Extraordinary synergy in the mechanical properties of polymer matrix composites reinforced with 2 nanocarbons

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One of the applications of nanomaterials is as reinforcements in composites, wherein small additions of nanomaterials lead to large enhancements in mechanical properties. There have been extensive studies in the literature on composites where a polymer matrix is reinforced by a single nanomaterial such as carbon nanotubes. In this article, we examine the significant synergistic effects observed when 2 different types of nanocarbons are incorporated in a polymer matrix. Thus, binary combinations of nanodiamond, few-layer graphene, and single-walled nanotubes have been used to reinforce polyvinyl alcohol. The mechanical properties of the resulting composites, evaluated by the nanoindentation technique, show extraordinary synergy, improving the stiffness and hardness by as much as 400% compared to those obtained with single nanocarbon reinforcements. These results suggest a way of designing advanced materials with extraordinary mechanical properties by incorporating small amounts of 2 nanomaterials such as graphene plus nanodiamond or nanodiamond plus carbon nanotube.

binary combinations | nanoindentation technique | polyvinyl alcohol | synergistic effects

Among the many unique attributes of nanomaterials, especially noteworthy are their large surface to volume ratios and outstanding mechanical properties. These properties offer venues for exciting areas of research as well as for technological innovations. Thus, an important use of nanomaterials is in reinforcing polymer matrices taking advantage of the ultra-high stiffness and hardness exhibited by them. Recent research has shown that small additions (up to ≈ 1 wt%) of certain nanomaterials such as carbon nanotubes enhance the mechanical properties markedly, sometimes by as much as 100% (1–8). Although the precise mechanism responsible for this dramatic enhancement is not entirely understood, it is generally believed that molecular level interactions between the nanomaterials and polymer matrices play a major role. The large interface area available for such interactions clearly hold the key for the dramatic enhancement in mechanical properties.

Of the variety of nanomaterials synthesized and characterized in recent years, nanocarbons of different dimensionalities are of particular interest, as exemplified by nanodiamond, nanotubes and graphene with dimensionalities of 0, 1, and 2, respectively (1–3). Extensive research has been carried out on the mechanical properties of composites made of polymer matrices with 1 of the nanocarbons as the reinforcement phase (1–8). We would expect the nature of interaction of the nanocarbon constituent with the matrix to vary with the dimensionality. For example, carbon nanotubes added to a polymer can interact over the length of the polymer chain whereas a nanodiamond particle can interact only at a point, possibly at the ends of a polymer chain. While each of the nanocarbons improves the mechanical properties of the polymer matrix, we felt intuitively that incorporation of 2

nanocarbons could lead to synergistic effects in the mechanical properties, as each of them interacts with the matrix differently. We have, therefore, carried out an investigation of the effect of incorporation of different binary combinations of the nanocarbons, nanodiamond (ND), single-walled nanotube (SWNT), and few-layer graphene (FG), on the mechanical properties of polymer matrix composites (PMCs) formed with polyvinyl alcohol (PVA). We have examined all of the 3 possible combinations of reinforcements, ND plus FG, FG plus SWNT, and ND plus SWNT. The results have been truly exciting and not entirely expected.

Results and Discussion

PVA is a water-soluble polymer and hence facilitates the synthesis of composites with uniform distribution of nanoparticles. ND, SWNTs, and FG, functionalized by acid treatment to form surface carboxyl and hydroxyl groups (2, 9, 10), interact well with the PVA matrix. The maximum content of the nanocarbon reinforcement was 0.6 wt% since higher levels of reinforcement only likely to cause agglomeration of the nanomaterials in the matrix. With different proportions of the major (0.4) and minor (0.2) nanocarbon additives, the elastic modulus, E , and hardness, H , of the PMCs were evaluated by the nanoindentation technique.

In Fig. 1*A* and *B*, we show the variation of the nanohardness, H , and the elastic modulus, E , of PMCs containing a single nanocarbon reinforcement as a function of the nanocarbon content. These data provide the reference for comparing the multiply reinforced composites investigated by us. All of the 3 nanocarbons improve the mechanical properties of PVA markedly, addition of SWNT enhancing H by ≈ 7 times and E by an order of magnitude. These enhancements are observed even with the addition of 0.2 wt% SWNT, the properties reaching a plateau on further increase in the SWNT content, probably due to the bundling of SWNTs at higher reinforcement content (11). Such bundling could reduce the effective interaction volume. Unlike the SWNT-PVA composites, the ND-PVA and FG-PVA composites show a gradual increase in E and H with the increasing nanocarbon content, the rate of increase being higher in the former.

