Mechanical properties of nanodiamond-reinforced polymer-matrix composites

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ABSTRACT

Poly(vinyl alcohol)-matrix reinforced with nanodiamond (ND) particles, with ND content up to 0.6 wt%, were synthesized. Characterization of the composites by transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS) reveal uniform distribution of the ND particles with no agglomeration in the matrix. Differential scanning calorimetry reveals that the crystallinity of the polymer increases with increasing ND content, indicating a strong interaction between ND and PVA. Nano-indentation technique was employed to assess the mechanical properties of composites. Results show that even small additions of ND lead to significant enhancement in the hardness and elastic modulus of PVA. Possible micromechanisms responsible for the enhancement of the mechanical properties are discussed.

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1. Introduction

Polymer-matrix composites (PMCs) such as the glass-fiber reinforced plastics (GFRPs) are widely used in engineering applications. This is because of a number of technical and economic advantages offered by the PMCs vis-à-vis metal- or ceramic-matrix composites. Typical advantages of these are the following. (a) PMC components are relatively easy to manufacture and do not require expensive equipments (such as high temperature furnaces for example), thereby making PMCs comparatively cost-effective. (b) Because of the low density of the polymers, specific properties of the PMCs tend to be far superior, making it highly advantageous to use them in lightweight structures in aerospace and transportation industries. These advantages are somewhat offset by the fact that conventional PMCs require large additions of filler material to attain the desired properties. In the recent past, nano-scale reinforcements are being explored to alleviate this problem. It has been shown that substantial enhancements in mechanical properties could be achieved with small additions of nanomaterials [1,2]. The improvement achieved in properties depends on the type of the nanofiller used, their size, distribution and its interaction with the polymer matrix. In addition to the enhancement in mechanical properties, these PMCs exhibit unique functional properties as well, making them potential candidates for multi-functional applications.

One way of classifying nano-fillermaterials is on the basis of their dimensionality (zero, one or two). Some examples are nano-clay or nanodiamond (zero-dimensional), single- or multi-walled carbon nanotubes and inorganic nanowires (one-dimensional) and single- or few-layer graphenes (two-dimensional). The mechanical properties of PMCs that are reinforced with one- or two-dimensional nanofillers have received considerable attention recently [3–8]. There have been very few studies on zero-dimensional nanofiller reinforced composites, except those of nano-clay reinforced ones [2]. Keeping this in view, we have examined the effectiveness of nanodiamond (ND), which has attracted attention in the recent past, in enhancing the mechanical properties of PVA.

ND, also known as ultradispersed diamond, combines unique properties of diamond core such as superior hardness and thermal conductivity with large readily modifiable surface [9–15]. It can be obtained in large quantities by detonation synthesis [9] and relatively inexpensive with broad applicability. Dolmatov [16] have studied the effect of ND (~2 wt%) addition on the mechanical properties of rubber. The particle size they used is about 44 nm. Kurin et al. [17] have made PVA-7wt% ND fiber coatings and observed ~200% increment in stiffness and large enhancement...
in breaking strength. But these composites suffer from poor ductility, which could be due to the large ND content. Behler et al. [18] have recently reported a ~400% increase of Young’s modulus and a ~200% increase of hardness by dispersing ND (~20 wt%) into electro spun polyamide11 fibers. However, higher concentrations of ND lead to agglomeration of the powders [18].

One way to avoid this problem is using lower filler additions, so that the properties of the polymers are preserved with moderate enhancement in mechanical properties. Furthermore, the rate of enhancement in the mechanical properties is highest when the nanofiller concentration is at the dilute limit. There are very few recent studies on the effectiveness of ND in enhancing the mechanical properties, when ND concentration is less than 1 wt% [19,20]. The objective of the present study is to investigate the mechanical properties of PVA-ND composites with small additions of ND (0.2, 0.4 and 0.6 wt%).

2. Materials and experiments

Powders of ND with phase purity higher than 98% and an average particle size of around 5 nm was purchased from Tokyo Diamond Tools, Tokyo, Japan. It was characterized by transmission electron microscopy (TEM), infrared (IR) spectroscopy [21], X-ray diffraction (XRD), small angle X-ray scattering (SAXS) and cathodoluminescence imaging (CL).

As the mechanical properties of the polymer-matrix composites depend on the efficient interaction between the polymer matrix and the filler material, the as-received (AR)–ND was functionalized to create surface carboxyl and hydroxyl groups [4,5], which interact with the polymer at molecular level. For this purpose, 100 mg of the ND was refluxed with 5 ml conc. HNO3 and 45 ml conc. H2SO4 for 12 h [21,22]. The acid-functionalized (AF)–ND was washed with distilled water and dried under vacuum. This was characterized using IR spectroscopy. ND so prepared was dispersed in aqueous media.

To prepare PVA-ND (~0.2, 0.4, and 0.6 wt%)composites, 2 gm of PVA was first dissolved in water. It was heated to 70–80 °C for complete dissolution. Required amount of AF-ND was dispersed in distilled water by sonication for 20–30 min. The mixture was then dried in Petri dishes at 35–40 °C over a period of 3 days. As the mechanical properties of the PVA are sensitive to the moisture content, the composites were desiccated over in CaCl2 for at least 7 days before conducting nano-indentation experiments [4,5].

