

Study of the Effect of Modified and Pristine Carbon Nanotubes on the Properties of Poly(vinyl alcohol) Nanocomposite Films

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ABSTRACT: Nanocomposites of poly(vinyl alcohol) (PVA) and single-walled carbon nanotubes (SWNTs) in pristine form, or modified with poly (sodium 4-styrene sulfonate), were prepared in the form of films. The effect of SWNTs modification on their dispersion in the polymer matrix and on certain properties of the resulting composites, including tensile mechanical and thermal properties and swelling ability upon exposure to various moisture levels was studied. The composite films based on the modified SWNTs: (i) were characterized by a much higher degree of transparency up to 10%w/w loads, due to better dispersion, (ii) presented a higher hydrophilicity, and (iii) tended to promote thermal degradation of PVA to a lesser extent, as compared with the composites based on pristine

SWNTs. A reinforcing effect was observed for the dry, 1% and 2.5% w/w modified-SWNTs–PVA nanocomposites, without serious detrimental effects on the elongation at break. The effect of moisture on the mechanical properties was more intense in the case of composites based on modified SWNTs, as compared with those based on pristine SWNTs, in line with the observed higher hydrophilicity in the former case. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: E471–E477, 2012

Key words: single-walled carbon nanotubes (SWNTs); PVA; nanocomposites; modified SWNTs; mechanical properties

INTRODUCTION

The remarkable mechanical, electrical, and thermal properties of carbon nanotubes (CNTs) make them promising candidates for replacing or supplementing the common fillers used in polymeric materials.¹ One of the challenges that this emerging technology for composite materials faces is the homogeneity in distribution of the CNTs in the polymeric matrix, made difficult by their inherent tendency to aggregate and their limited solubility in common solvents used for casting of polymeric films. Improved dispersion and interfacial interactions in the composites are achieved by the modification of CNTs by either covalently bonding chemical groups or by adsorption of polymeric chains onto their surfaces.^{2–7}

Poly(vinyl alcohol) (PVA) has been used as a host polymer matrix for CNTs.^{2,3,8–16} These nanocomposite materials are in the form of films^{2,3,8–11} or fibers,^{15,16} containing either single-walled (SWNTs) or multiwalled (MWNTs) nanotubes at initial loads ranging in most cases from 0.1–5% w/w. Improve-

ment of their dispersion in the matrix is achieved: (a) by addition of surfactants in the casting solution of the polymer,^{12,13} (b) by covalent bonding of either hydroxyl groups¹⁴ or PVA molecules^{3,12} on the side-walls of CNTs and (c) by adsorption of polymer chains on the surface of the nanotubes, a method referred to as "polymer wrapping". An example of the latter practice is the case of HiPco-SWNTs whose dispersion in PVA was facilitated by sodium dodecyl sulfate and poly(vinyl pyrrolidone).¹¹ Each approach has certain advantages and disadvantages (it has been noted, for example, that surfactants may deteriorate the mechanical properties of the composite material¹⁵ and that covalent functionalization disrupts the π conjugation in the graphene sheet and thus may be deleterious for the electrical properties of the composites¹), but all the above treatments have been reported to enhance the homogeneous dispersion of the nanotubes in the PVA matrix and to succeed, to a higher or a lesser extent, in exploiting the nanotubes properties in the nanocomposites. Regardless of the dispersion method, improvement of the mechanical properties is reported in most cases for loads ranging from 0.1 to 5%w/w,^{3,12,14,15} while the percolation threshold for electric conductivity has been found to lie between 5 and 10% w/w loads.¹⁰ Improved dispersion of the carbon nanotubes in PVA matrices is also important for the

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potential use of the nanocomposites in various applications, such as separation membranes,¹⁷ optical biosensors,¹⁸ and actuators.¹⁹

Recently, poly(sodium 4-styrene sulfonate) (PSSNa) has been used to “wrap” SWNTs.²⁰ The modification was verified by IR measurements and the vapor sorption properties of the wrapped SWNTs in three solvents of varying polarity indicated a significantly higher hydrophilicity as compared with the pristine SWNTs.

