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Influence of surface functionalization on the thermal and electrical properties of nanotube-PVA composites.

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Abstract :

We present an experimental study of the electrical and thermal properties of nanocomposites made of polyvinyl alcohol (PVA) and multiwall carbon nanotubes (CNTs). The CNTs are initially dispersed and stabilized in water by two methods: covalent acidic oxidation or by surfactant adsorption. The CNT dispersions are mixed with a PVA solution, filtered and dried to make composite materials. The resistivity of the composites decreases strongly with increasing the temperature for composites made of surfactant stabilized or oxidized CNTs. However the rate of resistivity decrease differs substantially depending on the considered composites. This rate exhibits a maximum well above the glass transition of the neat PVA for oxidized CNTs. This reflects strong interactions of oxidized CNTs and the polymer confined at the CNT interfaces. By contrast, surfactant stabilized CNTs exhibit weaker interactions and the maximum of resistivity decrease occurs at the glass transition temperature of the neat PVA. The present results show the critical importance of covalent or non-covalent surface functionalization for the conductive properties of nanocomposites. The latter are affected by modification of the thermal properties of the polymer through either the presence of additives in bulk or confinement and strong interactions at the CNT interfaces.

1. Introduction

Carbon nanotubes (CNTs) are light, anisometric and conducting particles (1). This combination of properties make them ideal fillers to achieve light and conductive polymer composites which can be useful for electromagnetic shielding devices, antistatic plastics, packaging, etc. The conductivity of the composites is usually dominated by the intertube contacts which are more resistive than the CNTs. This is why it is expected that the conductivity of nanotube composites should strongly depend on the surface properties of CNTs and on the polymer confinement at the CNT interfaces.

In the recent years, several studies have focused on composites made of polyvinyl-alcohol (PVA) loaded with carbon nanotubes (2-21). In particular, the conductivity of PVA nanotube composites loaded up to 5wt% with carbon nanotubes and carbon nanofilaments has been investigated as a function of temperature (10). The authors reported a nearly constant conductivity in the temperature range from 20 to 220°C. More recently the thermo-electrical properties of aligned CNT-PVA fibers which contained greater fractions of CNTs have been studied as well (21). It was shown that the resistivity decreased substantially at the glass transition temperature (T_g) of the PVA in the first heating stage. This effect was ascribed to structural relaxations with slight loss of nanotube alignment and reorganizations that favor better intertube contacts. In subsequent heating-cooling stages, the resistivity was found to be more stable.

The present study is focused on composites which also contain a large CNT weight fraction of about 25wt%. The materials are studied in the temperature range from 20°C to 200°C. In contrast with previous studies of CNT-PVA fibers, the investigated materials do not exhibit in-plane alignment. This allows the minimization of contributions arising from variations of the number of intertube contacts due to changes in orientation. In addition, we investigate isotropic composite mats comprised of multiwall nanotubes stabilized either by covalent functionalization or by surfactant adsorption. Such surface treatments allow the CNTs to be dispersed in water and thereby the use of water based processes to achieve nanocomposites. The systems have been characterized by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and electrical measurements. Composites made of covalently functionalized CNTs exhibit a strong decrease of resistivity with a maximum rate at a temperature well above the T_g of the neat polymer. DSC reveals that the T_g of the PVA in bulk is not affected by the presence of the CNTs. This suggests that the electrical behavior is dominated by polymer fractions at the interface of the CNTs. Polymers can indeed exhibit shifts of their glass transition as they are confined near the functionalized CNTs (20, 22). By contrast, and in analogy with the behavior of PVA-nanotube fibers (21), composites with surfactant stabilized CNTs exhibit a strong decrease of resistivity with a maximum rate in the vicinity of the T_g of the neat polymer. This distinct behavior reflects weaker PVA-CNT interactions. However, the surfactant route to achieve composites through water based processes has another consequence. Indeed, surfactants are not only distributed at the interface of the CNTs but also in the bulk polymer matrix. The presence of SDS does not substantially affect the glass transition of the polymer but it significantly lowers the melting transition. This is reflected by a second maximum in the rate of resistivity decrease below

200°C. The obtained results demonstrate the critical importance of the route chosen to make composites and in particular of the CNT surface properties for the thermo-electrical properties of their composites.

