



Contents lists available at ScienceDirect

## Progress in Organic Coatings

journal homepage: [www.elsevier.com/locate/porgcoat](http://www.elsevier.com/locate/porgcoat)



# Tannic acid based hyperbranched epoxy/reduced graphene oxide nanocomposites as surface coating materials

Udangshree Boro, Niranjana Karak\*

Advanced Polymer and Nanomaterial Laboratory, Center for Polymer Science and Technology, Department of Chemical Sciences, Tezpur University, Napaam, 784028 Assam, India

### ARTICLE INFO

#### Article history:

Received 25 June 2016

Received in revised form 7 September 2016

Accepted 31 October 2016

Available online xxx

#### Keywords:

Hyperbranched epoxy

Reduced graphene oxide

Tannic acid

Surface coating material

### ABSTRACT

Hyperbranched epoxy resin (TAE) was synthesized by a simple polycondensation reaction using bio-based tannic acid as a branch generating moiety. The nanocomposites of TAE with different doses (0.25, 0.5, and 1 wt.%) of reduced graphene oxide (RGO) were prepared by solution technique. TAE was cured with poly (amido-amine) hardener at a temperature of 100 °C followed by post curing at 120 °C. FTIR, <sup>1</sup>H NMR, <sup>13</sup>C NMR etc. studies support the hyperbranched structure of the synthesized epoxy resin. Transmission electron microscopy (TEM), X-ray diffractometry (XRD), scanning electron microscopy (SEM) and UV–vis spectroscopic analysis confirmed the formation of polymer nanocomposites. The results of performance studies showed that polymer nanocomposites exhibited better performance than the pristine polymer. The tensile strength, scratch hardness, impact strength, initial degradation temperature and gloss were all improved by the formation of nanocomposite. Thus results indicate the studied nanocomposite has the potential for use as a surface coating material.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Epoxy resins represent a class of engineering materials which are extensively used in structural, composite systems and surface coating applications [1,2] because of their unique properties such as excellent adhesion to many substrates, high strength, low shrinkage, excellent chemical resistance, fatigue resistance and corrosion resistance. More than 90% of the epoxy resin used in the world is diglycidyl ether of bisphenol A (DGEBA) which is largely dependent on fossil resources [3]. Many advanced applications of DGEBA are limited due to its inherent brittleness, low toughness and very low (1–5%) elongation at break [4]. Therefore, researchers are trying to substitute fossil feed-stocks with bio-based materials for preparation of epoxy resin without sacrificing the attractive properties typical of conventional systems [5]. Vegetable oils are the most commonly used bio-based materials for synthesis of epoxy resins. But due to the presence of the long aliphatic chains and the low reactivity of hydroxyl/epoxy groups, epoxidized plant oil always leads to unsatisfactory thermal and mechanical properties. Similarly, glycerol, sorbitol, isosorbide etc. are also used to produce bio-based epoxy resins which are now industrially available [6].

However, low glass transition temperatures due to their flexible structures limits their use as structural and engineering materials, besides the productivity and availability of such bio-based resources depends on climatic conditions. So researchers are trying to find other bio-based materials which can be fruitfully used to overcome these limitations. Tannic acid, a naturally available non-hazardous polyphenolic compound containing 25 hydroxyl groups, recently gained significant interest among researchers due to its low cost and worldwide unlimited availability. Unlike vegetable oils, the production of tannic acid does not depend on climatic conditions and is hence available in all seasons as it can be obtained from bark, roots, stems and leaves of certain plants. Hence tannic acid has a great potential to be used directly as a branch generating moiety in the synthesis of hyperbranched polymers without any modification.

Although hyperbranched polymers have numerous unique properties such as high solubility, low melt and solution viscosity as well as high reactivity [7] such virgin polymers are unable on their own to reach the high performance expected in today's world for advanced applications in terms of mechanical, thermal and chemical resistance, electrical properties, thermal conductivity and so on.

In this context nanotechnology plays a significant role. In recent years polymer nanocomposites with carbon nanomaterials have gained attention of researchers because the incorporation of such

\* Corresponding author.

E-mail address: [karakniranjana@gmail.com](mailto:karakniranjana@gmail.com) (N. Karak).

nanomaterials can effectively enhance the thermal, mechanical, chemical and electrical properties of the pristine systems [8,9]. Among different carbon nanomaterials, reduced graphene oxide (RGO) has been extensively investigated as the substitute for graphene, a single layer of  $sp^2$ -hybridized carbon atoms, since it is difficult to produce graphene in large scale [10–14]. RGO shares interesting electrical and mechanical properties of graphene and its nanocomposites offer various applications in sensors, nano-electronics, catalysis, and energy storage and energy conversion devices. Several procedures are currently used for the synthesis of reduced graphene oxide including chemical and thermal methods. Chemically derived single-layered RGO sheets can be obtained by the chemical reduction of graphene oxide (GO) generated from the oxidation of pristine graphite via Hummers' method followed by exfoliation [15]. The main disadvantage of the chemical method is the irreversible aggregation of the product graphene oxide, furthermore the highly toxic nature of the reducing agents (hydrazine, sodium borohydride, hydroquinone etc.) makes it environmentally unsound. In this context the use of green technology for the reduction of GO by using vitamin C [16–18], polyphenol [19], tea solution [20], reducing sugar [21], glucose [22], melatonin, [23] wild carrot root [24], bovine serum albumin [25] and bacteria [26,27], *Amaranthus dubius* [28] etc. has been widely reported. Various phytochemicals obtained from different natural resources such as leaves, peel or other parts of plants are also used as reducing agents. *Colocasia esculenta* is abundantly available in many countries. Phytoextracts of *Colocasia esculenta* have sufficient potential to reduce the oxygen containing group of GO [29].