In this work, the PSSNa-modified SWNTs (m-SWNTs), as well as the parent pristine SWNTs (p-SWNTs), were used for the preparation of PVA-based nanocomposites at various SWNTs loads, in order to study the effect of modification on the dispersion of the nanotubes in the polymer matrix and on certain properties of the resulting composites, including thermal and tensile mechanical properties, and swelling ability upon exposure to various moisture levels. PSSNa is miscible with PVA,^{21,22} and thus expected to improve dispersion of the nanotubes in the polymer.

EXPERIMENTAL

Materials

PVA in the form of powder was supplied by Aldrich (Milwaukee, USA, cat. No 36313-8) with the following specifications: 98–99% hydrolyzed, $M_w = 31$ –50 K.

The pristine SWNTs (code number P3-SWNT) were supplied by Carbon Solutions (Riverside, CA). According to the manufacturer, the pristine SWNTs were produced by the arc discharge method and contained 3–6% carboxylic groups (purity 80–90%), their outer diameter was 1.4 nm and their length ranged from 0.5–1.5 μm . The modified SWNTs were kindly supplied by the laboratory of Membranes and Microporous Materials for Environmental Separations located in NCSR Demokritos. Details on the SWNTs modification procedure with hydrophilic PSSNa of molecular weight $M_w = 70$ K, can be found in Ref. ²⁰.

Preparation of composite films

Aqueous solutions of PVA (10–15% w/w) were prepared by stirring appropriate amounts of the polymer powder in deionized water at 90°C for 6 h. Aqueous suspensions of 2% w/w p-SWNTs or m-SWNTs, were prepared by sonication for 2 h. Appropriate amounts of the nanotube suspension was then added to the PVA solution, to produce the desired final composition of the composite. The final mixture, containing PVA at 8–10% w/w, was magnetically stirred for 30 min, followed by sonication for

2 h. Subsequently, 5 mL of the mixture were transferred to Petri dishes, allowing for evaporation of water at atmospheric conditions. The composite matrices prepared thus, contained p-SWNTs or m-SWNTs at loads ranging from 0.5–10% w/w and thickness 30–50 μm (obtained by a micrometer gauge reading to 1 μm). A 10% w/w aqueous PVA solution was also used for the preparation of neat PVA films by the same method. All films were thermally treated by heating for 20 min at 130°C (i.e., at a temperature between the glass transition and melting temperature) and subsequently kept in a desiccator until use.

Characterization techniques

The dispersion of either p-SWNTs or m-SWNTs in water, in aqueous solutions of PVA and in PVA composite films was evaluated by means of an optical microscope (Pol U-Amplival, Jena, Germany) equipped with a CCD camera. The dispersion of the SWNTs in composite films of thickness ~ 50 μm was also assessed by UV/Vis spectrophotometry (model V-630 Jasco, Japan). The samples were placed on a quartz substrate and then scanned from 300–1000 nm. The absorbance at 600 nm was also recorded, separately.

The composite films were characterized with respect to their degree of crystallinity and the glass transition temperature (T_g) by temperature modulated differential scanning calorimetry (TMDSC). Measurements were performed with a 2920 MDSC model of TA Instruments (New Castle, DE) under nitrogen atmosphere at a heating rate of 5°C/min with a modulated signal of $\pm 0.796^\circ\text{C}$ every 60 s. The degree of crystallinity was determined from the total TMDSC signal of a first heating run (from 25 to 230°C) and the T_g from the reversing signal of a second heating run (from 25 to 170°C).

To investigate the effect of SWNTs on the thermal stability of the films, thermogravimetric analysis (TGA) was performed on films of neat PVA films and of PVA doped with p- and m-SWNTs at 5% w/w, at a heating rate of 2°C min⁻¹, using a SETSYS Evolution TGA-DTA/DSC instrument (Setaram, France). All experiments were performed in an argon inert atmosphere which minimizes the mass loss due to nanotube oxidation while allows PVA to thermally decompose.