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2. Experimental Section

2.1 Materials and equipments

We have used multiwall nanotubes provided by Arkema (batch 4028) and produced by a Catalyzed Chemical Vapor Deposition (CVD) process. The average external diameter of the tubes is 10-15 nm. Sodium dodecyl sulfate (SDS), the surfactant used to stabilize CNTs in water, was obtained from Acros. Nitric acid (65%) was purchased from Prolabo and the PVA from Sepic (M_w 198 kg.mol⁻¹, Hydrolysis 98%). Functionalization was checked by acid-base titration methods following the procedure described by Hu et al. (23). Sodium hydroxide (98%) and sodium hydrogen carbonate (99.5%) used for titration were obtained from Aldrich. They allow the total pourcentage of acidic sites and carboxylic acid groups to be respectively determined. Thermogravimetric analysis (TGA) was used to determine the amount of PVA in the nanotube composites. The experiments were performed using a Setaram TAG 16 instrument under argon flow at a heating rate of 5°C/min. Differential scanning calorimetry (DSC) was used to determine the glass temperature transition of the polymer in the presence or not of carbon nanotubes. A Perkin-Elmer Pyris instrument at a heating rate of 10°C/min under nitrogen atmosphere was used. Samples of ca. 12 mg in aluminum pans were used. Temperature and enthalpy calibrations were performed with the melting transition of an Indium standard sample. The conductivity of the samples was measured in a home made temperature controlled chamber shown in **Figure 1** (the internal temperature of the chamber was checked with a temperature sensor equipped with a platinum thermocouple). The composite mats are connected to two electrodes with silver paste. The silver paste was purchased from Radiospare under the reference RS 185-3593. The resistance is measured using a Keithley 2000 multimeter connected to a computer for simultaneous measurements of temperature and resistance. The nanocomposites are kept overnight in a vacuum oven before

each measurement to remove moisture. The resistance measurements are performed at fixed length. The composites are kept with a fixed length by holders made in Invar to avoid electromechanical artifacts due to possible thermal expansion of the materials.

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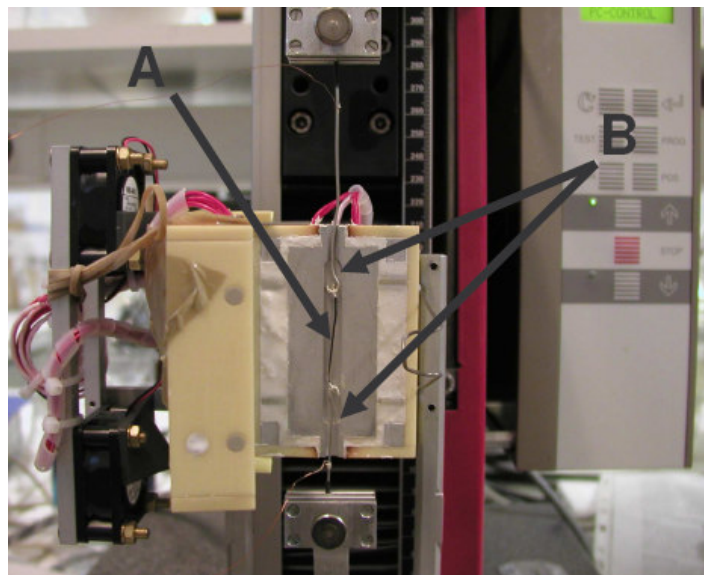


Figure 1. Experimental set-up used to investigate the conductivity as a function of temperature. A thin film layer of nanocomposite is connected to two electrodes with silver paste. The film is placed in a temperature controlled chamber, which is here opened. The length is kept fixed during the measurements. The arrow A shows the sample under investigation. The arrows B show the Invar holders.

2.2 Preparation of nanotube dispersions and nanotube composite mats.

- SDS-carbon nanotube dispersions: Arkema CNTs (0.9wt%) are dispersed in water using sodium dodecyl sulfate (SDS) as dispersant (1.2wt%). The dispersion is homogenized using a sonication treatment (35 min at 20 Watts, 20 kHz). Distilled water is added afterwards to achieve a final CNTs weight fraction of 0.7%.

