Influence of graphene on self-assembly of polyurethane and evaluation of its biomedical properties

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ABSTRACT

Novel aliphatic polyurethane (PU) nanohybrids have been prepared using varying amount of graphene by dispersing it in the early stage of polymerization (in situ) and achieved uniform distribution throughout the matrix, required for the improvement of properties. The alteration of self-assembly in presence of graphene have been explored through X-ray diffraction, small angle neutron scattering, atomic force and optical microscopy in the length scale of nanometer, tens of nanometer, hundreds of nanometer and micron range, respectively, indicating the layer by layer self-assembly of polymer and graphene in nanohybrids. The cause of self-assembly has been studied through spectroscopic techniques like FTIR and UV–vis measurements revealing strong interaction between polymer chain (both hard and soft segments) and graphene which is further confirmed from the depression of melting point and decrease in heat of fusion with increasing graphene content in the nanohybrids. The toughness of nanohybrids in solid state improves considerably as compared to pure PU and the mechanical strength in liquid state also dramatically increases with graphene content showing a dip at a particular frequency depending on the strength of self-assembly (greater for higher graphene content nanohybrid) followed by its reformation at higher frequency. Sustained drug release has been achieved in presence of graphene explaining the phenomena from the greater tortuousity in nanohybrids arising from the 2-D graphene and small but uniform cluster size of self-assembly as compared to pure PU. The suitability of the developed nanohybrids has been testified for its use in biomedical arena by checking the complete biocompatibility of the nanohybrids as compared to pure PU using bone marrow derived mesenchymal stem cells.

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1. Introduction

Polyurethanes (PUs), a versatile polymeric material, represent a class of polymers that are widely used in medical, automotive and industrial fields [1]. It has usually been synthesized using polyol, diisocyanate and chain extender and due to its ease of processability and possibility of altering the chemical compositions, these polymers are widely used [2]. The properties of PUs can be modified either by changing the composition or by the chemistry of polyol, diisocyanate and chain extender or by using the appropriate filler in the polymer matrix [3]. The blocky nature of PU arises from its hard and soft segment and depending upon these segmental composition and specific interactions between them (soft–soft, hard–soft, and hard–hard segments), varying shapes like globular, fibrillar, cylindrical or lamellar structures are formed originating from the interconnected hard/soft domain network [4]. Recently, self-assembled PUs have been widely used in tissue engineering, shape memory materials, molecular recognition and drug delivery applications and the nature of these polymeric self-assemblies can be altered by changing the chemical structure and constituents of polymer or by using fillers in the matrix [5–7]. There are various types of fillers being used to

enhance the polymer properties depending upon the shape, size, aspect ratio and surface modification of the fillers [8]. PUs have drawn much attention as compared to other polymer/shape memory alloys because of their high shape recoverability, good processing ability, low cost and wide temperature range for recovery and such polymers have a wide range of applications in medical sciences as smart actuators and in aerospace and textile engineering [9,10]. Due to outstanding physical, mechanical properties and good biocompatibility, PU has been extensively used in various applications [11]. Very recently, carbon in different forms like carbon black, carbon nanotubes (CNTs) and layered silicates have extensively been used for the preparation of polymer nanohybrids [12,13]. Carbon has different allotropic structure like 0-D (fullerenes), 1-D CNTs and nanoribbons, and 2-D graphene sheet structure. Fullerene allotrope of carbon can be made by wrapping a section of graphene sheet and CNTs and nanoribbons by rolling and slicing of graphene sheet [14]. CNTs dispersed in hyperbranched PU has been reported to be effective as shape memory and mechanical properties [15,16]. On the other hand, round shaped polyhedral oligomeric silsesquioxane (POSS) attached to thermoplastic PU suppresses the enzymatic degradation of PU by preventing the ester linkages from enzymatic attack [17]. Graphene, a two-dimensional sheet composed of sp^2 carbon atoms having a number of extraordinary optical, electrical, thermal and mechanical properties [18,19]. Due to its high surface area (2630 m^2/g), good electronic conductivity *i.e.* (mobility of charge carriers ~ 2 × 10^5 cm^2 V^{-1} s^{-1}), mechanical strength (Young's modulus ~1100 GPa) and biocompatibility of the graphene sheet, it has potential to be used as filler for polymeric matrices [20]. Mostly graphene oxides or functionalized graphene have been used as filler for PU to enhance the mechanical, thermal [21], gas barrier, electrical conductivity [22], and shape memory effect [23] using predominantly aromatic based PUs have been reported in the literature. Further, pure graphene sheets exhibit the biocompatible nature using bone marrow derived mesenchymal stem cells (BMMSCs) and have the potential to be used in tissue regeneration [24] but it is required to have support like polymer for its use as potential implant. To the best of our knowledge, there is no report about graphene induced self-assembly in PU and the effect of the self-assembly on practical applications such as controlled drug delivery and its potential use as biomaterials.