The effect of SWNTs modification on the water sorption properties of composites was assessed by two methods. First, 60–80 mg samples coming from neat and 5% w/w m-SWNTs or p-SWNTs doped films, were equilibrated at various relative humidities (RH), in a glove box containing saturated salt aqueous solutions, and the water uptake was determined by weighing in stoppered bottles. The relative

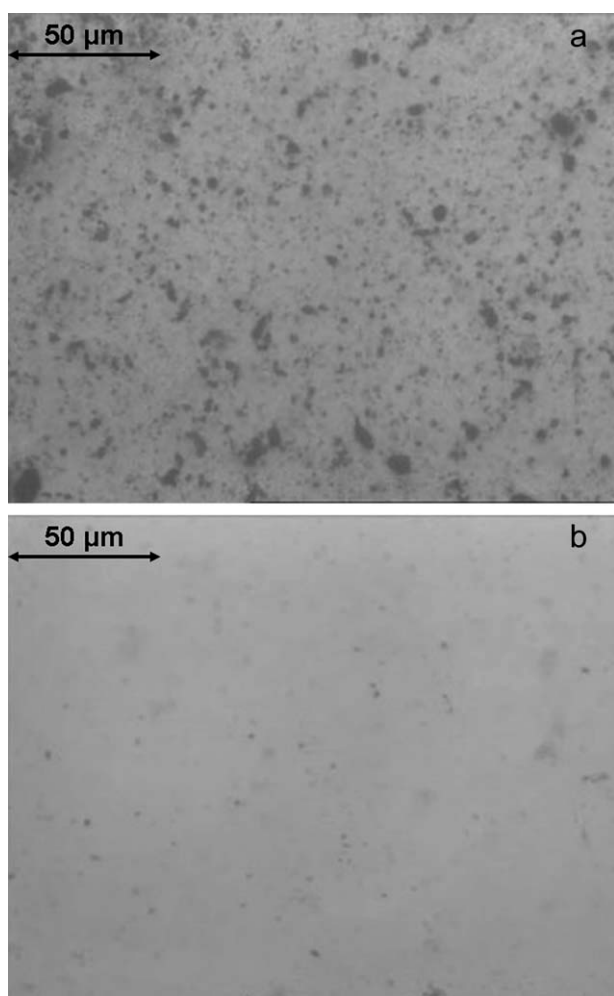


Figure 1 Optical microscopy of PVA films containing: (a) 5%w/w p-SWNTs and (b) 5% w/w m-SWNTs.

humidities were established by the use of zinc nitrate hexahydrate (Fluka, Germany), ammonium nitrate (Merck, Darmstadt, Germany) and potassium chloride (Merck, Darmstadt, Germany) for 42, 65, and 86% RH, respectively.

Second, a White Light Reflectance Spectroscopy methodology was applied to compare the hydrophilicity of supported composite films containing 5% w/w pristine or modified SWNTs with that of pure PVA, at 30°C. Detailed description of the methodology and the apparatus can be found elsewhere.^{23,24} Briefly, films of thicknesses $l_o = 790$ nm, supported on oxidized silicon substrate were prepared by spin coating the aqueous dispersions, prepared as described in the previous section. Measurements were performed in a home-made experimental setup consisting of a white light interferometry unit, a temperature-controlled measuring chamber in conjunction with a delivering subsystem for controlled concentrations of the water vapor. Moisture-induced changes in the polymeric film thickness result in changes in the recorded interference spectrum (pro-

duced by multiple reflections at the polymer–air, polymer–SiO₂, and SiO₂–Si interfaces). Film expansion Δl is evaluated by fitting the experimental spectrum with an appropriate expression for the total incident energy on the spectrometer at each wavelength.^{23,24}

Tensile mechanical properties of neat and SWNTs-doped films were tested in specimens of lateral dimensions 4.0×0.5 cm² and thickness 30–50 μ m, using a tensile tester (TENSILON UTM-II-20 of Toyo Baldwin, Japan). Stress–strain tests with an initial gauge separation of 2 cm were performed at a constant rate of elongation of 10 mm min⁻¹, at $23 \pm 1^\circ$ C. The samples were either dried or pre-equilibrated at 42, 65, and 86% RH. For each type of films, at least six samples were tested.