The enhancement in the mechanical properties of PVA is due to the inducement of crystallization of the polymer with the addition of the nanomaterials (4, 6, 7). Differential scanning calorimetry shows no change in the melting point, T_m , of PVA in the composites examined, but the crystallinity increases. The

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Fig. 1. Mechanical properties of hardness (A) and elastic modulus (B) with the variation of nanocarbon content. SWNT reinforced nanocomposites gives the superior mechanical properties compared to the FG and ND.

values of the degree of crystallinity, χ , of the composites, defined as the ratio of heat required to melt 1 g dry PMC sample to that of the standard enthalpy of the pure crystalline PVA ($\Delta H \approx 138.6 \text{ Jg}^{-1}$), are summarized in Table 1 along with the mechanical properties. The data reveal that the addition of a nanocarbon to PVA increases χ . To examine whether χ determines the enhancement in mechanical properties, we have plotted E and H against the relative change in χ in Fig. 2. The values of pure PVA (Table 1), processed and evaluated under identical conditions as those of the PMCs, were used for reference. Fig. 2 suggests that crystallinity and mechanical properties are related in ND- and FG-containing PMCs. The mechanical properties of SWNT-containing PMCs seem to be independent of crystallinity.

A few comments on the large changes in the mechanical properties observed in SWNT-PVA composites would be in

Fig. 2. Variation of percentage relative change in the hardness (*A*) and elastic modulus (*B*) with the relative change in crystallinity. (*H* and *E*) increases with increasing relative change in crystallinity for FG and ND reinforced composites, where as for SWNT reinforced composites, they are independent of the relative change in crystallinity.

order, since such changes have not been reported hitherto in the literature. There is a limited number of studies of nanotube-polymer composites, and they generally involve high reinforcement content (1, 2, 11–15). Furthermore, many of the studies pertain to composites reinforced by multiwalled carbon nanotubes. Liu et al. (12), who examined the PVA-0.8 SWNT composite, report an increase of 78% in E and of 48% in tensile strength, values much smaller than these observed by us in the present study. These workers did not observe any increase in crystallinity and attributed the enhancement in mechanical properties to the homogeneous distribution of fillers in the

Table 1. Mechanical properties of PVA and PVA-nanocarbon composites

Filler material	Hardness, MPa	Elastic modulus, GPa	Degree of crystallinity, %
PVA	38.0 ± 0.01	0.66 ± 0.03	42.0
PVA-0.2 FG	39.0 ± 0.03	0.69 ± 0.03	42.8
PVA-0.4 FG	44.1 ± 0.03	0.73 ± 0.05	46.3
PVA-0.6 FG	55.7 ± 0.05	0.89 ± 0.08	47.4
PVA-0.2 ND	43.7 ± 0.01	0.87 ± 0.04	52.5
PVA-0.4 ND	52.8 ± 0.03	0.96 ± 0.13	54.9
PVA-0.6 ND	68.4 ± 0.02	1.33 ± 0.35	56.6
PVA-0.2 SWNT	277.8 ± 2.02	6.93 ± 0.05	52.4
PVA-0.4 SWNT	280.1 ± 9.82	7.30 ± 0.61	54.6
PVA-0.6 SWNT	290.2 ± 19.42	7.80 ± 0.34	63.6

Fig. 3. Variation of elastic modulus (E) and hardness (H) for 2 binary composites PVA-0.4ND-xSWNT (A) and PVA-0.4EG-xND (B).

matrix. Zhang et al. (13) examined composites of PVA with KOH-treated SWNTs and report that H and E increase by 78% and 110%, respectively, whereas Li et al. (11) report 30% and 75% increases for the 5 wt% SWNT-epoxy composite. These workers observe that intercalation of the nanotubes is the cause for relatively poor enhancement in mechanical properties. Cadek et al. (4) have attributed the increase in mechanical properties of composites to the interfacial bonding between the matrix and the nanotubes as reflected by the increase in crystallinity. They also argue that the mechanical properties of the composites depend critically on the aspect ratio of the nanotubes, which in their case was ≈ 100 . In the present study, the SWNTs had aspect ratios of 700 to 1400. Furthermore acid functionalization of SWNTs could contribute to better bonding with the polymer, because of the presence of the surface carboxyl and hydroxyl groups.

In Fig. 3A and B, we show the variation of E and H in 2 composites containing 2 nanocarbons of different dimensionali-

Fig. 4. Percentage synergy in hardness and elastic modulus for different binary composites. Percentage change in synergy is the improvement in mechanical properties of the composite due to the presence of double reinforcement with reference to the individual properties of the composites.

ties, PVA-0.4ND-xSWNT and PVA-0.4FG-xND, respectively. In Table 2, we have summarized the mechanical properties of the various PVA composites formed with 2 nanocarbons. The synergistic benefit due to the addition of 2 different nanocarbons was estimated as follows, as exemplified in the case of the PVA-0.2SWNT-0.4ND composite. The addition of 0.2SWNT alone to PVA leads to an enhancement in H of PVA by p as shown in Fig. 1A. Likewise, q represents the enhancement in H of PVA due to the addition of 0.4 ND alone. The synergistic effect or percent synergy attained by adding both 0.2SWNT and 0.4ND to PVA was computed by the following relation:

$$[\mathbf{M}_H - (p + q)] \times 100 / (p + q).$$

Here, M_H is the measured value for the composite. This equation is unique for cases where the properties increase linearly with the reinforcement content.