Thus attempt is made to synthesize a tannic acid based hyperbranched epoxy (TAE) and its nanocomposite with RGO obtained through a greener route. This may address the existing shortcomings of epoxy thermosets and ultimately the nanocomposite could be utilized as binder for surface coatings and paints.

## 2. Experimental

### 2.1. Materials

Bisphenol A and epichlorohydrin were purchased from G.S. Chemical, India. Bisphenol A was recrystallized from toluene before use. Tannic acid (TA, Sigma-Aldrich, Belgium) was dried in a vacuum oven at 55 °C prior to use. Sodium hydroxide (Merck, India), poly (amido-amine) hardener (Petro Araldite Pvt. Ltd, India), tetrahydrofuran (THF, Merck, India), concentrated sulphuric acid (98%, Merck, India), hydrogen peroxide ( $H_2O_2$ , 30%, Merck, India), concentrated hydrochloric acid (30%, Merck, India), potassium permanganate ( $KMnO_4$ , Analytical Rasayan, India), graphite flakes (60 mesh, purity 99%, Loba Chemie, India), sodium chloride (NaCl), and anhydrous sodium sulphate were used as received without any further purification. Leaves of *Colocasia esculenta* were collected from the local area of Tezpur University, India.

### 2.2. Preparation of tannic acid based hyperbranched epoxy resin

A three neck round bottom flask equipped with a water condenser and a thermometer was used for the polycondensation reaction. The round bottom flask was charged with 10 g (0.0438 mol) of bisphenol A, 0.75 g (0.00044 mol, 7.5 wt.% of bisphenol A) of tannic acid, 36.5 g (0.394 mol) g of epichlorohydrin. Then all the reactants were stirred continuously by using magnetic needle at a temperature of 80 °C until it became a homogenous mass. 5N NaOH was then slowly added to it from a dropping funnel maintaining the temperature at 110–115 °C. After 5–6 h the reaction mixture transferred into a viscous mass, then the reaction was stopped and allowed to settle in a separating funnel. The desired

organic layer was washed with 15% aqueous NaCl followed by distilled water 2–3 times. Anhydrous sodium sulphate was added to the resin and kept for 1.5 h to absorb the water. After diluting with THF it was filtered and the filtrate was collected in a one neck round bottom flask. THF and unreacted epichlorohydrin were removed from the resin by a rotary evaporator under vacuum. After drying a viscous, sticky product was obtained, encoded as TAE. Further resins with different (2.5 and 5) wt.% of tannic acid were also prepared by using the same strategy.

### 2.3. Preparation of graphene oxide (GO)

GO was synthesized from graphite flakes by using modified Hummer's method [15]. An amount of 2 g graphite powder was stirred in 40 mL of 98%  $H_2SO_4$  on a magnetic stirrer for 1.5 h. Then 6 g of  $KMnO_4$  was gradually added into the above solution by maintaining the temperature less than 10 °C (by using ice bath). The mixture was stirred at 35 °C for 12 h in a water bath. Then 90 mL of water was added to it by stirring vigorously for 1 h. A dark brown suspension was obtained. A 30%  $H_2O_2$  solution was added dropwise to it until the colour of the solution became yellow. The resulting GO suspension was washed by repeated centrifugation, first with 5% of HCl solution to remove the excess manganese salt followed by water until the pH of the solution became neutral.

### 2.4. Preparation of phytoextract and reduction of GO to RGO

About 2 g of *Colocasia esculenta* leaves was washed 2–3 times with water then ground using a domestic grinder followed by stirring for about 1 h by using 50 mL of water at 50 °C. Then the obtained aqueous phytoextract was filtered under ambient conditions. The filtrate was used for the reduction of GO.

Well dispersed GO in water was reduced by using phytoextract of *Colocasia esculenta* leaves. An amount of 6 mL phytoextract containing 0.1 M of  $FeCl_3$  solution was added dropwise into the GO suspension. After reduction it was allowed to settle down and repeatedly washed with water by centrifugation until it became neutral. The obtained reduced graphene oxide is encoded as RGO.

### 2.5. Preparation of TAE/RGO nanocomposites

RGO (0.25, 0.5, and 1 wt.% with respect to the weight of resin) was dispersed in dimethylformamide (DMF) by magnetic stirring for 6 h followed by sonication for 10 min. After getting a stable dispersion of RGO in DMF, it was added into TAE followed by continuous magnetic stirring for 3–4 h followed by sonication for 15 min. The obtained polymer nanocomposites with 0.25, 0.5, and 1 wt.% of RGO, mixed with the required amount of poly (amido-amine) hardener, are encoded as PNC0.25, PNC0.5, and PNC1 respectively.

### 2.6. Curing

Curing of TAE and nanocomposites of TAE/RGO was done by using poly (amido-amine) as a hardener. An amount of 100 phr of the hardener was mixed with resin and nanocomposites by hand mixing at room temperature in the presence of a small amount of THF. A thin film of the mixture was cast on glass slides (75 mm × 25 mm × 1.3 mm) and on metal plates. The solvent was removed from the films by using a vacuum. The films were cured at 100 °C for 1–1.5 h followed by post curing at 120 °C for about 20 min.

After curing the glass slides were kept under vacuum in a desiccator overnight. Then the slides were taken out and checked for curing by pinching with a needle. Swelling value was determined to check the extent of curing. For this purpose the cured films were removed from the glass slides, cut into small pieces, weighed and

Download English Version:

<https://daneshyari.com/en/article/4999259>

Download Persian Version:

<https://daneshyari.com/article/4999259>

[Daneshyari.com](https://daneshyari.com)