RESULTS

The modification of SWNTs improved dramatically their dispersion in water, as well as in the casting solution of PVA. Moreover the former suspensions remained stable for a considerably longer period (more than four weeks) than the corresponding suspensions of p-SWNTs. The reduced tendency of m-SWNTs to form aggregates in the PVA composite films, as compared to p-SWNTs, is shown in the optical micrographs of Figure 1.

The absorbance of PVA composite films at 600 nm vs. the SWNTs load is depicted in Figure 2. As shown, this relationship is linear for both p-SWNTs and m-SWNTs doped films, indicating homogeneous dispersion.¹⁴ However, the significantly higher absorbance of the p-SWNTs doped films probably results from light scattering arising from p-SWNTs agglomerates¹⁴ in accordance with the observations

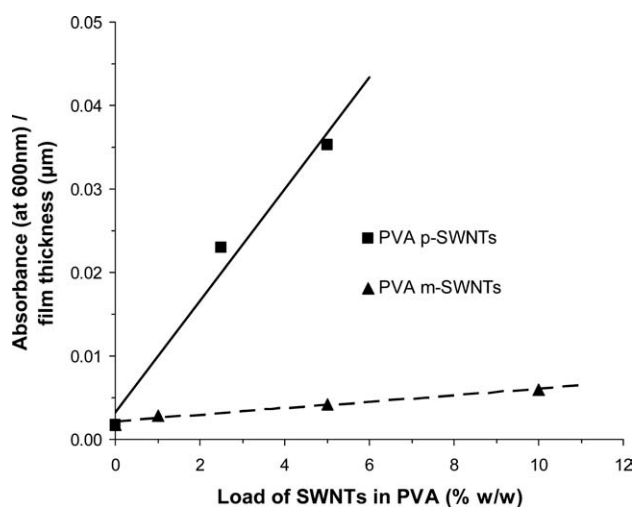


Figure 2 Absorbance at 600 nm per thickness of composite film, as a function of the load of pristine or modified SWNTs.