- Oxidized-carbon nanotubes dispersions: Oxidized-multiwalled carbon nanotubes are obtained by adding 1.5 g of CNTs to 250 mL of nitric acid solution 3.6 M under reflux. After 3 days of acid treatment, the suspension is rinsed with distilled water until neutralization. Acid treatment is not expected to significantly shorten the length and diameter of nanotubes, but it induces the formation of carboxyl groups at the nanotube interface (23). To quantitatively evaluate this effect, 200 mg of oxidized-MWNT are used for acid-base titration

(23). It was found that oxidized nanotubes have 1% of COOH groups (uncertainty 0.2%) while raw nanotubes have between 0 and 0.2% of COOH groups using this method. One can therefore consider the ratio of COOH groups on raw nanotubes as negligible. The weight fraction of remaining CNTs is then adjusted to 0.7wt% with distilled water. This treatment leads to dispersions of CNTs with covalently bonded hydroxyl and carboxyl groups at their interface (24). These hydrophilic groups allow the stabilization of CNTs in water (25, 26).

- SDS-carbon nanotubes/PVA and oxidized-carbon nanotubes/PVA composite mats: Prior to preparation of PVA-nanotube composite mats, PVA ($M_w = 198000$ g/mol, hydrolysis 98%) is dissolved in pure water. The weight fraction of the polymer solution is 5wt%. 5 g of the PVA solution is added to 10 g of the homogeneous SDS-stabilized or oxidized-CNT dispersions described above (0.7wt% in both cases). After addition of the PVA solution, the dispersion is kept 5 minutes in an ultrasonic bath and then filtered under vacuum on a regenerated cellulose membrane (pore size = $0.45 \mu\text{m}$, diameter = 4.7 cm, thickness = 0.155 mm) to obtain CNT/PVA composite sheets as shown in **Figure 2**. The thickness of the dried sheets ranges between $200 \mu\text{m}$ and $350 \mu\text{m}$ typically. Layers that are 1.8 mm wide and 2 cm long are cut with a cutter knife for thermo-electrical measurements. CNT mats of similar surface area but without PVA have also been prepared to serve as references for thermo-gravimetric analysis as explained below.



Figure 2. Picture of a CNT-PVA composite mat. The diameter of the mat is 4 cm.

The CNT, PVA and SDS contents are determined by TGA. Thermographs for SDS-CNT and oxidized-CNT materials, with or without PVA, are respectively shown in **Figure 3** and **Figure 4**. We take $W_{1(30-600)}$ as the weight loss from 30 to 600°C. It corresponds to the decomposition of the SDS for SDS-CNT mats or to the decomposition of the carboxylic acid and hydroxyl groups for oxidized-CNT mats prepared without PVA. $W_{2(30-600)}$ is the weight loss from 30 to 600°C due to the decomposition of the SDS and the PVA chains or of the carboxylic acid and hydroxyl groups and the PVA chains for composite materials.

The CNT weight fraction is given by: $CNT_{wt\%} = 100 - W_{2(30-600)}$ (eq 1)

The CNT to SDS ratio is given by: $\frac{CNT_{wt\%}}{SDS_{wt\%}} = \frac{100 - W_{1(30-600)}}{W_{1(30-600)}}$ (eq 2)

We can deduce from equations (eq 1) and (eq 2) and the data in **Figure 3** that the composition of CNT/PVA composites with SDS stabilized CNTs is the following: CNT 26wt%, PVA 66.8wt% and SDS 7.2wt%. Note that this estimation is based on the fact that we consider the ratio of CNT to SDS similar in mats with or without PVA. SDS molecules at the surface of CNTs can remain in the final mats in both cases. A fraction of SDS remains trapped in the PVA but we assume that this fraction is small relative to the amount of surfactant adsorbed at the surface of the CNTs.

Following the same procedure for oxidized CNTs and using the data shown in **Figure 4** we deduce that the composition of oxidized CNT/PVA composites is the following: CNT (only the carbonaceous part that doesn't include the functional groups) 27.7wt%, PVA 69.1wt%, functional carboxylic and hydroxyl groups 3.2wt%.

