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In situ synthesis of a microbial fouling resistant, nanofibrillar cellulose-hyperbranched epoxy composite for advanced coating applications

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ABSTRACT

High performance polymeric materials have a wide variety of applications right from household smart paints and coatings to biomedical devices. This study reports a novel *in situ* synthesis of a hyperbranched epoxy nanocomposite (HENC). Nanofibrillar cellulose (NFC) was modified with a branch generating moiety, triethanol amine (MNFC) and simultaneously embedded with silver nanoparticles. This MNFC was utilized as a core to synthesize HENC *via* an *in situ* approach by reacting with bisphenol A and epichlorohydrin. The chemical structure of HENC was confirmed by FTIR, ^{1}H and ^{13}C NMR studies, with degree of branching 0.83. The poly (amido amine) cured HENC thermosets exhibited very high tensile strength (up to 160.34 MPa), without compromising the elongation at break (25.7%). Further, excellent wood to wood substrate adhesion (~2423 MPa) was provided by the HENC. Inherent antimicrobial activity of silver nanoparticles was conferred onto HENC, as evident from the assays against *Staphylococcus aureus* (minimum inhibition concentration, MIC ~120 μg/mL) and *Candida albicans* (MIC ~132 μg/mL). The HENC system thus renders a microbial fouling resistant, mechanically strong coating material with excellent adhesive power. The most fascinating part of the investigation is the synthetic protocol, which is devoid of tedious solution or melt-mixing methods to generate nanocomposite.

1. Introduction

Polymeric nanocomposites are attaining great impetus in recent times by exploiting the synergistic effect of polymers and nanomaterials. Literature has broadly showcased the utility of such systems in a number of advanced applications, ranging from high performance structural materials to biological scaffolds [1–5]. Melt mixing is the commonly adopted technique for preparation of polymeric nanocomposites, industrially [6]. Solution methods are also employed in similar context [7]. However, the most serious practical problem associated with these techniques is inefficient mixing. Moreover, solution technique uses a huge amount of organic solvents resulting in the emission of volatile organic components [8]. Hence, *in situ* synthesis of polymeric nanocomposites is an essential measure for scaling up the production, especially in case of resinous materials. With such approaches, a range of nanocomposites have been synthesized using different nanomaterials [9,10]. Yet, as the synthesis of bisphenol based epoxy needs an aqueous basic system to scavenge the HCl, generated during the diglycidyl ether linkage formation; *in situ* incorporation of nanomaterials is quite difficult. In most of the cases, a clear phase separation is witnessed between the polymer and the nanomaterial. Aqueous dispersibility of certain nanomaterials, however helps in this method. Zhang et al. in 2006, reported the synthesis of an *in situ* epoxy by using high dose of nanosilica, by a sol-gel process [11]. Recently, a carbon nanofiber reinforced epoxy nanocomposite was generated by an *in situ* technique, where a strong interfacial interaction was witnessed [12]. Bao and co-workers also reported the *in situ* preparation of functionalized graphene oxide/epoxy nanocomposite by thermal polymerization technique [13]. However, *in situ* synthesis of hyperbranched epoxy nanocomposites is rare in literature. Hyperbranched epoxy systems are superior in properties than their linear analogs, in terms of viscosity, processability, reactivity and compatibility with other matrices [14]. Such nanocomposites have been endorsed for structural adhesives, tissue scaffolds, high performance materials, biomedical and antimicrobial coatings etc [15].

Accumulation of unwanted growth of microorganisms on the surface of a substance detrimentally affects its performance and longevity. In search of a remedy to this problem, a range of antimicrobial materials and coatings have been put forwarded [16–18]. However, due to the extensive toxicity to non-target organisms, most of such materials

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were banned by different regulatory bodies [19]. Hence, it necessitates the requirement of a microbial fouling resistant coating material with adequate mechanical performance and stability [20]. Metal nanoparticles have been extensively used for achieving antimicrobial efficacy, though they cannot contribute significantly to the mechanical performance of the nanocomposite system [1]. Thus, there is a need for another material to attain the dual benefits of high mechanical performance and microbial resistant capacity. In this work, silver nanoparticles (AgNP) decorated nanofibrillar cellulose (NFC) would be used as the nano-platform for *in situ* generation of the hyperbranched epoxy nanocomposite. Cellulose nanofibers have demonstrated remarkable augmentation of thermo-mechanical properties of epoxy systems on minimal incorporation within the matrix [15,21]. Utility of NFC further facilitates the sustainability of the nanocomposite system.

The authors therefore wish to report a facile *in situ* synthesis for generating a microbial fouling resistant hyperbranched epoxy nanofibrillar cellulose composite with high mechanical performance.

2. Experimental

2.1. Materials

Fresh stems of *C. esculnta* were collected from the Assam Kaziranga University campus, Jorhat, India and sun dried after crushing and grinding. Bisphenol A (BPA), epichlorohydrin (ECH), sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2), acetic acid, tetrahydrofuran (THF), silver nitrate ($AgNO_3$) and dichloromethane (DCM) were procured from MERCK, India and used without further purification.