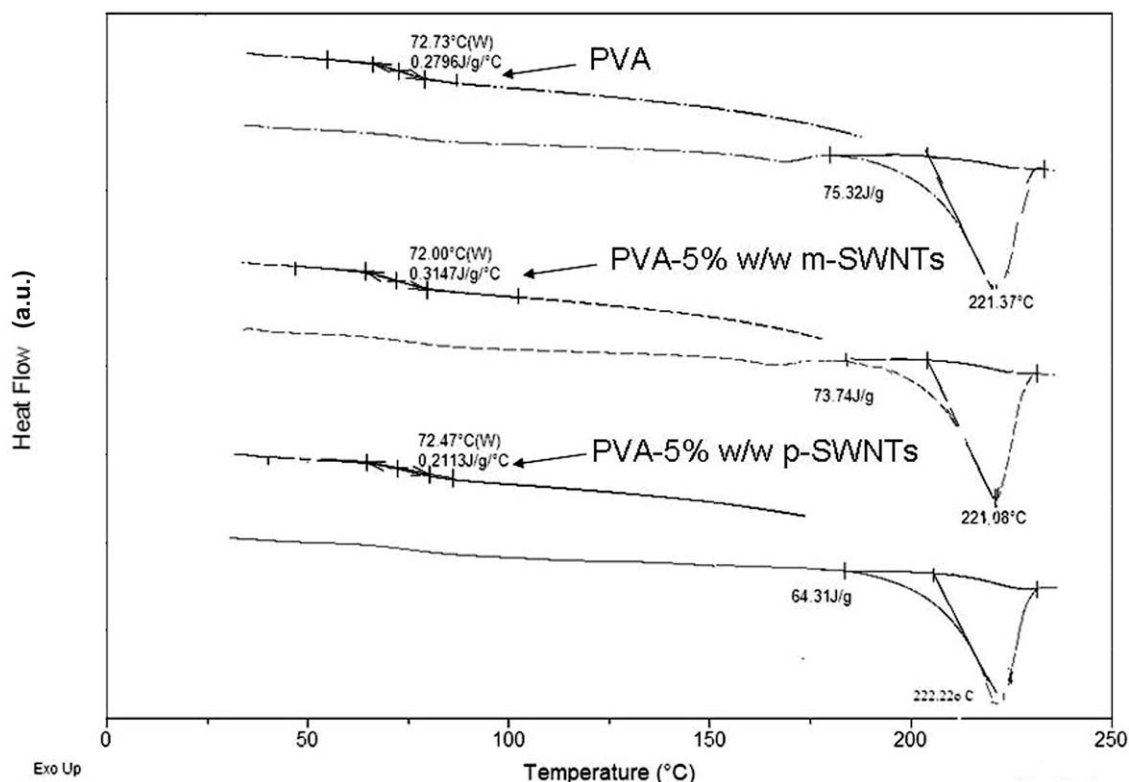


Figure 3 TMDSC signals during the first (up to 230°C- total signal) and the second (up to 170°C- reversing signal) heating runs of neat PVA films and of PVA films loaded with 5% w/w modified or pristine nanotubes. Each curve is vertically shifted for reasons of clarity.

made by optical microscopy. Hence the modification of SWNTs with PSSNa leads to significant improvement of the dispersion and transparency, which expands to initial loads up to 10% w/w.

The effect of carbon nanotubes on the crystallinity of PVA has been studied in many cases. Certain studies report that carbon nanotubes nucleate an ordered polymer phase on their surface and the measured increase in crystallinity is correlated to the corresponding mechanical reinforcement of the polymer upon inclusion of MWNTs.^{2,8,25} However, in other studies, no discernible changes¹⁴ or even a drop¹¹ in PVA's crystallinity upon inclusion of functionalized SWNTs is reported. The melting point and the degree of crystallinity of pure PVA films, determined here by TMDSC were found to be $219.9 \pm 1.5^\circ\text{C}$ and $49.5 \pm 2.8\%$, respectively. No statistically significant effect on both quantities upon inclusion of SWNTs was observed (examples shown in Fig. 3), except for a small increase in the crystallinity of the films containing 0.5% w/w m-SWNTs ($54.2 \pm 2.5\%$). The glass transition temperature (T_g) was not essentially affected as well, in line with results of Ref. 10.

The effect of SWNTs on the thermal stability of PVA films was investigated by TGA up to the temperature of 350°C, at which the main degradation

step of pure PVA is completed,^{26–28} while PSSNa has not yet started to decompose.²⁹ TGA results are shown in Figure 4(a) and the corresponding derivative curves (DTG) are plotted in Figure 4(b). The onset temperature of degradation, defined by the intercept of the tangent of the derivative curve on the temperature axis, the maximum rate of weight change and the temperature of the maximum rate are summarized in Table I, for neat PVA films and for composites with 5% w/w load of p-SWNTs or m-SWNTs. These results indicate that SWNTs promote the degradation of PVA. Similar conclusions have been drawn in other studies and attributed to the acidic nature of the pristine nanotubes.¹³ However, we note that the onset temperature is lower, and the peak rate of degradation is higher, for p-SWNTs compared with m-SWNTs.

The effect of modification of the nanotubes on the hydrophilicity of PVA was studied in free-standing, and on supported, films of pure PVA and of composites with 5% w/w pristine or modified SWNTs. The results on weight gain of the free-standing films upon equilibration to three moisture contents (42, 65, 86% RH) showed that the pure PVA and p-SWNTs composite films sorbed comparable amounts of water (i.e., 3.3, 10.2, and 17.5% g of water/g PVA for the pure PVA film and 3.0, 9.4, and 16.7% g of