In Fig. 4, we have plotted percent synergy for the different composites. The synergistic effect is dramatic in the ND plus FG composites, with 4- and 1.5-fold increases in E and H , respectively, in PVA-0.4FG-0.2ND composite. In the case of the PVA-0.4ND-0.2FG composite, synergistic effect is somewhat less, amounting to 92% and 71%, respectively, in E and H . The synergy is not as apparent in the SWNT plus ND composites since the addition of SWNT alone gives rise to fairly large values of E and H . Variation in the percent crystallinity (%) of the PMCs with 2 nanocarbons is around $\approx 2\%$, suggesting that increase in crystallinity is not the cause of the observed synergy.

To examine if the synergetic benefits can increase further by the incorporation of higher percentages of the nanocarbons, we have examined the mechanical properties of the PVA-0.4ND-0.6SWNT composite. The H and E values of this composite were 534.3 ± 90.6 MPa and 12.96 ± 1.22 GPa, respectively. These

Table 2. Mechanical properties of the reinforced composites incorporating two nanocarbon

Composite wt%	Hardness, MPa	Elastic modulus, GPa	Synergy, %		Degree of crystallinity, %
			Hardness	Elastic modulus	
PVA-0.4SWNT + 0.2FG	366.5 ± 23.99	9.3 ± 0.43	36.4	30.1	56.5
PVA-0.4SWNT + 0.2ND	314.2 ± 10.15	7.5 ± 0.05	12.5	2.5	55.1
PVA-0.4FG + 0.2ND	66.4 ± 5.43	1.6 ± 0.1	141.4	397.7	55.1
PVA-0.4FG + 0.2SWNT	336.9 ± 22.21	8.6 ± 0.34	20.4	25.6	57.5
PVA-0.4ND + 0.2FG	61.18 ± 0.002	1.3 ± 0.07	71.1	90.7	54.8
PVA-0.4ND + 0.2SWNT	352.9 ± 34.78	9.3 ± 0.36	23.6	33.6	57.2

properties are superior to those of the nanocarbon-polymer composites reported in the literature. A possible reason for the high E and H values in the PVA-0.4ND-0.6SWNT composite could be because that the ND particles prevent clustering of SWNTs due to van der Waals interactions. Surfactants are generally used to generate isolated SWNTs, but here it appears ND particles are able to do the same. From Fig. 4, it is interesting to note that, in general, the synergistic benefits for both modulus and hardness accrue together. A possible reason for this strong correlation could be the fact that the nanocarbon reinforcements interact with the polymer chains at the molecular level. Such interaction not only enhances the polymer chain's stiffness (thereby increasing the composite's global modulus) but also its plastic flow resistance, which in turn leads to increased hardness. The present results suggest possible exciting ways of obtaining high performance polymer matrix composites.

Conclusion

In conclusion, it has been possible to prepare composites of polyvinyl alcohol with 2 nanocarbon additives. While nanodiamond, single-walled nanotubes, and graphene individually give rise to significant improvement in the mechanical properties of PVA, incorporation of binary combinations of these nanocarbons results in extraordinary synergy in mechanical properties. We should point out, however, that our study has been limited to the measurements of hardness and elastic modulus and do not include ductility and toughness. In any case, our results suggest that it would indeed be profitable to explore polymer composites with such binary reinforcements.

Materials and Methods

FG was prepared by the exfoliation of graphite oxide following the procedure described recently (3). SWNTs were prepared by DC arc-discharge process. After preparation, the SWNTs were treated with HCl and heated in H_2 several times to remove the metal nanoparticles and amorphous carbon (16). ND with phase purity higher than 98% and an average particle size of around 5 nm was purchased from Tokyo Diamond Tools.

All 3 nanocarbons were functionalized by acid treatment by the following procedure. A mixture of concentrated nitric acid, concentrated sulfuric acid, water, and corresponding nanocarbon was heated in a microwave oven for about 5–8 min under hydrothermal conditions. The mixture was heated at 100 °C for 6–8 h in an oven. The product thus obtained was washed with distilled water and filtered through a sintered glass funnel. The product so obtained was functionalized with $-CO_2H$ and $-OH$ groups (2, 9, 10). The composites of PVA with the functionalized nanocarbon were prepared in aqueous media. Since the mechanical properties of the PVA are sensitive to the moisture content, the composites were desiccated over $CaCl_2$ for 7 days or more before performing nanoindentation experiments.

Nanoindentation experiments were performed using a Hysitron tribolindenter with a Berkovich tip (a 3-sided pyramidal diamond tip) to determine the hardness and the elastic modulus. Ten indentations were made in each case, and the average value was taken as the property of the composite. A max load of 1 mN was used at loading and unloading rates of 0.1 mN/s with a hold time of 10 s at the peak load. In all of the cases, care was taken that the penetration depth was <1000 nm. Hardness and elastic modulus were determined by the Oliver-Pharr method (17). Differential scanning calorimetry measurements were carried out in the 50 °–250 °C range with samples of ≈ 8 mg at a scan rate of 0.16 K/s, using a Mettler-Toledo DSC equipment. DSC curves are shown in Fig. S1.

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