In this work, the main aim is to study the effect of embedding 2D graphene sheet in PU matrix and to explore the layer by layer self-assembly (nanoscale to microscale) in PU in presence of graphene. Special technique has been adopted to uniformly disperse the graphene in polymer matrix. The effect of self-assembly on mechanical, thermal and rheological properties has been studied in detail both in solid and liquid state showing structure property relationship of supramolecular PU. The structure of nanohybrids has also been studied through small-angle neutron scattering (SANS) and X-ray diffraction (XRD) techniques. The thermal properties have been studied through thermogravimetric analyzer (TGA) and differential scanning calorimeter (DSC). Control release of drug has been demonstrated by regulating the size of assembly in presence of graphene.

2. Experimental

2.1. Materials

Poly(tetramethylene glycol) (PTMG) (Sigma–Aldrich, number-average molecular weight, M_n = 2900 g/mol), 1,6-hexamethylene diisocyanate (HMDI), and 1,4-butanediol (BD) (Merck, Germany) were used as received. Graphene nanoparticles were purchased from Redex Nano Lab (Noida, India). The catalyst dibutyltindilaurate (DBTDL) and solvent, dimethyl formamide (DMF) were purchased from Himedia and Merck, respectively.

2.2. Synthesis of polyurethane and its nanohybrids

The polyurethane (PU) was synthesized in two steps: prepolymer preparation using PTMG and HMDI followed by addition of chain extender BD, DMF as solvent and catalyst (DBTDL: 0.1 ml of 1 wt.% toluene solution) to complete the polymerization reaction with rapid stirring at 70 °C for 24 h. The molar ratio of PTMG: HMDI: BD was kept 1: 5: 4, respectively. The polymer was obtained by pouring the solution in deionized water and dried in vacuum oven under reduced pressure at 65 °C for 50 h. The hard segment content of polymer was maintained at 30% by using a predetermined amount of polyol, diisocyanate and chain extender. Polymer nanohybrids were prepared by using graphene nanoparticles (2, 4, 6 and 8 wt.% with respect to polymer weight) during the first phase of polymerization process after suitably dispersing the graphene nanoparticle in PTMG. The nanohybrids are designated as PU-G2, PU-G4, PU-G6 and PU-G8 for 2, 4, 6 and 8 wt.% of graphene in the nanohybrids, respectively. The molecular weight of PU and its nanohybrids are ~38,000 g/mol (PDI ~ 1.5), measured through gel permeation chromatography using DMF as eluent at 70 °C with 1 ml/min flow rate. The formation of polymer and its nanohybrids scheme are given below.

$$PTMG + graphene \rightarrow mix \xrightarrow{HMDI} mix \xrightarrow[DBTDL]{BD} PTMG$$

$$- Gr \text{ nanohybrids}$$
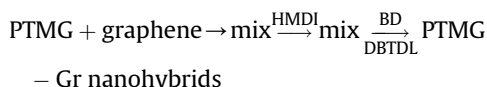
2.3. Structural analysis

X-ray diffraction was measured using a Bruker AXS D8 Advance wide angle X-ray diffractometer with a graphite monochromator using Cu Kα source with a wavelength of 0.154 nm. The generator was kept at 40 kV and 20 mA. The thin films of the samples, prepared through solution casting technique, were placed on a quartz sample holder at room temperature at the scanning rate of 1°/min. Small angle neutron scattering (SANS) experiments were done on the spectrometer at the Dhruva reactor at Bhabha Atomic Research Centre, Mumbai, India. The SANS experiment was performed in the scattering vector (q) range of 0.17 $nm^{-1} \leq q \leq$ 3.5 nm^{-1}. The Scattering from the samples were corrected for background contribution. Debye-Bueche and other models were fitted separately in lower range of q. The characteristic length (Λ_c) was obtained through the equation $\Lambda_c = 2\pi/q_m$, where q_m is the scattering vector q corresponding to the peak position in scattering pattern and the temperature of experiment was kept constant at 30 °C.

2.4. Spectroscopic examinations

Fourier transform infrared (FTIR) spectrum was measured in reflectance mode at room temperature from 650 to 4000 cm^{-1} using a Nicolet 6700 FTIR with a resolution of 4 cm^{-1}. The UV−visible measurement was performed in the range of 200−1100 nm in the reflectance mode using solid specimens (Cary Bio-100, Agilent).

2.5. Thermal studies

The melting point and heat of fusion of PU and its nanohybrids were measured using differential scanning calorimeter (DSC, Mettler 832) over a temperature range of −90 to 200 °C at a scan rate of 10 °C min^{-1}. The peak temperature and heat of fusion were