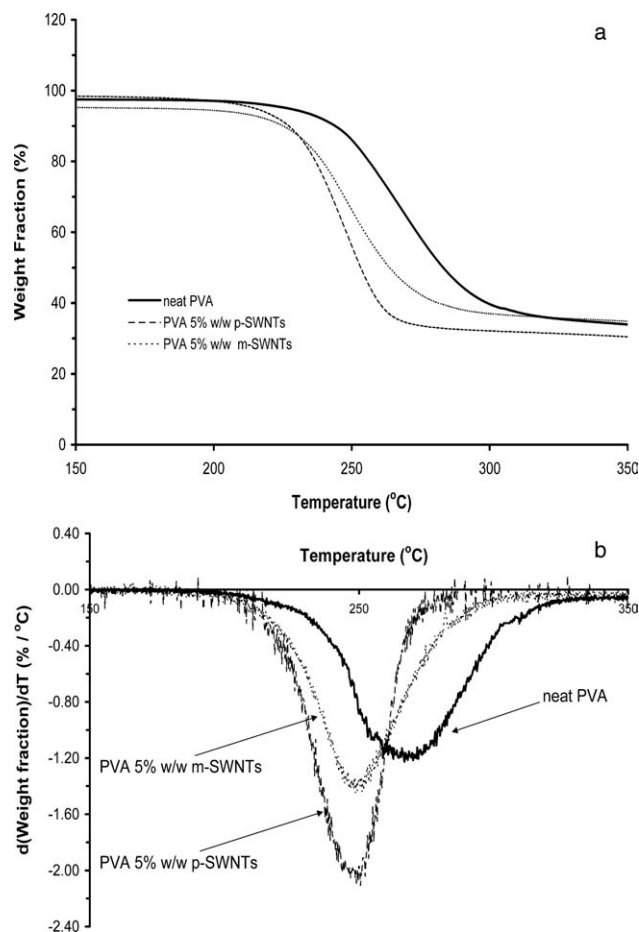


Figure 4 (a) TGA curves and (b) derivative TGA graphs of neat PVA films and films doped with 5% w/w p- or m-SWNTs.

water/g PVA for the composite film at each RH, respectively). On the other hand, the presence of PSSNa wrapping increased the water sorption to 5.4, 15.1, and 18.2% g of water/g PVA at each RH.

The same tendency was observed in corresponding supported films, subjected to successive equilibrations with progressively higher relative humidities, at 30°C. The equilibrium fractional film expansion $\Delta l/l_0$, due to swelling, at each RH, was determined by the methodology described in the experimental section and presented in Figure 5. The data of Figure 5 indicate that for RH > 30%, swelling of the film with 5% w/w m-SWNTs tends to be

TABLE I
TGA Results

| | Onset temperature (°C) | Peak rate of degradation (% w/w°C ⁻¹) | Peak degradation temperature (°C) |
|-------------|------------------------|---|-----------------------------------|
| Neat PVA | 235 | -1.20 | 269 |
| PVA-p-SWNTs | 219 | -1.99 | 249 |
| PVA-m-SWNTs | 222 | -1.40 | 249 |

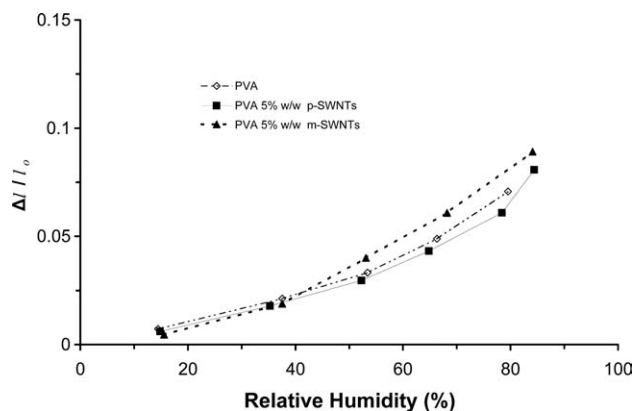


Figure 5 Fractional film swelling $\Delta l/l_0$ of supported, neat and SWNTs-loaded PVA films at different relative humidities and 30°C.

higher than that of pure PVA and that of the corresponding composite with p-SWNTs. As expected, the hydrophilicity of the wrapping PSSNa enhances the water uptake of the composite film. The results are also in line with moisture adsorption experiments performed in net pristine and modified SWNTs.²⁰