2.2. Isolation of nanofibrillar cellulose (NFC)

Fibers were isolated from the dried stems of *C. esculenta* by a chemical method described elsewhere [15]. Briefly, the ground mass of the dried stems was treated with 50% H_2O_2, 5% w/v NaOH and 50% glacial acetic acid sequentially, at 50 °C. Firstly, the mass was treated with 50% H_2O_2 (pH 5) with a mass to solution ratio of 1:50. After 2 h of reaction at 50 °C, the mass was washed till a neutral pH was obtained. This was followed by the treatment of the mass with 5% w/v NaOH, by soaking it in 250 mL NaOH solution for 2 h at 50 °C. The residue was washed repeatedly to maintain a neutral pH and treated with 50% glacial acetic acid for 2 h. Finally, the acid treated fibrils were washed with water by centrifugation at 8000 rpm for 15 min.

2.3. Modification of NFC (MNFC)

An amount of 1 g of NFC was taken in a round bottom flask, where 0.5 g of triethanol amine (TEA, MERCK, India) was added. The mixture was treated at 60 °C. After 30 min of reaction, 0.078 g of $AgNO_3$ (assuming 100% conversion of $AgNO_3$ to AgNP) was added and the reduction was carried out for another 4 h with constant mechanical stirring at the same temperature. This AgNP impregnated modified NFC was encoded as MNFC and dispersed in DMSO for further use.

2.4. Preparation of nanocomposites

BPA (4 g, 0.02 mol) and ECH (6 g, 0.06 mol) were taken in a round bottom flask, fitted with a condenser. The reaction mixture was subjected to continuous mechanical stirring at elevated temperature. After 30 min of reaction, MNFC (in DMSO) was slowly added to the reaction mixture in three different weight ratios, separately. After attaining a reaction temperature of 110 °C, 5 N NaOH aqueous solution was added very slowly and the reaction was continued for another 3 h at the same temperature. During the reaction time, increasing viscosity was observed by monitoring the stirring rate. The viscous resin formed after 3 h of reaction, was collected from the aqueous layer with the help of a separating funnel. The collected resin was repeatedly washed with brine solution. Then, the resin was allowed to dry at 70 °C for 48 h. Three different nanocomposite systems were prepared according to the amount of MNFC, *viz.* 1, 2 and 3 wt percentages and encoded as HENC1, HENC2 and HENC3 respectively. Further, a linear epoxy (PE) and a TEA based hyperbranched epoxy (HE) were also considered for comparative studies. HE was synthesized as per the reported procedure [22].

2.5. Casting and curing

Homogenous mixtures of PE, HE, HENC1, HENC2 and HENC3 with poly(amido amine) hardener were prepared by hand stirring for a few min by using minimum amount of THF. Hardener was taken equimolar to the epoxy equivalent of the resins. The mixture was cast at room temperature on glass plates (150 × 100 × 1.44 mm^3) for 48 h. After the films became touch free they were cured at a definite temperature for specific time.

2.6. Characterization

FTIR spectra of NFC, MNFC, HENC3 resin and thermoset were recorded in a FTIR spectrophotometer (Impact-410, Nicolet, USA) using KBr pellet. ^1H and ^{13}C NMR spectra of HENC3 resin were recorded in a Bruker Avance III 500 MHz FTNMR spectrometer, using tetramethylsilane (TMS) as an internal standard and $CDCl_3$ as the solvent. Distribution of MNFC within the polymeric matrix as well as its shape size accord were analyzed by transmission electron microscopic images captured in a TEM, JEOL-JEM 2100 instrument at 200 keV.

Tensile strength and elongation at break were measured for rectangular cured films (60 × 10 × 0.3 mm) with the help of a Universal Testing Machine (Aimil Instrumentation and Technologies Ltd., India). Lap shear tensile adhesive strength was determined for HENCs as well as for HE and PE by applying the resins on overlapping wood substrates of size 25 × 25 × 0.3 mm^3. Impact strength was determined by falling weight (ball) method (ASTM D 1709). Bending test was performed by a mandrel with diameter 1–100 mm (standard ASTM D 522) [15]. Gloss values of the cured resins were determined by a glossmeter (Minigloss meter, Sheen, UK), over the coated steel plates at an angle of incidence, 60°. Scratch hardness was measured by a scratch hardness tester, Model no. 705, (Sheen, UK) equipped with a stylus accessory.

Weighed amount of the cured HENCs, HE and PE films were immersed in sufficient amount of THF for 48 h to carry out the swelling test. After 48 h, the weight of the swollen film was measured according to the reported methods [14].

2.7. Microbial fouling resistance assay

The test organisms used for the fouling resistance study were *Staphylococcus aureus* (ATCC 11632) and *Candida albicans* (ATCC 10231). Luria Bertani broth and Potato Dextrose broth (HiMedia, India) were used to culture the bacterium, *S. aureus* and the fungi, *C. albicans*, respectively. *S. aureus* culture was incubated for 24 h, at 37 °C and *C. albicans* culture was maintained for 48 h at 28 °C.

First phase of the study was carried out by determining the minimum inhibitory concentration (MIC) of MNFC, HENC3 and $AgNO_3$ against the aforementioned microorganisms. Solutions of 50 mg mL^{-1} concentration were prepared for each sample in 1% DMSO and used as the stock solutions. Micro-dilution technique was employed to obtain a final concentration range of 10–150 μg mL^{-1}. Then, 100 μL of the samples were poured into 96 well plates. A commercial antimicrobial agent, ampicillin was taken as the control for comparison. Each microbial strain (100 μL) was added to the wells of two different plates and incubated separately. Subsequently, 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT solution, 40 μL) was added to the wells. No change in color confirmed the inhibition of microbial growth, while formation of blue color indicated microbial survival [20].

Again, the growth of the microorganisms was monitored in presence