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Carbon dot – Unique reinforcing filler for polymer with special reference to physico-mechanical properties

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ABSTRACT

This work reports the reinforcing efficiency of carbon dots (CDs) in carboxylated acrylonitrile butadiene (XNBR) latex at very low concentration. Amine and carboxyl functionalized CDs have been synthesized from citric acid and glycine. The CDs are covalently conjugated to XNBR latex using 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC.HCl) and N-hydroxysuccinimide (NHS) as coupling agents. The covalent conjugation of CDs with XNBR latex has been confirmed by Fourier transform infrared spectroscopy (FTIR), dynamic light scattering (DLS) and X-ray photoelectron spectroscopy (XPS). The optical properties of CDs and XNBR-CDs conjugate have been characterized by ultraviolet (UV) - visible, fluorescence spectroscopy, time-resolved fluorescence spectrophotometer and haze meter. The tensile stress-strain properties of XNBR latex dramatically increases by the addition of CDs to XNBR latex. The maximum tensile stress of 2 phr of CDs loaded XNBR latex is nearly 215% higher than the maximum tensile stress of neat XNBR latex. There is a concomitant decrease in the tan δ peak height and increase in the tan δ peak temperature of XNBR latex with the incorporation of CDs to XNBR latex. In addition, the storage modulus (G′) value of sample containing 2 phr of CDs is 161% higher than the storage modulus value (G′) of neat XNBR latex. The onset of degradation temperature (T_i) value of sample containing 4 phr of CDs is 40 °C higher than the T_i value of neat XNBR latex. On the other hand, the maximum degradation temperature (T_{max}) of XNBR latex containing 1 phr of CDs is 11 °C higher than the T_{max} value of neat XNBR latex. Morphology of pristine CDs and XNBR-CDs conjugate has been analyzed using transmission electron microscopy (TEM). To the best of our knowledge, this is the first report which analyzes the effect of CDs on the physico-mechanical properties of elastomer contrary to the other novel fillers of carbon family.

1. Introduction

The members of the carbon family fullerene, graphene and nanotube have attracted scientist due to their unique properties and numerous applications in various field [1–4]. Carbon dots (CDs), a newcomer in the family of carbon nanomaterials are currently the centre of conversation in nanotechnology. The CDs having size from 1 to 10 nm possess excellent brightness, chemical inertness, low toxicity and high resistance to photobleaching which imparts huge demand to CDs [5,6]. The enormous potential applications of CDs for sensing, bio imaging, lasers, photo catalysis, light emitting diodes and desalination of sea water make these nanoparticles promising alternative to many other nanomaterials [7]. In literature, there are few reports which discuss the procedure for encapsulating hydrophilic CDs in the hydrophobic polymer environment for improved solar cell energy conversion and opto-electronic devices [8–11].

Landi et al. have incorporated CDs and single wall carbon nanotubes (SWNTs) into poly (3-octylthiophene) [12]. Reportedly, the nanocomposite exhibits high electron affinity and high electrical conductivity which can be used for light weight polymeric solar cell applications [12]. Yu et al. have investigated the temperature dependent fluorescence in CDs and revealed that CDs exhibit dual photoluminescence [13]. De et al. have prepared an in situ generated photo-luminescent transparent biocompatible hyperbranched epoxy/CDs nanocomposite [14]. The study revealed that the in situ prepared nanocomposites possessed superior optical and biocompatible properties compared to pristine epoxy as well as

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the ex situ prepared nanocomposites [14]. Hao et al. have investigated the effect of CDs in polyethylene glycol (PEG) to produce PEG/CDs nanocomposites film for tunable blue-red light emission [15].

The use of CDs for in vitro and in vivo application of oligomeric PEG molecules has been studied by Yang et al. The results suggested that CDs were biocompatible and their performance as fluorescence agents was competitive in PEG molecules [16]. De et al. has fabricated a highly tough thermostable hyperbranched epoxy nanocomposite by the incorporation of CDs reduced copper oxide (Cu_2O) nanohybrid which exhibits excellent photocatalytic activity under solar light [17].

Chen et al. have successfully functionalized the carbon dots with polymethyl methacrylate (PMMA) via chemical and physical interaction. It was shown that the as-prepared Carbon dot-PMMA film shows good transparency in sun light and the overall thermal stability increased in comparison to the pure PMMA film [18]. Wang et al. have demonstrated the preparation of aminopropylmethylpolysiloxane (AMS) functionalized luminescent carbon dots (AMS-CDs) by one step solvothermal method that could form CDs cross-linked Silicone rubbers (SRs) by self- or co-cross-linking with AMS [19]. Xie et al. have prepared highly daylight photoluminescent and full band UV shielding silane-functionalized graphene quantum dot (SiGQD) nanofluids and their polymerized organic–inorganic hybrid Ormosil gel glasses via a facile and efficient technique [20]. Zhang et al. have demonstrated a facile and versatile approach to fabricate fluorescent polymers using novel polymerizable carbon nanodots. It was shown that this methodology is highly efficient and versatile approach to various fluorescent materials for optical sensing, biomedical imaging, cell labeling and even UV protection for optical devices [21]. Xie et al. have prepared silane prefunctionalized CDs (SiCDs), ormosil nanohybrid gel glass composite (Si-CD-Gel) glasses and macrostructure monoliths (100% SiCD-Gel glasses) which is having good long term optical, thermal and mechanical stabilities [22].