The results of the tensile mechanical tests in p- and m-SWNTs-doped PVA films are summarized in Table II. In relation to the modulus E of the composites, a reinforcing effect of m-SWNTs is observed for the 1% and 2.5% w/w nanotube inclusions, which practically fades out at 5% w/w. The corresponding values for p-SWNT-based composites show no significant effect for the 1 and 2.5% w/w, while for the two higher nanotube loads, E tends to decrease, as compared with pure PVA. Thus, improvement of the Young's modulus E is observed for m-SWNTs loading up to 2.5% w/w. To evaluate these results on the basis of relevant theoretical models, we have to take into account that the reinforcing volume fraction of the modified nanotubes in the composite is lower than that corresponding to the weight fraction of embedded m-SWNTs, due to the wrapping PSSNa material, which according to Ref. 20 is $\sim 40\%$ w/w of the m-SWNTs. On this basis, we may apply the Halpin-Tsai equation, as modified for random distribution of carbon nanotubes in the polymer^{11,14}:

$$E_c = \left[\frac{3}{8} \cdot \frac{1 + 2(l_{NT}/D_{NT})\eta_L V_{NT}}{1 - \eta_L V_{NT}} + \frac{5}{8} \cdot \frac{1 + 2\eta_T V_{NT}}{1 - \eta_T V_{NT}} \right] E_P \quad (1)$$

with $\eta_L = \frac{E_{NT}/E_P - 1}{E_{NT}/E_P + 2(l_{NT}/D_{NT})}$ and $\eta_T = \frac{E_{NT}/E_P - 1}{E_{NT}/E_P + 2}$.

where E_c , E_{NT} , and E_P are the tensile modulus of composite, nanotube, and polymer, respectively and l_{NT} , D_{NT} , V_{NT} are the length, diameter, and volume fraction of nanotubes in the composite, respectively. According to the manufacturer, $D_{NT} = 1.4$ nm and

TABLE II
Young Modulus (E) and Elongation at Break ($\Delta L/L_0$) of PVA Composite Films

| | SWNTs (% w/w) | E (GPa) | $\Delta L/L_0$ (%) |
|---------------|------------------|-----------------|-----------------------|
| Neat PVA | 0 | 2.16 ± 0.08 | 7.5 ± 3.6 |
| PVA – p-SWNTs | 1 | 2.11 ± 0.08 | 6.1 ± 1.6 |
| | 2.5 | 2.19 ± 0.30 | 8.1 ± 2.2 |
| | 5 | 1.82 ± 0.15 | 7.6 ± 2.0 |
| | 10 | 1.79 ± 0.05 | 5.2 ± 1.2 |
| PVA – m-SWNTs | 1 | 2.63 ± 0.15 | 6.1 ± 1.0 |
| | 2.5 | 2.78 ± 0.14 | 4.4 ± 1.1 |
| | 5 | 2.28 ± 0.12 | 4.8 ± 2.0 |
| | 10 | 1.37 ± 0.16 | 4.2 ± 2.3 |

l_{NT} has a mean value of $0.75 \mu\text{m}$. The V_{NT} values used in eq. (1) were calculated by taking into account that PSSNa does not contribute to the volume fraction of the nanotube, hence the estimated V_{NT} were 0.0058 and 0.0145, for 1 and 2.5% w/w m-SWNTs composites, respectively. The experimental tensile modulus for neat PVA (E_P) and for the 1 and 2.5% w/w m-SWNTs composites (E_C) were taken from Table II. On the basis of eq. (1), the calculated value for E_{NT} is ~ 0.3 TPa for the 1% w/w composites and 0.1 TPa for the 2.5% w/w ones. The experimental value of E_{NT} for a single SWNT, as well as of SWNTs ropes of small diameter, is reported to be in the order of 1 TPa, and with increasing rope diameter (from 3 to 20 nm), E_{NT} was found to decrease by more than one order of magnitude.³⁰ Analogous reduction of the anticipated reinforcing effect of SWNTs, as that determined here, has been also found in other cases where SWNTs have been dispersed at relatively high loads in PVA. For example, DMA analysis of PVA nanocomposites with 10–60% w/w pristine SWNTs¹⁰ showed that the reinforcement effect was more drastic in the rubbery than in the glassy state. In the latter case, the best fit of the results to an appropriate theoretical expression for composite materials was obtained by values of $E_{NT} = 0.15$ TPa. Zhang et al.¹¹ tested PVA composites based on poly(vinyl pyrrolidone)-wrapped SWNTs dispersed at 5% w/w load in the polymer matrix with the aid of surfactant. Analysis of the observed increase in E , on the basis of the Halpin–Tsai model, as well as SEM studies, indicated that ropes of SWNTs aggregated during film formation, leading to a lower aspect ratio as compared with that of isolated SWNTs and ropes of SWNTs. The fact that the high modulus of SWNTs is not fully exploited upon their inclusion in polymeric matrices is attributed, not only to their tendency to aggregate, but also to bending and to inadequate stress transfer at the polymer–nanotube interface. In the case of m-SWNTs studied here, there is a possibility that

