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Aligned ZnO nanorods as effective reinforcing material for obtaining high performance polyamide fibers

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A B S T R A C T

The present study is an attempt to demonstrate that a small amount of rigid anisotropic nanostructures such as ZnO nanorods can be successfully used to transform commodity grade polymer to high performance grade fibers. ZnO nanorods with aspect ratio 14 and nanoparticles of circular shape were synthesized, melt-blended with nylon 6, melt spun, and subsequently, drawn to obtain composite fibers. The effect of shape and amount of nanostructure on the properties and morphology of the composite fibers was investigated. It was found that unlike the inclusion of ZnO nanoparticles, the incorporation of ZnO nanorods inside the nylon 6 fibers resulted in formation of highly oriented fibrillar morphology, which was instrumental in an increase of tensile strength by 115% to a value of ~1 GPa and initial modulus by 142% to a value of 4.26 GPa while retaining high extensibility. Consequently, the composite fibers show high work of rupture, which makes them suitable for high impact applications.

1. Introduction

Polymer nanocomposite is a fast growing research area to develop new materials with enhanced performance properties. Nanoparticles have been widely used in polymer composites because of their high surface area, which results in improved interaction with the matrix. Incorporation of nanostructures inside polymer matrix can result in enhancement in properties, such as mechanical [1], thermal stability [2,3], electrical [4], UV resistance [5], gas barrier [6], fire retardancy [7], antimicrobial [8] etc. The mechanical performance of nanocomposites is expected to depend upon the shape and size of nanofillers and their interfacial interaction with the polymer matrix. Several nanostructures such as particles [9] (nano in 3D), clays [10] (nano in 2 D) and carbon nanotubes (CNTs; which are nano in 1 D) [11,12] have been used for preparing various polymer based composites.

Fibers are mechanically superior materials compared to films, moulds and casts for various applications. Their properties principally depend upon the orientation of the molecular chains in the direction of the fiber axis. Because of the limitation on nature of available polymeric materials and their processability, the known fibers have not been able to achieve the theoretically estimated properties. Incorporation of nanostructures in the polymeric fiber has opened up new approaches for pushing the limits of properties to a higher level. Processing of composites in the form of fibers is expected to enhance the properties of these composites by coaligning nanostructures with molecular chains along the fiber axis. In order to achieve the benefits of nanostructures, it is essential to incorporate high aspect ratio nanostructures, such as CNTs, and ensure their homogeneous dispersion and uniform distribution in the polymer matrix. However, the dispersion of nanomaterials, especially the high aspect ratio nanostructures such as CNTs, is a major challenge in processing of composites.

Solution processing is the most commonly used technique for the production of reinforced nanocomposite fibers. The process facilitates the de-aggregation and dispersion of CNTs in the appropriate solvent using mechanical or ultrasonic agitation. This has been reported to have drastic improvement in the dispersion, and hence, the mechanical properties of the reinforced composite fibers. The enhancement in the mechanical properties have been achieved using carbon nanotubes (SWCNT/MWNT) reinforced solution spun fibers with different polymers including poly(p-phenylene benzobisoxazole) [13], polyacrylonitrile [14,15], polyaniline [16] and polyvinyl alcohol [17,18]. However, the method relies on dispersion of filler in specific solvent, which limits the choice of polymers. The method would thus be suitable for only

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those polymer-solvent systems, in which the required CNTs could be readily dispersed. Further the use of solvents is environmentally undesirable and significantly increases the cost of processing.

Melt processing of polymers into fibers is a preferred technique at the industrial scale because of its simplicity, economy, environmentally friendliness and production speed. The process involves melting of the polymer and addition of CNTs to the polymer matrix by melt-shear mixing. However, the dispersion of nanofillers in the melt poses a greater challenge. Therefore, the properties reported for melt processed composites are not impressive [11,19]. Most of the reported composites with CNTs are solution based, where the dispersion of CNTs was facilitated using solvents. This approach has been used for producing reinforced fibers based on pitch [20], poly(propylene) (PP) [11], poly(ethylene terphthalate) (PET) [21] and poly(carbonate) [22]. Other than CNTs, the same approach has also been reported for nanoclays (2D nano-structures) to form composite fibers with improved tenacity using nylon [23], PP [10] and PET [24].

ZnO nanostructures are rigid hydrophilic entities that offer an alternate choice for reinforcement other than widely used CNTs. ZnO has attracted remarkable attention in research because of its wide range of potential applications such as catalysis, solar cells, optoelectronic device, chemical and biological sensors. Various methods have been employed in the literature to prepare different morphologies of ZnO nano-structures such as spheres, stars, flowers [25], and rods [26–29].

A few studies [30–32] have proposed that elongated nanostructures such as nano-rods are expected to show better reinforcement when they are made to align inside a composite. However, only ZnO nanoparticles have been incorporated in nylon 6 fibers and were shown to induce gamma crystal formation in composites [33]. While, ZnO nanorods have been incorporated in PP [34] and PU films [35] and were shown to enhance mechanical and antibacterial properties [36] of these films.

As discussed above, incorporation of high aspect ratio rigid nanostructures, such as ZnO nanorods, inside an oriented fiber may offer an alternative route for realizing mechanically strong composite fibers. However, incorporation of these ZnO nanostructures inside polymer fibers has not been accomplished and needs to be investigated.