However, till today, there are no reports in literature which discuss the unique method for dispersing CDs in the polymer matrix and understanding its reinforcing efficiency with special reference to polymer-filler interaction. On the other hand reinforcing efficiency of nanoclay, graphene and nanotubes in polymer matrices are well explored [23–25]. For the first time in literature, this work attempts to explore the reinforcing efficiency of CDs in polymer latex. In this work water soluble CDs have been doped and well dispersed in polar hydrophilic carboxylated acrylonitrile butadiene rubber (XNBR) latex via covalent conjugation. CDs have been covalently conjugated to XNBR latex using EDC (1-3-dimethylaminopropy l-3-ethylcarbodiimide) /NHS (N-hydroxysuccinimide) mediated amide coupling.

The optical characterization of CDs and XNBR-CDs conjugate was investigated by using ultraviolet (UV) - visible, fluorescence spectroscopy and haze meter. The covalent conjugation of XNBR latex with CDs was confirmed by Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS). Hydrodynamic radii of XNBR latex with increasing concentration of CDs were determined by dynamic light scattering (DLS). The effect of CDs ratio and extent of CDs dispersion on the mechanical and rheological properties of XNBR latex has been analyzed using universal testing machine (UTM) and modular compact rheometer (MCR). Thermogravimetric analysis (TGA) has been used to evaluate the thermal stability of XNBR latex and XNBR-CDs conjugate. Morphology of the pristine CDs and XNBR latex with different concentration of CDs has been studied using transmission electron microscopy (TEM). The superior reinforcing effect and retention of fluorescence of CDs in the XNBR latex is expected to hasten the development of unique polymers having remarkable photophysical and physico-mechanical properties for multifaceted applications.

2. Material and methods

2.1. Material

Carboxylated acrylonitrile butadiene rubber (XNBR) latex, XNB 300 with acid content (COOH) of 6%, acrylonitrile (ACN) content of 28% and density of 1 g/cm^3 was supplied by Apcotex Industries Limited, Mumbai, India. Citric acid monohydrate, glycine, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC.HCl) and N-hydroxysuccinimide (NHS) were obtained from Alfa Aesar, Hyderabad, India. All chemicals were used as received. Nanopure water from millipore was used in all experiments.

2.2. Preparation of samples

2.2.1. Synthesis of N-doped CDs

The CDs were prepared by hydrothermal treatment of citric acid as a carbon source and glycine as a nitrogen source. In a typical synthesis of CDs, citric acid (10 mmol) and glycine (10 mmol) were dissolved in 15 mL water and mild heating was done at 120 °C to prevent the carbonization of surface functional group for 12 h, the optimized condition for CDs with high quantum yield (QY). After heating, the autoclave was allowed to cool naturally. The resulting solution was diluted to 50 mL and centrifuged at 8000 rpm to remove the large agglomerated particles and the unreacted organic moieties. The light yellow aqueous solution containing CDs was collected and filtered through 0.2 μm filter. The purified CDs solution was stored at 4 °C for further use.

2.2.2. Covalent conjugation of XNBR latex with CDs and preparation of film

Primarily, for covalent conjugation of CDs to XNBR, the quantitative estimation of $-NH_2$ group on the surface of CDs was done by using ninhydrin reagent [26] and the -COOH group were determined by titration with 0.05 M NaOH solution. To prevent the interference from $-NH_2$ groups on the surface of CDs during titration with NaOH the $-NH_2$ groups were blocked by formaldehyde [27]. The XNBR was covalently conjugated to CDs using EDC/NHS mediated amide coupling. The carboxyl group of XNBR was activated by adding 0.1 M EDC and 0.2 M NHS to 10 mL of XNBR solution at room temperature. To this activated rubber solution 10 mg (0.1 phr) of CDs were added and stirred for 3 h. Excess of EDC and NHS were removed by dialysis (MWCO- 1KDa). Similarly, CDs were conjugated to XNBR latex in different ratios as shown in Table 1. The solution of XNBR-CDs was casted in a petri dish for film preparation. The average thickness of the films was about 0.5 ± 0.05 mm.

Table 1
Composition of samples prepared.

Sl. no.	Sample designation	Amount of XNBR (parts)	Amount of CDs (phr[a])
1.	XNBR	100	0
2.	XNBR + 0.1 phr CDs	100	0.1
3.	XNBR + 0.5 phr CDs	100	0.5
4.	XNBR + 1 phr CDs	100	1
5.	XNBR + 2 phr CDs	100	2
6.	XNBR + 4 phr CDs	100	4

[a] phr = parts per hundred ml of rubber latex.