nonisothermal cure kinetics of the prepared nanocomposite coatings are studied by the aid of differential scanning calorimetry (DSC). The results of differential and integral isoconversional approaches are coincidently indicating a lower activation energy for the epoxy/GO-PAMAM nanocomposite coatings over the whole range of conversion, particularly at later cure stages where crosslinking is agreed to be mainly controlled by the diffusion, with respect to the samples containing pristine GO. The facilitated crosslinking in epoxy nanocomposites containing GO-PAMAM has been discussed on the bedrock of autocatalytic and noncatalytic nature of the monitored cure kinetics using mathematical models.

1. Introduction

High-performance polymer nanocomposites are the combinatorial outcome of the chemistry and engineering. Nanoscale fillers/additives play the most vital role in obtaining nanocomposites with superior properties. Graphene is a two-dimensional nanosheet of sp^2-bonded carbon with a single atom thickness (≈ 0.345 nm) that can be physically, mechanically or chemically detached from graphite. This special allotrope of carbon reveals prominent features such as exceptional mechanical properties (T.S. $\cong 130$ GPa, $E_Y = 1$ TPa), thermal conductivity (K $\cong 2500$ W m^{-1} K^{-1}), and electrical conductivity (Electron Mobility $\cong 15000$ cm^2 V^{-1} s^{-1}) that makes it applicable in different fields including biosensors, drug delivery systems, super capacitors, and polymer nanocomposites [1–4]. There has been numerous researches on polymer nanocomposites containing graphene and its derivatives over the last decade to obtain hybrid materials possessing outstanding characteristics [5]. Nevertheless, there still exist major difficulties associated with the dispersion of graphene nanoplatelets in the polymer matrices as a consequence of strong tendency of graphene to form clusters/agglomerates [6]. This is mostly because of the strong

interactions of the graphene layers with each other that tightly keep them together and make it almost impossible for the resin molecules to penetrate inside the galleries. This is accompanied with the almost high immiscibility of the flakes with most of the organic resins [7]. Since the properties of graphene-based composites are strongly governed by the state of dispersion and/or the degree of exfoliation of the nanoplatelets, there has been a great deal of efforts put forth over recent years to overcome such problems.

Chemical functionalization is known as the simplest at the same time the most efficient route to prevent agglomeration/restacking of graphene nanosheets in the polymer matrices [8]. The chemical species grafted on the sheets could inhibit the restacking process through two different mechanisms: electrostatic repulsion and steric hindrance. On the other hand, by tailoring the functional groups on the surface, one may simply enhance the miscibility of the particles with the surrounding environment [9] which, in turn, reduces the driving force that causes the particles emigrate from the matrix and hence increases the stability of the dispersion [10,11]. Another important notation regarding graphene is that there exist no reactive sites on the graphene platelets that makes it almost impossible to put chemically

functionalities on the surface [12]. Oxide form of graphene, i.e. graphene oxide (GO), known as the most widely used grapheneous material, could be synthesized through the eminent modified Hummers method from natural graphite by treatment with strong acids [13,14]. Obviously, some kinds of functional groups do exist on the surface of GO platelets, e.g. hydroxyl, epoxide, ketone, and carboxyl which could be tailored via surface functionalization of GO [15]. Overall, techniques used for surface functionalization of GO could be categorized into two main classes including covalent and non-covalent functionalization. These two have been widely practiced for different polymers [16,17]. The attachment of small or large molecules onto the GO surfaces could lower the degree of nanosheet agglomeration through electrical repulsion and physical hindrance, as evidenced by octadecylamine [18], hexachlorocyclotriphosphazene [19], isophoronediamine [20], and aliphatic amines [21]. Due to inadequate active groups per common modifier molecule or their weak interaction with the graphene, the use of dendritic structures would be a wise choice for chemical functionalization of grapheneous nanoparticles [22–24].

Dendritic polymers, as the fourth generation of the macromolecules, and as their name speaks for themselves, are highly branched structures which, in turn, fall into three sub-categories: dendrimers or dendrons, hyperbranched polymers and dendrigrafts. Although these categories have structural differences, e.g. different molecular symmetry, different molecular weight distribution, however it can be said that they are all composed of three fragments: a core, branching units and functional end-groups [25]. Fig. 1 demonstrates schematic structures of the dendritic polymers.

As it is clear from the structures, by increasing the generation of the dendrimers, the number of functional end-groups exponentially increases. Hence, compared to linear polymers at the same molecular weight, much larger number of functional groups is available. Furthermore, the unique structure of the dendrimers provides them with unprecedented properties like as Newtonian rheological behavior, low viscosity, high solubility, nano-particulate form. Besides, it is also possible to replace the pristine functional groups with the desirable ones if necessary [26,27].