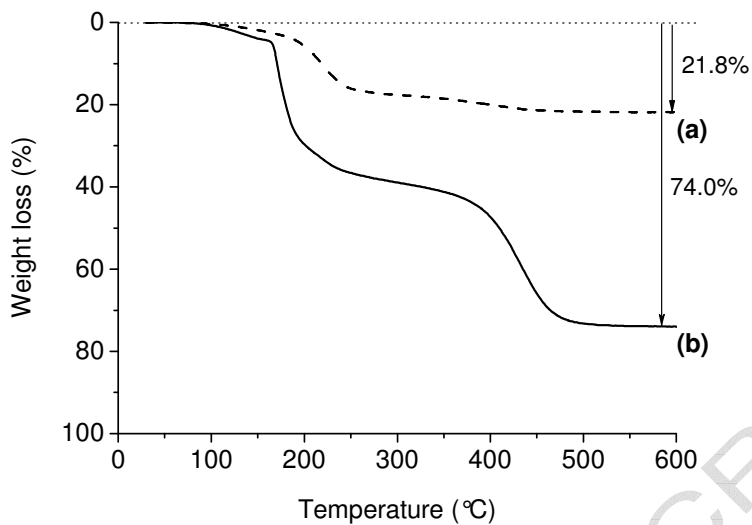


Figure 3. Thermogravimetric analysis of (a) SDS-CNT mat $W_{1(30-600)}=21.8\%$ and (b) SDS-CNT/PVA composite $W_{2(30-600)}=74.0\%$.

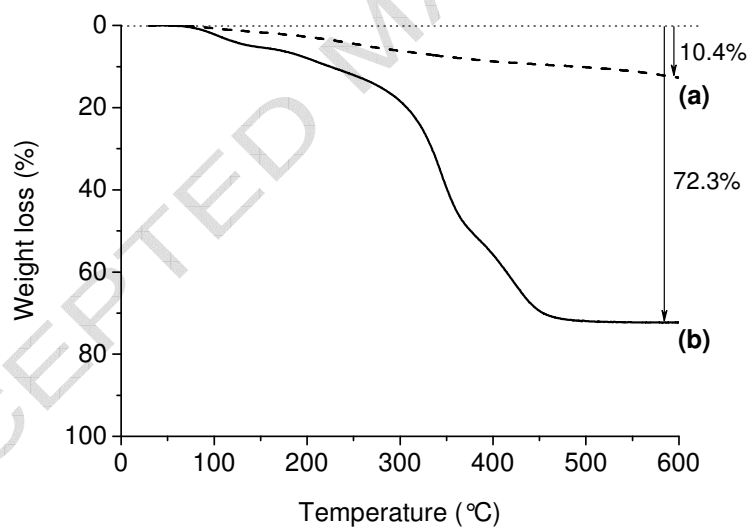


Figure 4. Thermogravimetric analysis of (a) oxidized-CNT mat $W_{1(30-600)}=10.4\%$ and (b) oxidized-CNT/PVA composite $W_{2(30-600)}=72.3\%$.

It is important to note that the composites exhibit a major difference in terms of composition. In the case of surfactant stabilized CNTs, SDS is distributed at the interface of the nanotubes

but also in the bulk polymer matrix. The polymer matrix is instead free of additives for composites made of oxidized CNTs.

3. Thermal and thermo-electrical characterizations

We present in this section the thermal properties of pure PVA and of CNT-PVA composites characterized by DSC.

3.1 Thermal properties

DSC is used to determine the glass (T_g) and melting (T_m) transition temperatures of the materials. The T_g is revealed by the change in heat capacity and a corresponding inflexion point in the thermograms, whereas T_m is characterized by a peak corresponding to the latent heat of melting. As shown in **Figure 5**, the T_m is about 208°C for the neat PVA, and 207°C for the composites made of PVA and oxidized CNTs. In the presence of SDS T_m is 170°C. Similar effects have been reported for mixtures of PVA and other additives. It was indeed already shown that the presence of moisture, physical or chemical cross-linkers, acids, salts, drugs or even colloidal particles can substantially alter the temperature transitions of PVA materials (27-34). The melting temperature is unchanged with oxidized CNTs because, as indicated above, the polymer matrix is in this case free of molecular and ionic additives.