In the present study, the feasibility of incorporation of ZnO nanorods inside nylon 6 fibers and their effect on mechanical properties of nylon 6 fibers has been investigated. The effect of shape of nanostructures, i.e. comparison of nanoparticles versus the nanorods, on structure and properties has been elucidated.

2. Experimental methods

Textile grade nylon 6 polymer (MFI ~30) was procured from Grodno Azot, Khimvolokno (Slavinskogo, Belarus). zinc acetate dihydrate, sodium hydroxide (NaOH), acetone and ethanol were procured from Merck, (Bangalore, India). ZnO nanoparticles/nanorods were synthesized using hydrothermal unstirred vessel as reported in the literature [26,28,37,38]. Nanocomposites of ZnO nanorods were prepared by melt blending nylon 6 with 0–2 wt% ZnO nanorods using twin screw extruder (TSE), Process 11, Thermo Scientific (Karlsruhe, Germany). The various samples were coded as: Nylon 6, 0.5 ZnR/Nylon 6, 1 ZnR/Nylon 6, 1.5 ZnR/Nylon 6 and 2 ZnR/Nylon 6, respectively for ZnO nanorods and 0.5 ZnP/Nylon 6, 1 ZnP/Nylon 6, 1.5 ZnP/Nylon 6 and 2 ZnP/Nylon 6, respectively for ZnO nanoparticles depending on the wt% of ZnO used. The dried chips were meltspun into monofilaments using melt spinning machine, Model LBS, Hills (Florida, USA) and subsequently drawn to a possible maximum draw ratio, which was 4.7 and 4.8 for ZnP/nylon 6 and ZnR/nylon 6 composite fibers, respectively, and 5 for neat nylon 6 at the room temperature.(Experimental details given in supporting information).

The morphology of ZnO nanorods, ZnO nanoparticles and ZnO/nylon 6 composite fibers was analyzed using a field emission scanning electron microscope (FE-SEM), Quanta 200F, FEI (Eindhoven, Netherlands). The dimensions of nanorods/nanoparticles were determined as an average of 100 readings using ImageJ software (NIH, USA). The fibers were immersed in the bath containing liquid nitrogen, and the frozen fibers were fractured by an impact to expose the cross-sectional morphology. The cross-section was observed under FE-SEM. Energy dispersive X-ray (EDX) analysis was done using X-max 80 mm^2, Oxford Instruments (Oxfordshire, UK). The mechanical properties of the drawn fibers (in the form of monofilaments) were measured using microtensile tester, Model-5848, Instron (Singapore). X-ray diffraction (XRD) patterns were obtained using X-ray diffractometer, X'Pert Pro, PANalytical (Almelo, Netherlands) and SAXSess mc^2, Anton Paar (Graz, Austria) having Cu Kα radiation ($\lambda = 0.154$ nm) source at 40 kV. Spectra of samples were analyzed using SAXSQUANT software. Samples were placed with fiber axis orientation parallel with respect to source and the deconvolution of the peaks was carried out using Wire 3.2 software. Birefringence was measured using LEICA DM 2500 P, Leica Microsystems Ltd (Heerbrugg, Switzerland) using phase compensator.

3. Results and discussion

3.1. Morphology of ZnO rods and particles

Morphology of ZnO rods and particles was analyzed using SEM as shown in Fig. 1(a) and (b), respectively. SEM study revealed that the synthesized ZnO rods had an aspect ratio of ~14 with average length of 691 ± 167 nm and average diameter of 50 ± 10 nm. The ZnO rods showed a typical XRD pattern (Supporting information) for high purity wurtzite hexagonal phase and the entire diffraction pattern matched well with the standard hexagonal ZnO (JCPDS number 36–1451 for ZnO).

3.2. Melt spinning and drawing behavior

The as-spun nylon 6 as well as ZnO/nylon 6 composite fibers were found to have denier of 150 ± 4, which on drawing decreased to 30.20 ± 0.1 in nylon 6, 30.25 ± 0.5 in ZnP/nylon 6 and 30.35 ± 0.3 in ZnR/nylon 6. The nylon 6 fibers could be drawn at the room temperature to a maximum draw ratio of 5, while ZnO/nylon 6 composite fibers could be drawn to a maximum draw ratio in the range of 4.7–4.9. The mechanical and structural characterizations were carried out on drawn fibers.

3.3. Morphology of composite fibers

The morphology of melt spun ZnO/nylon 6 composite fiber is shown in Fig. 2. In all the cases the surface of fibers was observed to be uniform. Moreover, no aggregates were observed in the case of ZnO/nylon 6 composite fibers. The incorporation of ZnO nanostructures resulted in composite fibers of uniform diameter 58 ± 3.5 μm in ZnP/nylon 6 and 59 ± 4.2 μm in ZnR/nylon 6 composite fibers compared to 57 ± 3.2 μm in nylon 6 fibers. The presence of ZnO nanostructures inside the fibers, both particles and rods (in particular those present near the surface of the fibers) can be observed using SEM when sufficiently high voltage electron beam is applied on the samples. This is similar to the observation reported for ZnO-PAN nanofibers in our previous study [39]. The images clearly show the presence of highly dispersed ZnO nanostructures in the fibers.