Considering the above paragraphs, it is out of wisdom to consider the dendrimers as promising candidate for surface modifying of nanoparticles such as GO in order to tailor its surface chemistry for consequent uses. Along with the mentioned properties, their spherical structure also helps them to penetrate in between the lamellar structure of GO and intercalate the stacks of layers which hopefully leads to a more exfoliated structure. One of the most focused dendrimers in literature is polyamidoamine, known as PAMAM, with plenty of amine functional groups on its surface. These amines are chemically capable of interacting with epoxide and carboxylic groups of GO and clearly covalent bonding is probable. The size and spherical structure of PAMAM also prevents the GO flakes to agglomerate/restack that ameliorates the dispersion stability [28].

Likewise, epoxy resin has a very special position among thermosetting materials because of its heavy-duty performance in a broad range of application from coatings and adhesives to electronic devices and biocompatible prosthesis [29,30]. Many favorable specifications are propounded for epoxies among which high chemical resistance, high hardness and excellent adhesion are attributable. However, these are accompanied with some drawbacks in properties such as brittleness, low thermal and electrical conductivity that confines its merit for high-tech applications. In this context, tremendous efforts have been devoted to tackle this challenging issue [31,32]. Incorporation of inorganic components, especially graphene and its derivatives, into the epoxy matrix has been offered as an easy and effective route to resolve such problem. For example, graphene nanosheets modified with poly(glycidyl methacrylate) containing localized pyrene groups through non-covalent functionalization approach revealed appropriate dispersion in epoxy causing considerable improvement in thermal conductivity of the epoxy composite compared to the blank epoxy [33]. The effect of the dispersion state on the mechanical, thermal and electrical properties of the epoxy resin was also examined elsewhere [6]. Despite the very low loading level of the reduced GO, glass transition temperature of the produced nanocomposite increased by 11 °C. Moreover, the electrical conductivity of the composite escalated by one or two orders of magnitude with respect to the neat epoxy. Wan et al. [34] reported that epoxy-based nanocomposites containing 0.25 wt.% GO modified by diglycidyl ether of bisphenol-A showed higher values of tensile modulus and tensile strength than that for the neat epoxy or the GO/epoxy composites, as a result of improved dispersion and compatibility of the modified GO nanosheets with the epoxy matrix. Bortz et al. [35] reported that uniaxial tensile fatigue life of the epoxy resin was improved by 1580% upon introduction of small amount of GO. Furthermore, not only acceleration in onset of crosslink density was observed, but also heat of curing reaction rose up, showing an increase in the degree of crosslinking density.

It is well-known that the state of crosslinking or the degree of epoxy resin curing in the presence of nanoparticles depends to a large extent
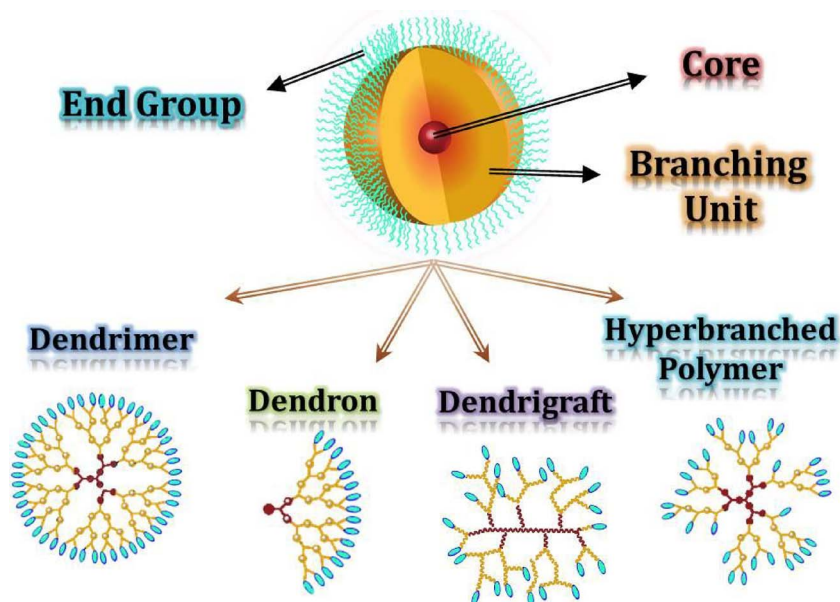
Fig. 1. Schematic structures of the dendritic polymers.