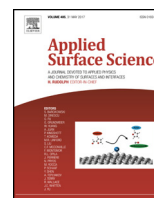




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Studies on biodegradable polyurethane-SWCNTs nanocomposite films by covalent approach: Physicochemical, electric and mechanical properties

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ABSTRACT

Biodegradable control polyurethane (PU) film as well as PU nanocomposite films (PU-SWCNTs), covalently incorporated with minor amount of hydroxyl single walled carbon nanotubes [(OH)_n-SWCNTs] have been formulated to investigate the influence of SWCNTs on the matrix of PU (3-dimensional network of soft and hard segments). Biodegradable polyol, polycaprolactone triol (PCL, ~70%), diisocyanate (TDI, ~21%) and 1, 4- butane diol (BDO) as chain extender were taken to react at 70 °C under inert atmosphere in the presence of amine catalyst (PMDETA) via prepolymer process to obtain the control PU film by casting approach, whereas *in situ* addition of (OH)_n-SWCNTs into the above formulation can afford the covalently incorporated PU-SWCNTs films by the identical protocol. PU and PU-SWCNTs films loaded with variable quantity of (OH)_n-SWCNTs (0.01, 0.03, 0.05, 0.1 and 0.3 wt.%) were characterized to identify the enhancement of their physicochemical properties such as optical, electrical conductivity, thermal and mechanical properties. These film samples were characterized by FT-IR, Raman, ATR-FT IR, UV-vis DRS, solid state ¹³C NMR, XRD, impedance measurements, DSC, TGA, EDX, SEM, AFM, optical microscope and tensile strength data.

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1. Introduction

Polymeric nanocomposites use to constitute the homogeneously dispersed organic or inorganic nanomaterial on polymer matrix with variable loading in the range of 0.5–10% [1]. Both bio-derived and biodegradable polymer matrices have intrigued researchers due to the depletion of fossil resources, used as monomers for the wide range of synthetic polymers [2–4]. Polymeric products like polypropylene, polystyrene, polyethylene and polymethylmethacrylate are accumulated as non-biodegradable wastes globally including variety of composites [5]. Since the biodegradable polymers are formulated alternatively from the renewable and biodegradable precursors, polymeric nanocomposites derived from this category of samples have to be tuned in terms of mechanical, electrical and thermal properties, these properties

are possible to achieve conventionally in nanocomposites of commonly available non-biodegradable polymers [6,7].

PU and PU nanocomposites can be developed by the versatile synthetic methodologies as environmental friendly process upon elimination of toxic chemicals and multi-step procedure to develop the potential products possessing the desirable biological, physicochemical, mechanical and conductive properties. These products are under investigation for the various applications like energy harvesting, self-healing, shape memory and tissue engineering. Aliphatic polyester, polycaprolactone polyol (polycaprolactone diol and polycaprolactone triol) is classified as one of the essential biodegradable precursor to replace the role of non-degradable petrochemicals, their degraded by-products use to be non-toxic [8–12]. Synthesis of PU from polycaprolactone diol or PCL found to be desirable for their properties like biodegradable, hydrophobic, biocompatible and bioresorbable due to their feasible conversion into mild products. For e.g., 6-hydroxyhexanoic acid can be converted into natural metabolite, adipic acid by microsomal ω-oxidation [13,14]. We are aiming to develop the biodegradable nanocomposite as film (~1.5 mm) with characteristic properties from the petro-based precursor (trifunctional polyol, PCL) to for-

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mulate PU as well as PU nanocomposite in the form of films, loaded with trace quantity of carbonaceous nanomaterial (SWCNTs) by casting method for the investigation of their optical, thermal, mechanical and conductivity properties [15–17].

Essentially, polycaprolactone diol ($f_n = 2$) has been explored by the several groups, whereas the PCL ($f_n = 3$) found to be chosen as the polyol precursor in limited cases for our knowledge. PU scaffold from the mixture of polycaprolactone diol and PCL via one-shot method is found to be an alternative for the cartilaginous tissue in plastic and reconstructive surgery [18–20]. In the present work, PCL is used as major component (~70%) for the development of biodegradable nanocomposite film with hydroxyl functionalized SWCNTs. In this formulation, hard segment of PU matrix is comprised of urethane link from the highly reactive aromatic diisocyanate (TDI) while the soft segment is associated with aliphatic polyester polyol (PCL, ~M.W. 2000).

Inorganic carbon nanotubes use to be exemplified as ubiquitous and subject of interest since their discovery in 1991 by Iijima [21]. Both pristine SWCNTs and functionalized SWCNTs in the form of nanomaterials tend to be utilized in variety of applications, nanoelectronics to nanocomposite fabrication due to its high aspect ratio with thermal, mechanical and electronic properties [22]. As such SWCNTs can exhibit enormous potential to explore the enhancement of fore mentioned properties, even upon loading well below 0.5% in polymers matrix [23,24]. It is typical to form polymer nanocomposites based on SWCNTs for several applications, by the versatile of methods such as *in situ* polymerization, non-covalent, solution, grafting and melt mixing etc.[25–29]. Among those methods, Song and Hesheng et al. have preferred to accomplish the formulation of PU nanocomposites using SWCNTs by two step *in situ* polymerization [30,31]. Since few challenges are accounted with SWCNTs such as poor miscibility with polymer and solvents, both solution processing and the preparation of composite samples containing carbon nanotubes (CNTs) found to be uncommon. In fact the chemical functionalization of CNTs has been a subject of several reviews, wherein the solubility, dispersion and stress transfer were demonstrated to illustrate the mechanical properties [26–28]. The facile interface between SWCNTs and polymer matrix enhances the load transfer among the nanotubes and polymer network to exclude interfacial collapse, particularly the functionalized SWCNTs tend to be affordable to form such robust polymer composites. Chemical functionalization favours the isolation of entangled or bundled SWCNTs for the suitable orientation.