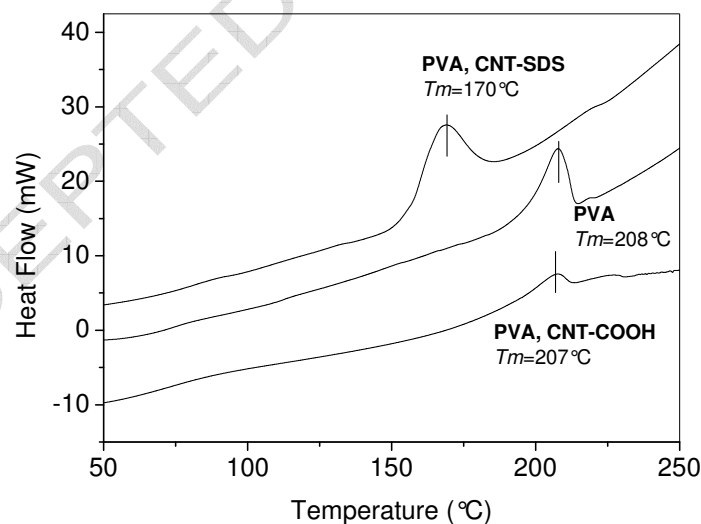


Figure 5: Thermograms of PVA, composites made of PVA and SDS stabilized CNTs (PVA, CNT-SDS) or oxidized CNTs (PVA, CNT-COOH). The melting temperature (T_m) is similar for neat PVA and composites comprised of oxidized CNTs. It is lowered by almost 40°C in the presence of SDS. The curves have been shifted by an arbitrary vertical offset for sake of clarity.

To see more clearly the glass transition we plot in **Figure 6** zooms of the low temperature range of the thermograms. The T_g is close for all the investigated materials. It is about 74°C for neat PVA and PVA loaded with oxidized CNTs. It is slightly greater $T_g=80^\circ\text{C}$ in the case of composites made of SDS stabilized CNTs. This shift can also be attributed to the presence of SDS in the bulk polymer matrix.

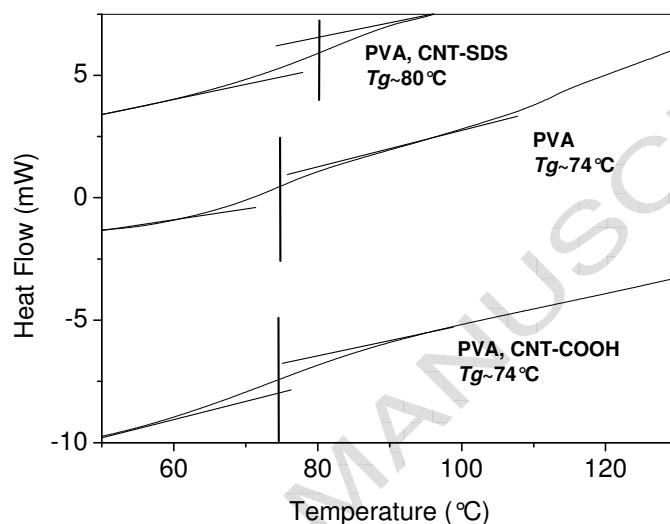


Figure 6: Zoom in the low temperature range of thermograms of PVA, composites made of PVA and SDS stabilized CNTs (PVA, CNT-SDS) or oxidized CNTs (PVA, CNT-COOH). The glass transition temperature (T_g) is almost similar for all the materials. It is just slightly greater for composites comprised of SDS stabilized CNTs: 80°C vs 74°C. . The curves have been shifted by an arbitrary vertical offset for sake of clarity.

3.2 Electrical properties

The resistivity of the composite materials is measured as the samples are heated up at a heating rate of 10°C/min. Experiments at lower rates, down to 1°C/min, yield similar results. A significant decrease of the electrical resistivity (ρ) is observed for both SDS stabilized nanotubes and oxidized nanotubes. The data are shown in **Figures 7a** and **8a**. In both cases, the resistivity is normalized by the resistivity at room temperature: $\rho_0=30\text{ Ohm.m}$ for oxidized-CNT/PVA composites and $\rho_0=0.05\text{ Ohm.m}$ for SDS-CNT/PVA composites. Even though the absolute values of the resistivity differs strongly, their normalized variations as a function of the temperature occur in the same ranges. This is because they are mainly driven by the thermal properties of the polymer as discussed latter. To more clearly evidence the rate

of decrease we plot in **Figure 7b** and **8b** the derivatives $d\rho/dT$. In the case of oxidized CNTs, the maximum of the rate of decrease occurs at 99°C. In the case of SDS stabilized CNTs, two peaks are observed in the derivatives at 80°C and 172°C. They reflect two maxima of the rate of resistivity decrease.