The composites, thus prepared, were characterized by several techniques. CL images of samples were obtained. Differential scanning calorimetry (DSC) was performed (~8 mg) at a scan rate of 0.16 K/s from 50–250 °C. TEM and small angle X-ray scattering (SAXS) were conducted to examine the particle size distribution and the inter-particle separation in the composites. TEM studies were conducted by re-dissolving the films in water and drying a drop of this on a carbon copper grid and were observed in a JEOL JEM 3010 microscope.

IR spectra were recorded using Bruker IFS 66/S spectrometer. X-ray diffraction (XRD) patterns were recorded using Cu Kα radiation on a Rigaku Rint XRD-3000 TT diffractometer. CL images were recorded using LEICA 544oi scanning electron microscope. SAXS measurements were carried out with a Bruker-AXS NanoSTAR instrument. The instrument has X-ray tube (Cu Kα radiation, operated at 45 kV/35 mA), cross-coupled Göbel mirrors, three-pinhole collimation, evacuated beam path, and a 2D gas-detector (HI-STAR) [23]. SAX data were recorded in the q range of 0.007 to 0.21 Å−1 (i.e., 2θ = 0.1°–3°).

Mechanical properties of the PVA-ND composites are determined using nano-indentation technique. Thin films of 0.5 mm in thickness (10 mm × 10 mm area) were used for indentation. These films are stuck to a steel plate with a thin layer of glue which dried thoroughly. Quasi-static nano-indentation was carried out using Hysteron Triboindener with a Berkovich tip (a three sided pyramidal diamond tip).

Since the hardness, H, and the Young’s modulus, E, obtained from the instrumented indentation experiments are sensitive to the area function of the indenter, it was first calibrated by employing a quartz standard sample. Since the loads that are used are small, the area function is calibrated at the low depth range. With the new area function, the H and E values measured on the standard Al and quartz samples were found to be within the 5% standard deviation given by the manufacturer, validating the calibration.

The mechanical properties of polymers are sensitive to the loading rate and the pause time at the peak load. Therefore, these indentation parameters were optimized until H and E, obtained from the nano-indentation are comparable with the available literature data [5,24]. A peak load of 1 mN was chosen, such that the substrate does not influence the measured properties. The loading and the unloading rates used were 0.1 mN/s with a hold time of 10 s at the peak load. Ten indentations are made on each sample and the average values of the E and H from these measurements are reported.

3. Results

TEM images of AR-ND, AF-ND and PVA-0.6 wt% ND are shown in Fig. 1(a), (b) and (c) respectively. Both the AR-ND and AF-ND have an average diameter of 5 nm. The inset shows the particle size range and their distribution. A change in the average diameter of the particles nor agglomeration on acid-functionalization was noted. The TEM image of PVA-0.6 wt% ND in Fig. 1(c) shows that the dispersion is uniform. The XRD patterns (see Fig. 1, supplementary information) of the AR-ND and AF-ND yield similar results. The IR spectrum of the AR-ND shows characteristic OH and C=O, C–O band peaks (Fig. 2). The intensity of these peaks increases upon acid-functionalization.

ND is known to show CL due to presence to defects such as nitrogen and vacancies. We used this property to characterize the PVA-ND films. Fig. 3(a) and (b) show the CL images of PVA-ND composite films with 0.2 and 0.6 wt% ND contents, respectively. The density of the bright spots increase with increasing ND concentration in the film indicating large amounts ND in PVA-0.6 wt% composite.

Fig. 4 shows the SAXS data of the prepared films where the intensity is plotted as function of the scattering factor. The scattering factor, q, and the inter-particle distance, d, values are shown in the inset table (Fig. 4). The inter-particle distance is calculated using the formulae $d = \frac{2\pi}{q}$ and the radius of gyration is calculated using $I = G \exp\left(\frac{-q^2 R_g^2}{2}\right)$ [25]. The particle separation decreases by 11% and the agglomerate size increases by 14% with increasing ND concentration from 0.2 to 0.6 wt% (see Fig. 2, supplementary information).

DSC traces of the PVA-ND composites show (see Fig. 3, supplementary information) that there is no change in the melting temperature, $T_m$, of the composites with the addition of ND. The degree of crystallinity, $\chi$, defined as the ratio of heat required to melt 1 g dry sample (obtained by integrating the area of the DSC curve between 220–235 °C), $\Delta H$, and the standard enthalpy of pure crystalline PVA, $\Delta H_c$ (~138.6 Jg−1 [4]), is plotted against the ND concentration in Fig. 5. It is seen from Fig. 5 that $\chi$ increases markedly first (by ~10% upon the addition of 0.2 wt% ND to PVA) and then increases gradually (from ~52.5 to 62% when ND concentration is increased from 0.2 to 0.6 wt%).