mechanical properties of the composite are also affected by the presence of the wrapping material, especially at higher loads. Measurements on PVA–PSSNa blends have shown that PSSNa has a deteriorating effect on the Young modulus, as well as on the ultimate strength and ductility, of PVA.²²

In Table II, it is also shown that for both types of composites, elongation at break is not materially affected by the increasing amounts of nanotube loads.

The hydrophilizing effect of PSSNa can be also detected on the dependence of the mechanical properties of the composites on the equilibrating humidity. As shown in Figure 6, drastic changes in the properties of pure PVA are observed at $\text{RH} \geq 65\%$, associated with the transition from the glassy to the rubbery phase. As shown previously,³¹ the T_g of pure PVA films equilibrated at $\text{RH} \geq 65\%$ falls well below the experimental temperature studied here (23°C). The plasticizing effect of water is more intense in m-SWNTs composites, as compared to p-SWNTs composites, (higher drop in E and higher increase in $\Delta L/L_0$), in line with the higher hydrophilicity of the former.

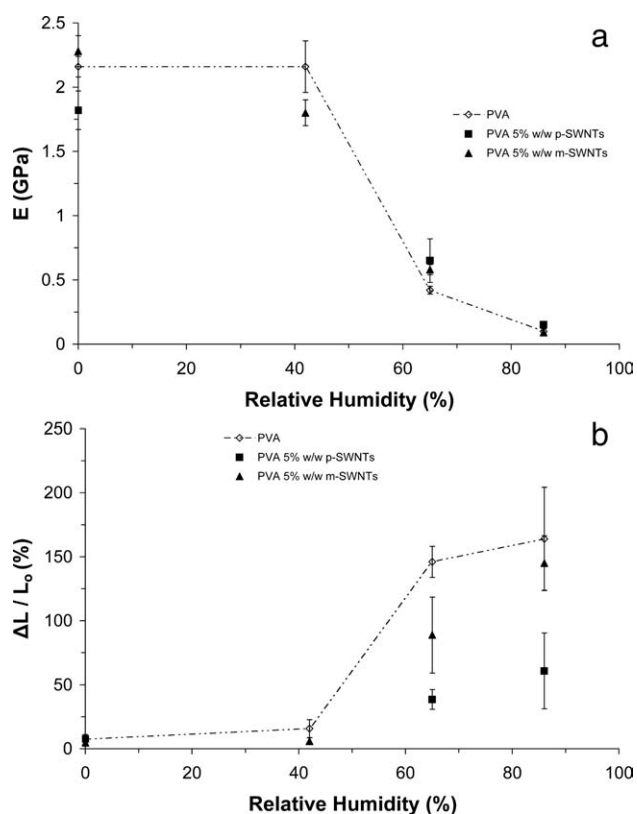


Figure 6 Mechanical properties of neat PVA films (\diamond) and of p-SWNTs (\blacksquare) or m-SWNTs (\blacktriangle) doped PVA films vs. equilibrating relative humidity at $23 \pm 1^\circ\text{C}$. (a) Young's modulus and (b) elongation at break. Each point represents the mean value and the standard deviation of at least six samples.

CONCLUSIONS

Adsorption of polymer chains on the surface of CNTs is one of the strategies studied to improve their dispersion in polymeric matrices for various applications. SWNTs wrapped with PSSNa, were found here to disperse more efficiently, than pristine SWNTs, in PVA, up to loads corresponding to the percolation threshold for electric conductivity of PVA–SWNTs composites, without serious detrimental effects on thermal and mechanical properties. On the other hand, the results draw attention to the possibility that the wrapping material may affect, in undesired ways, other properties of hydrophilic nanocomposites, especially when exposed to ambient humidity levels.

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