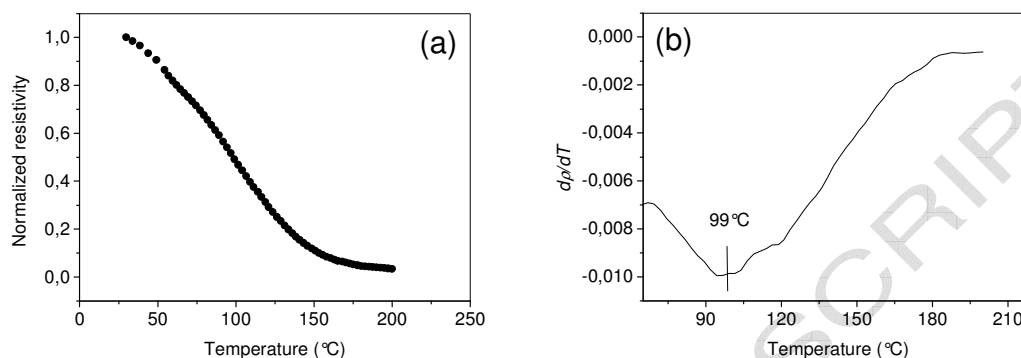


Figure 7: Normalized electrical resistivity (a), and its derivative (b), of composites made of PVA and acid oxidized CNTs. The maximum of rate of decrease occurs at 99°C.

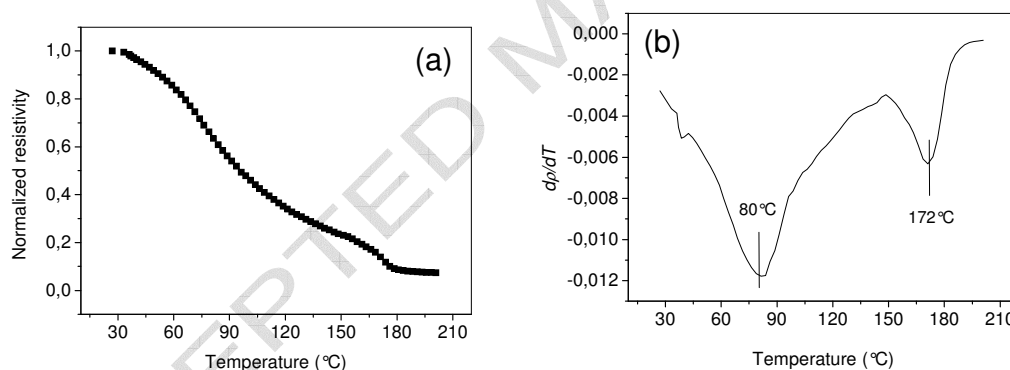


Figure 8: Normalized electrical resistivity (a), and its derivative (b), of composites made of PVA and SDS stabilized CNTs. Two peaks are observed in the derivative. They indicate two maxima of the rate of resistivity decrease: at 80°C and 172°C.

For comparison and confirming that the observed behavior is essentially governed by the properties of the polymer, mats of pure nanotubes have been tested. Those mats are simply obtained by a membrane filtration process. The conductivity of such a mat as a function of temperature is plotted in **Figure 9**. The data are normalized by the resistivity at room temperature such as for composite materials. The resistivity of pure CNT mats decreases with temperature but this decrease is much less pronounced than for composites.

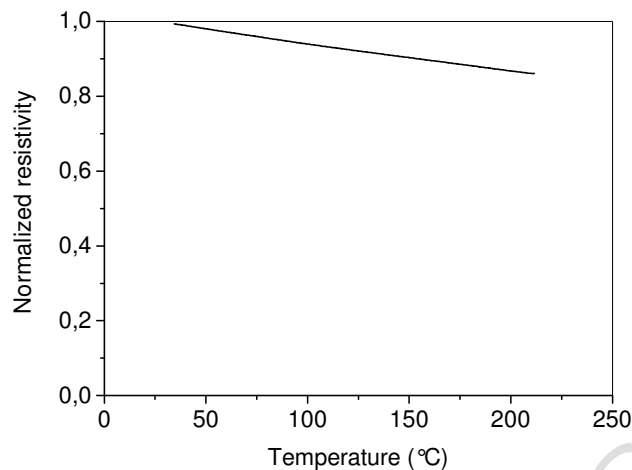


Figure 9: Normalized electrical resistivity of nanotube mats (without PVA) as a function of temperature.