The hardness and elastic modulus are determined using Oliver–Pharr method [26] and are listed in Table 1. These values, normalized with the respective values of blank PVA (in order to highlight the relative changes in mechanical properties with the addition of ND), are plotted as against wt% ND in Fig. 6. It is
Table 1
Mechanical properties of PVA-ND composites.

<table>
<thead>
<tr>
<th>ND content (%wt)</th>
<th>Crystallinity, χ (%)</th>
<th>Elastic modulus, E (GPa)</th>
<th>Hardness, H (MPa)</th>
</tr>
</thead>
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<td>42.0</td>
<td>0.67 ± 0.01</td>
<td>38.3 ± 0.02</td>
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<tr>
<td>0.2</td>
<td>52.6</td>
<td>0.87 ± 0.01</td>
<td>43.7 ± 0.03</td>
</tr>
<tr>
<td>0.4</td>
<td>55.0</td>
<td>0.96 ± 0.02</td>
<td>52.8 ± 0.12</td>
</tr>
<tr>
<td>0.6</td>
<td>56.6</td>
<td>1.33 ± 0.02</td>
<td>68.4 ± 0.3</td>
</tr>
</tbody>
</table>

Fig. 1. TEM images of (a) AR-ND (b) AF-ND with particles size distribution in the inset and (c) PVA-0.6 wt% ND.

Fig. 2. IR spectra showing the variation of AR-ND and AF-ND showing the increase in intensity of C=O and C–O peaks.

Fig. 3. CL images of (a) PVA-0.2 wt% ND and (b) PVA-0.6 wt% ND composites.

evident that both $H$ and $E$ of the PVA increase significantly upon the addition of ND. In Fig. 6, it can be seen that the scatter in $E$ is relatively large for 0.6 wt% ND composite. This is possibly due to the agglomeration of the ND particles at higher concentrations (see Fig. 2, supplementary information). While the average value of $H$ increases by $\sim 80\%$, $E$ almost doubles with the addition of 0.6 wt% ND. The reasons for such a substantial increment in mechanical properties are discussed in the following section.

4. Discussion

The mechanical response of a composite depends on many factors. These include (a) the size and distribution of the reinforcement phase in the matrix and (b) the characteristics of the interface between the reinforcement phase and the matrix. Uniform distribution of the reinforcement is essential for obtaining high quality composites. Detailed characterization of the PVA-ND composites produced in this work shows that the ND is distributed uniformly with no agglomeration. Since the size of the particle is of nm-scale, their number density (per unit volume) will be high, amplifying the strong interaction with molecular mechanisms of
elastic as well as plastic deformation features of the polymer. The DSC results obtained in this study, which show increased crystallinity of the polymer with the ND addition, suggest that the adhesion between the polymer and the ND particles is strong, promoting crystallization of the matrix, which in turn enhances the mechanical response of the composite. In light of this, possible mechanisms responsible for the enhancement in elastic and plastic properties of the PVA with the addition of ND are discussed below.

At the most basic level, the stiffness (characterized by $E$) is determined by the atomic bonding characteristics as well as the structure of the material. Despite having covalent bonding, which is one of the strongest bonds, polymers suffer from poor stiffness. This is because $E$ of a polymer is determined by the van der Waals bonding that exists between different polymer chains, which allows for relative sliding of the polymer chains rather easily. Since the functionalized ND particles may form chemical bonds with the polymer chains, they affect the inter-chain bonding characteristics, making it difficult for the relative sliding to take place. In this context, it is worth noting that similar enhancements in $E$ were reported PVA reinforced with few-layer graphene [5], or MWNT [3] or SiC nanowires [4]. Post fracture microscopy of the PVA-SiC nanowire composites by Vivekchand et al. [4] showed a thin layer of matrix on the filler material, indicating a strong interaction between the two. Similar interaction can be inferred in the present case as well, as a significant increase in the degree of crystallinity (by 14% with the additions of 0.6 wt% ND) was noted.

Similar arguments can be used to rationalize the enhancement in $H$, which reflects the resistance of the composite to plastic deformation. In this case, the controlling characteristic is the efficiency with which the applied load is transferred from the softer but contiguous matrix phase to the stronger reinforcement phase. Again, the strong adhesion between ND and PVA due to functionalization of the former and ND crystallinity, favor effective load transfer. Another possible factor is that the hard ND resists the formation and/or propagation of shear bands, the primary mode of deformation in amorphous and semi-crystalline polymers, resulting in enhancement of hardness.

5. Conclusions

PVA polymer-matrix composites reinforced with small concentrations of functionalized ND were synthesized and evaluated. Detailed structural characterization, employing a variety of analytical techniques, shows that the nanoparticles are distributed uniformly and do not agglomerate. Further, they appear to interact with the polymer matrix strongly, increasing the crystallinity substantially. The mechanical properties of the PVA-ND composites are determined using nano-indentation technique. With only 0.6 wt% addition of ND, which is relatively small, significant enhancements to the hardness and Young’s modulus of the PVA were observed. It was suggested that excellent adhesion between the matrix and the functionalized ND particles is the main reason for this marked improvement in mechanical performance. These results indicate that ND can be successfully used as a filler material for making polymer composites.

Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ssc.2009.06.017.

References