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Thermo-electrical properties of PVA–nanotube composite fibers

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Abstract

We present in this work an experimental study of the resistivity of composite nanotube fibers made of polyvinyl alcohol and multiwalled carbon nanotubes. These fibers which exhibit exceptional mechanical properties could be used for new conductive and multifunctional textiles or composites. We report on their electrical properties and draw two main conclusions: (i) when the fibers contain a large fraction of amorphous polymer, a substantial decrease of the resistivity is observed in the vicinity of the glass transition temperature (T_g) of the pure PVA. On the basis of X-ray diffraction characterizations, we believe that this behavior results from the relaxation of stress in the polymer–nanotube composite. Slight structural modifications and partial loss of nanotube alignment at T_g could yield an increase of the density of intertube contacts and thereby to a decrease of the electrical resistivity. (ii) Annealing the fibers at high temperature reduces the fraction of amorphous PVA which becomes more crystalline. As a result, the conductivity becomes more stable and does not exhibit any abrupt variation at T_g. Instead the conductivity is non-metallic with an effective semi-conductor type behavior as observed in other nanotube composites or even in pure nanotube assemblies.

Keywords: Composite; Nanotube; Fiber

1. Introduction

Carbon nanotube composites have been and are still extensively studied for their electrical and mechanical properties. In the recent years, several studies have focused on composites made of polyvinyl alcohol (PVA) loaded with carbon nanotubes [1–14]. PVA can also be used to make composite fibers which contain a large fraction of nanotubes [15]. Composite nanotube–PVA fibers exhibit an extremely high toughness, superior to that of any other materials [16,17]. They are also electrically conductive and could be therefore the basis for lightweight, strong and conducting textiles or composites. The electrical resistivity (ρ) of such fibers at low temperature is dominated by the electronic properties of the nanotubes, the number of intertube contacts [7] as well as their tunneling nature as in other nanotube polymer composites [18]. However, to the best of our knowledge, their resistivity at temperatures above room temperature has not yet been investigated. This is a critical property for potential future applications. Nevertheless, the conductivity of PVA–multiwalled nanotube composite films loaded up to 5 wt% with carbon nanotubes and nanofilaments has been recently reported [9]. The authors reported a nearly constant conductivity in the temperature range from 20 to 220 °C. Here we focus our study on composite fibers which contain more carbon nanotubes with weight fractions of 11 and 23 wt%. Loading composites is a natural route to achieve improved electrical and mechanical properties. As shown further, the large fraction of nanotubes leads to substantial differences from the behavior of less concentrated composites. In contrast to previous studies, the resistivity of PVA–nanotube fibers exhibits a strong decrease at T_g. In contrast also with the electrical behavior at low temperature, the resistivity is here dominated by the properties of the polymer. X-ray diffraction is used to identify a possible origin of

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such a thermo-electrical behavior. Actually, we observe some loss of nanotube alignment as the fibers are heated up even at fixed strain. We believe that this is due to the relaxation of mechanical stress stored during the synthesis and drying of the fibers. This relaxation is occurring when the polymer chains become more mobile. This mobility allows slight structural modifications which are sufficient to yield a strong decrease of the resistivity. To confirm further the importance of the glass transition temperature and of the presence of amorphous PVA in this electrical behavior, we have performed two sets of experiments. First, we have annealed composite fibers to increase the crystallinity of the PVA and to reduce the fraction of amorphous polymer. Annealing is here achieved by heating the fibers up to 200 °C and by holding it at 200 °C for 5 min. The heating rate from room temperature to 200 °C is 5 °C/min. As expected, annealed materials behave differently. Their electrical resistivity slightly decreases with the temperature. They behave like polymer-free nanotube fibers which are like a semi-conductor with $\rho = \rho_0 e^{(E_0/2kT)}$ [19]. We stress that annealed PVA–nanotube composites exhibit a much better thermal stability than untreated fibers. They could thus be more suitable for applications where the stability of the conductivity is an important issue. Secondly, we have investigated the behavior of fibers with two different fractions of nanotubes which are 11 and 23 wt%. As naturally expected, the resistivity of the more concentrated fibers is lower. The decrease of ρ at T_g is observed in both cases. But this decrease is much more pronounced with fibers that contain a larger fraction of polymer. This confirms the critical role of the insulating polymer in the electrical behavior of such composite fibers above room temperature. Lastly, we note that measuring the conductivity of highly loaded nanotube composites is a simple and effective way to reveal the glass transition temperature of the polymer. In the presently studied samples, we can deduce that the glass transition temperature of the polymer is not substantially affected by the presence of the nanotubes in spite of their high concentration.