Another concern about the polymer nanocomposite is identified that if SWCNTs gathered by agglomeration, which could cause the loss of inherent properties supposed to be incorporated into the 3-dimensional network of polymer matrix. To ascertain the uniform distribution of SWCNTs on polymer matrix, we have established an efficient and viable strategy to accomplish the effective interfacial adherence of functionalized $(\text{OH})_n$ -SWCNTs with polymer matrix via covalent bond [32–34]. In general, functionalization of SWCNTs requires the treatment of hazardous reagents and stringent reaction conditions with multi-step synthetic route to obtain the poor yield of functionalized SWCNTs [35–38]. Carboxyl and hydroxyl functional groups were substituted on carbon nanotubes by simple mechanical grinding of the reactants at ambient condition by mechano-chemical reaction [39,40]. Our two steps synthetic strategy to substitute hydroxyl groups on side walls of SWCNTs to obtain good yield of $(\text{OH})_n$ -SWCNTs has excluded any multi-step or rigorous condition during the reaction, which can retain the unique properties of SWCNTs as well [32].

At present, PU nanocomposite formulated in this work is described to be unique due to the fact that the biodegradable trifunctional polyol, PCL has been chosen to form prepolymer followed by covalent incorporation with $(\text{OH})_n$ -SWCNTs in the presence of chain extender (BDO). In literature, reports to develop

the polymeric nanocomposites with biodegradable properties exist under progress to match with the properties of conventionally available non-biodegradable polymers. Moreover, our report demonstrate the efficient and fairly cost effective use of trace quantity (0.01–0.3 wt.%) of $(\text{OH})_n$ -SWCNTs in the formulation of PU-SWCNTs nanocomposite in the form of film (~1.5 mm). In general, PU-SWCNTs nanocomposite film formulations use to encounter the opportunity to exhibit agglomeration of SWCNTs while used as pristine sample (*p*-SWCNTs). Currently, *in situ* addition to incorporate the functionalized $(\text{OH})_n$ -SWCNTs towards the generation of covalent bond across the network of PU matrix can exclude the possibility of agglomeration and improves the opportunity of effective interfacial interaction and preferred homogeneous distribution of SWCNTs on the film of PU network.

2. Experimental details

2.1. Materials

Polycaprolactone triol (PCL, CAPA 3201, ~M.W. 2000, soft waxy solid at RT, OH value: 85.85, melting point: 40–50 °C) has been received as the gift sample from Perstrop India Limited. Pristine SWCNTs, 2, 4-toluene diisocyanate (TDI), 1, 4-butanediol (BDO), N, N, N', N'', N'''-pentamethyldiethylenetriamine (PMDETA) and dry toluene were procured from Sigma Aldrich, USA. Tetrahydrofuran was purchased from Merck specialties Private Limited and distilled after stored overnight in calcium chloride. The other reagents were procured from the chemical suppliers available at India.

2.2. Methods

Tensile strength and Youngs moduli were measured using an Instron 3369 tensile testing system, USA. ABB MB3000 spectrometer was used to collect ATR-IR on control PU and nanocomposite films. Raman spectra for the functionalized SWCNTs and nanocomposite films were collected from the Confocal Raman spectrometer (Nanophoton Corporation, Japan, excited at 532 nm). AFM imaging was carried out by NT-MDT (NTEGRA Prima, Netherlands). UV–vis DRS data was characterized using a LAMBDA 650 UV/vis spectrophotometer. OLYMPUS BX50 with transmitted light was used to record the optical microscopic images of nanocomposite films. DSC profiles were recorded between ambient temperature to 300 °C using TA-Instruments DSC Q200. TGA thermogram for the samples was carried out by Q50 TGA, TA Instruments. XRD pattern of PU was studied by X-ray diffraction analysis by X-ray diffractometer (Rigaku miniflex). The probe sonicator Sonics VCX 750 (750 W, 20 KHz, Sonics & materials, Inc., Newtown, USA) operated at 60% amplitude to get homogeneous material.

2.3. Control PU film

PCL (4 g) was taken in three necked RB flask, melted at 50 °C in oil bath and allowed to stir using mechanical stirrer under nitrogen atmosphere for 15 min under inert atmosphere. PCL and 2, 4-toluene diisocyanate (TDI) were taken in 1:2 ratio to obtain prepolymers. TDI (1.20 ml) was then added and continued to stir at the temperature in oil bath. After 10 min, dry THF (10 ml) and tertiary amine, PMDETA (1.26 μ l) were added to polyol. The reaction temperature was raised to 75 °C and stirred constantly for 90 min. In the mean while reaction mixture was added occasionally with THF (3 ml) to maintain its viscous state as well as to avoid the gel formation. Now, the chain extender (1, 4-butane diol, 60 μ l) was added and continued to stir for 15 min. The viscous reaction mixture was removed from the oil bath and the composition was transferred to a petri dish. The curing step was carried at ambient temperature for a week followed by curing at 75 °C under vacuum for 6 h. After

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