5. Discussion

Improvements of conductivity of nanotube composites upon heating have been already reported in the literature (19, 21) with a correlation of the glass transition and the rate of maximal resistivity decrease for nanotube composite fibers (21). Several effects can come into play. In aligned structures, changes of the degree of orientation with increasing temperature can affect the contact probability of the conducting particles (35) and thereby the number of intertube contacts and the conductivity of the composite. This effect was proposed to partially contribute to the decrease of resistivity observed in nanotube fibers (21). Even if the present materials are isotropic, mechanical relaxations at the glass transition still allow the CNTs to locally reorganize in response to van der Waals interactions and mechanical constraints stored during the drying of the composite mats. Such relaxations can generate closer and more conductive intertube contacts. From a qualitative point of view, the similarity of the behavior of aligned fibers and of the present non aligned mats suggest that changes of orientation do not dominate the improvement of electrical conductivity. Instead local reorganizations and improvements of intertube contacts seem to be preponderant. In addition, the influence of surface functionalization shows that interfacial phenomena are critical. First, from a quantitative point of view, oxidized-CNT/PVA composites are much less conductive than SDS-CNT/PVA composites. Acidic oxidation is expected to degrade nanotubes and their electronic properties. In particular the external tubes, through which internanotube contacts are established, are the most degraded by the oxidation treatments. Degradations of the

delocalized π electrons system can explain more resistive intertube contacts and the observed differences of oxidized-CNT/PVA composites from SDS-CNT/PVA composites. Second, and as shown above, the T_g of the bulk PVA is not affected by the presence of oxidized CNTs. However, the maximal rate of resistivity decrease is clearly above the T_g of the bulk PVA: 99°C vs 74°C. This suggests that reorganizations at the interfaces are more pronounced at temperatures above the T_g of the neat PVA. Such an effect can arise from a modification of the polymer dynamics when it is confined and strongly interacting with the CNTs. It has indeed been shown in other nanocomposites (22) that nanoparticles can increase the glass transition temperature of the polymer at the interface of the nanoparticles. This is a local effect that occurs only at the interfaces of the nanoparticles. It is therefore difficult to evidence it by bulk measurements such as in our DSC analysis. Oxidized CNTs are expected to strongly interact with the PVA via hydrogen or even covalent bonding. This is why its glass transition can locally be shifted to higher temperatures. The observation of anomalies quite above the main melting peak of PVA in DSC curves in **Figure 5** of oxidized-CNT/PVA composites can also be a consequence of strong interactions of PVA and oxidized CNTs. They are not observed in SDS-CNT/PVA composites. But the rate of resistivity decrease exhibit two maxima in the case of CNTs stabilized with SDS. The first maximum is at 80°C, a temperature that matches the T_g of the PVA-SDS mixture. This behavior is reminiscent of the behavior of composite fibers made of non-functionalized CNTs. It suggests that PVA-CNT interactions are weaker than in the case of oxidized CNTs. However, the presence of SDS induces a decrease of the melting temperature transition down to 170°C. At this temperature structural relaxations are enhanced and reflected by the second maximum in the rate of resistivity decrease.

6. Conclusion

It has been shown that the conductivity of CNT-PVA composite mats increase with increasing the temperature. This effect is characterized by a rate which exhibit different maxima depending on the surface properties of the CNTs and of the presence of additives in the bulk polymer matrix. Oxidized CNTs exhibit strong interactions with the PVA which yield pronounced local reorganizations only at temperatures well above the T_g of the neat polymer. However, oxidized CNTs can be stabilized without any additive. The absence of additives in the bulk polymer matrix is reflected by the conservation of the glass and melting temperature transitions. Non oxidized CNTs exhibit weaker interactions with the PVA and a maximum of the resistivity decrease at the glass transition temperature of the bulk PVA. Nevertheless, the

presence of surfactant additives in the bulk yields a decrease of the melting temperature of the polymer. The latter is shifted below 200°C and reflected by a second maximum in the rate of resistivity decrease. The present results show that surface functionalizations play a critical role in the thermo-electrical properties of CNT composites. In particular, the type of formulation, via either covalent functionalization or surfactant adsorption, can yield substantial differences through the presence of additives in the bulk or through surface interactions and polymer confinement at the CNT interfaces.

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