2. Experimental

2.1. Materials and equipments

We use multiwalled nanotubes provided by Arkema (batch 3056) and produced by a Catalyzed Chemical Vapor Deposition process. The average external diameter of the tubes is 10–15 nm. After purification in HCl acid, they contain a fraction of remaining iron catalysts of about 3 wt% and no other forms of impurities. The nanotubes are washed several times with distilled water to fully remove HCl. The small fraction of remaining iron impurities is mainly encapsulated in the nanotubes. But it can still slightly contribute to the electrical conductivity of the fibers. However, since we show that the variation of conducting behavior is dominated by the polymer, one can simply consider this fraction of impurities as an additional conductive filler in the system. The PVA was obtained from Seppic (M_w 198 kg mol^{-1}, hydrolysis 98%). Thermal gravimetric analysis (TGA) was used to determine the amount of PVA in the nanotube composite fibers and films. The experiments were performed using a Setaram TAG 16 instrument. Differential scanning calorimetry (DSC) was used to determine the glass transition temperature of the raw polymer, in the absence of nanotubes. A Perkin–Elmer Pyris instrument at a heating (or cooling) rate of 10 °C/min under a nitrogen atmosphere was used. Samples of 25 mg were put per aluminum pans. The conductivity of the samples was measured in a home-made temperature controlled chamber shown in Fig. 1 (the internal temperature of the chamber was checked with a temperature sensor equipped with a platinum thermocouple). The studied fibers are connected to two electrodes with silver paste. The silver paste is provided by Radiospare under the reference RS 185-3593. The contact resistance certainly varies as a function of temperature. But it was checked by four probe measurements that the contact resistance is negligible compared to the resistance of the investigated samples. The resistivity is followed using a Keithley 2000 multimeter connected to a computer for simultaneous measurements of temperature and resistivity. The fibers are kept overnight in a vacuum chamber before each measurement. This allows removing residues of water. The conductivity difference from fibers which were not kept in the vacuum chamber is about 10% at room temperature. The resistivity measurements are performed at fixed strain. The clamps which impose the fixed strain are outside the chamber. The fibers are held by holders made in Invar. This alloy is specifically chosen for its small thermal expansion coefficient of 10^{-6} K^{-1}. The length of the holder parts in the chamber is about 4 cm. It can thus be estimated that the maximal length variation induced by thermal expansion of the holders in the present experiments does not exceed 8 μm when heating the samples from room temperature to 200 °C. Considering that the length of the smallest tested nanotube fiber is 1.5 cm, we deduce that the strain is kept fixed within an uncertainty of 0.05%. The orientation of the carbon nanotubes within the fibers is characterized by

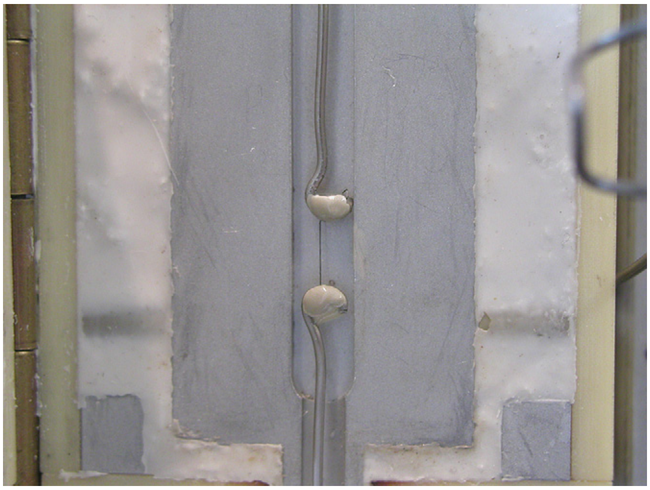

Fig. 1. Experimental set-up used to investigate the conductivity as a function of temperature. The fiber is connected to two electrodes with silver paste. The fiber is placed in a temperature controlled chamber, which is here opened. The strain is kept fixed during the measurements.

X-ray diffraction using a Nanostar Bruker diffractometer equipped with a 2D detector. As described in previous Refs. [7,20–22], the degree of alignment of the nanotubes is directly deduced from Gaussian fits of the angular distribution of the scattered intensity at a given wave vector. The latter is taken as the wave vector of the diffraction peak which corresponds to the intertube spacing. Its value is 1.85 $\mathring{A}^{-1}$, a value roughly similar to the wave vector of the 002 diffraction peak of graphite. Unfortunately crystallinity of the polymer could not be quantified. The width of X-ray scattering peaks is affected by the confinement of the polymer in the investigated nanocomposite structures.

2.2. Thermal properties of the PVA

The glass transition temperature of pure PVA used in this study is about 76 °C. As shown in Fig. 2, heating the polymer induces a reduction of the fraction of amorphous polymer which directly contributes to the variation of the heat capacity at the glass transition temperature. We note that subsequent heating and cooling stages progressively reduce the fraction of amorphous polymer. But a single heating–cooling cycle is not sufficient to crystallize all the polymers.

2.3. Preparation of the fibers

We spin fibers via a continuous method with the fundamental mechanism already described in the literature [13]. MWNTs (0.9 wt%) are dispersed in water using sodium dodecyl sulfate (SDS) as dispersant (1.2 wt%). The dispersions are homogenized by sonication. The fibers are continuously spun by injection of the homogeneous nanotube dispersions in the co-flowing stream of an aqueous solution of PVA (5 wt%). This induces polymer bridging coagulation of the nanotubes. The resultant fibers are directly extracted from the coagulating bath, then dried at room temperature and referred to as ‘raw’ and ‘unwashed’ fibers. Their diameter is about 50 μm. Their composition is determined by thermal gravimetric analysis. It is found that they contain a nanotube weight fraction of about 11%. Another type of fiber has been made by washing the fibers in pure water after their extraction from the coagulating bath. This treatment allows some fraction of polymer to be removed. The fibers are then dried and referred to as ‘raw’ and ‘washed’ fibers. The nanotube weight fraction as determined by TGA is now about 23%. Their diameter is smaller than that of unwashed fibers. It is about 30 μm. ‘Annealed’ fibers are fibers which have been heated from room temperature up to 200 °C and then cooled down at room temperature. As shown above for pure PVA, this treatment is expected to promote the crystallization of the polymer. In addition, according to recent studies dealing with the mechanical properties of PVA–nanotube composites, it is expected that carbon nanotubes can enhance the crystallization of the PVA [2,5,10,11,13,14,17]. Annealing the fibers is thus a way to reduce the fraction of amorphous polymer while increasing its crystallinity. We stress that in both cases the fibers are drawn vertically from their washing bath for washed fiber or directly from their coagulating bath for unwashed fibers. This drawing creates in both cases some tensile stress which is stored by the fibers when they dry. As shown in previous papers [7,20,21], coagulation in flow and drying under vertical drawing yield a preferential alignment of the nanotubes along the main axis of the fibers.

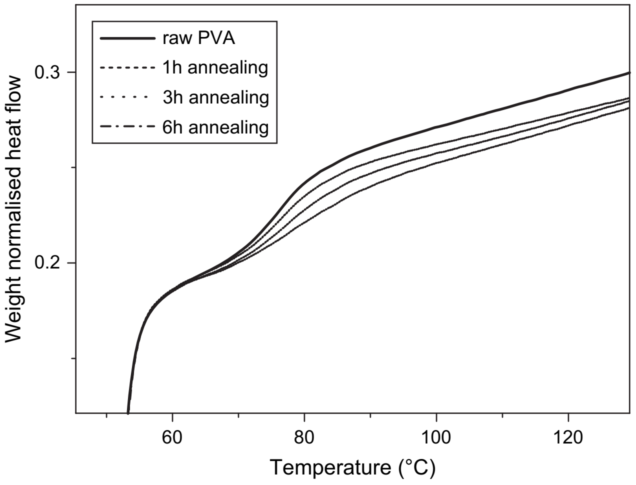

Fig. 2. DSC curves of PVA samples which have not been annealed (raw PVA) and which have been heated for 1, 3 and 6 h at 180 °C (from the upper curve to the lower one). The variation observed at 76 °C reflects the glass transition temperature of the polymer. It corresponds to a variation of Cp, the heat capacity of the amorphous PVA. Heating the fiber at high temperature (up to 180 °C) substantially reduces this variation of Cp. This confirms the increase of crystallinity and the disappearance of amorphous PVA upon thermal cycles.

3. Results and discussion

All the data of electrical measurements are plotted in Fig. 3. The resistivity of raw, annealed, washed and unwashed fibers is studied as a function of the temperature. The heating rate is 5 °C/min and the duration of the hold at 200 °C is 5 min.

These results reveal important and different features of PVA–composite nanotube fibers. First of all, the fraction of amorphous polymer and its glass transition temperature play a significant role. As observed in Fig. 3, this is manifested in the first heating stage of raw washed as well as in raw unwashed fibers. The resistivity strongly decreases in the vicinity of the glass transition temperature. As shown in Figs. 4 and 5, this decrease is even more clearly revealed when we look at the derivative of the resistivity $d\rho/dT$.

The predominant role of the polymer disappears when the PVA–nanotube fibers are annealed. Crystalline domains do not exhibit glass transition temperature. As a result there are no abrupt changes of resistivity in the vicinity of T_g in the second, third, and further heating or cooling stages. We note that, in contrast to the DSC experiments, the conductive behavior does not progressively evolve upon subsequent cycles. A strong decrease is observed in the first cycle whereas the conductive behavior is constant for further cycles. We don’t expect that all the polymer is crystallized after the first heating cycle. Nevertheless, since nanotubes promote the crystallization of

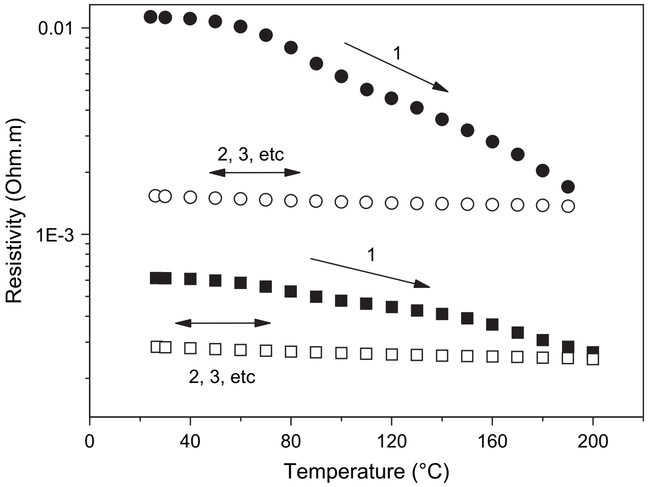

Fig. 3. Resistivity of nanotube fibers as a function of temperature over several cycles for raw (circles) and washed (squares) fibers. In the first heating stage (1, black labels) the resistivity of non-annealed fibers decreases markedly in the vicinity of the glass transition temperature of the polymer ($T_g = 76$ °C). The resistivity of washed fibers is much lower than that of unwashed fibers. The fibers after having been annealed at 200 °C are then cooled down (2, open labels) from 200 °C to room temperature. It is observed that the variation of the resistivity as a function of the temperature becomes much weaker for both washed and unwashed fibers. Then, repeated and subsequent heating and cooling cycles do not change the electrical behavior (2, 3, etc.).

PVA [2,5,10,11,13,14,17], we believe that a single heating cycle stage followed by a cooling stage is sufficient to crystallize the PVA at the interface of the nanotubes. This can freeze and lock the conductive network formed by the nanotubes. As a consequence the conductive behavior remains unchanged even if remaining fractions of amorphous polymer, far from the interfaces of the nanotubes, are still affected by heating and cooling stages. As shown later, the resistivity after the first cycle exhibits a weak variation upon temperature changes. It is also observed that the resistivity of unwashed fibers is greater than that of washed fibers by more than one order of magnitude. This can be understood by considering the greater fraction of insulating PVA in unwashed fibers. The polymer between the nanotubes provides a barrier for electron tunneling at the intertube contacts. More importantly it is observed that the decrease of resistivity at T_g is significantly more pronounced for unwashed fibers than for washed fibers. The resistivity of unwashed fibers decreases by a factor of 6.8 between room temperature and 200 °C whereas that of washed fibers decreases only by a factor of 2.2 in the same temperature range. The predominant role of the fiber composition suggests that the strong decrease at T_g is arising from slight structural modifications in spite of the conditions of fixed strain. Indeed mechanical stress is stored during the drying and washing of the fibers. Its relaxation when the polymer chains become mobile at T_g can allow partial reorganizations of the nanotubes. But we stress that this is not linked to the crystallinity of the polymer. Increase of crystallinity takes place upon cooling and locks the nanotube network in the subsequent heating–cooling cycles. To test the hypothesis of structural modifications in the first heating stage we have performed X-ray diffraction experiments. Those are expected to reveal potential variations of the nanotube alignment when the fibers are heated up at fixed strain. We show in Fig. 6 the angular distribution of the scattered intensity at the wave vector of 1.85 Å^{-1}. As already reported in the frame of other studies [7,20–22], this angular distribution can be fitted with a Gaussian function. The full width at half maximum (FWHM) of the Gaussian function provides an estimate of the average orientation of the nanotubes along the main axis of the fibers. We find that the FWHM for raw fibers is 54.3 ± 1.0° (correlation coefficient 0.97) whereas it is 61.4 ± 1.3° (correlation coefficient 0.97) for annealed fibers (data fitted with the software Origin 6.0). This difference confirms a slight loss of nanotube alignment as the fibers are heated up. Such a loss of alignment increases the

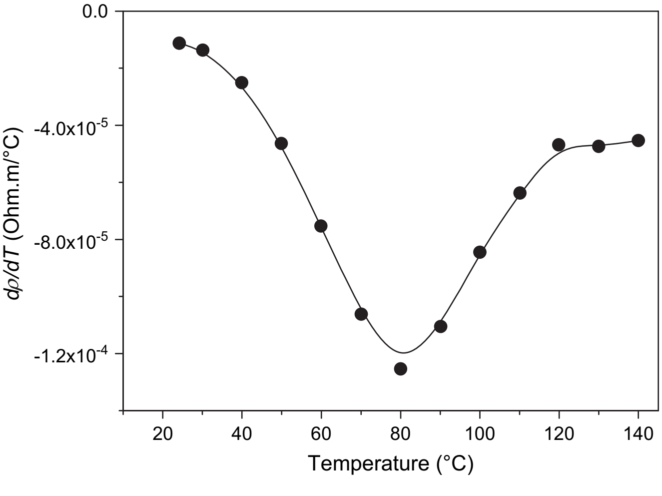

Fig. 4. Derivative of the resistivity of raw unwashed fibers over the temperature as a function of the temperature. A minimum at approximately 80 °C is observed. This temperature is close to 76 °C, the glass transition temperature of the polymer.

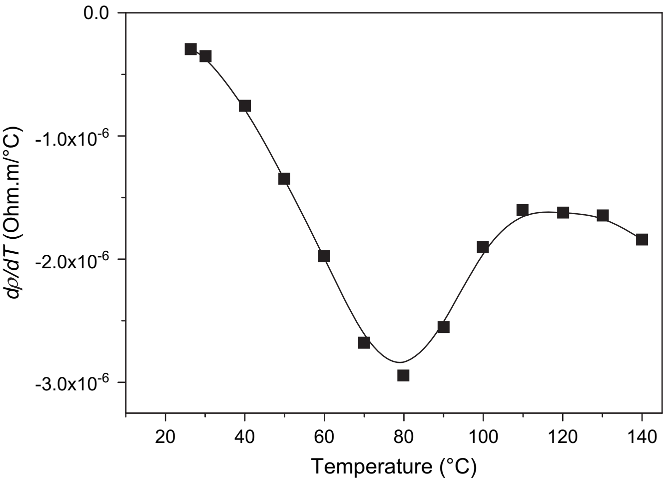

Fig. 5. Derivative of the resistivity of raw washed fibers over the temperature as a function of the temperature. A minimum at approximately 80 °C is observed. This temperature is close to 76 °C, the glass transition temperature of the polymer.

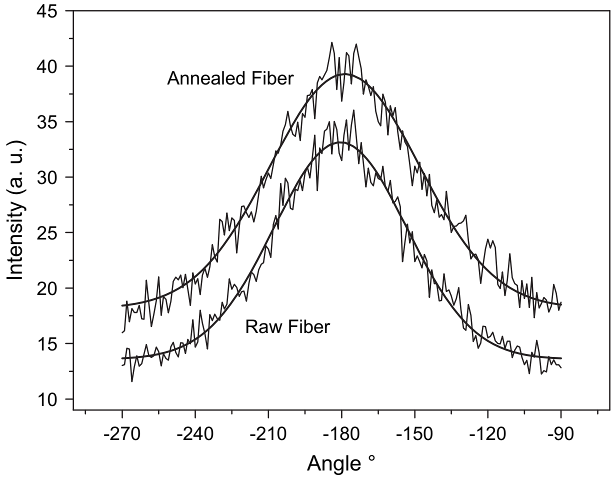

Fig. 6. Angular distribution of the scattered X-ray intensity of a raw nanotube fiber (lower curve) and of the same fiber after it has been heated at 200 °C (upper curve). The distributions are fitted by Gaussian functions. The FWHM of these functions, respectively, are 61.4° and 54.3° for annealed and raw fibers.

excluded volume of the nanotubes and thereby their contact probability [23,24]. A greater number of intertube contacts is naturally expected to increase the conductivity of the material. In addition to this, it is possible that the microscopic nature of the contacts varies upon heating. Indeed, nanotubes which acquire some mobility in the amorphous polymer above T_g can approach each other because of van der Waals interactions. This effect can also participate in the variation of conductivity.

When more crystalline, the mobility of the PVA chains does not change at the glass transition temperature and the variation of the resistance is now dominated by intertube contacts as in classical composite fibers, films and other nanotube based composites [18]. It is interesting at this stage to note the discrepancy with the behavior reported in Ref. [9] for composites loaded with nanotubes. In this previous study, the authors did not observe a strong variation of the resistance at T_g in PVA composites loaded with carbon nanotubes, whereas they reported such a variation in different systems loaded with carbon nanofilaments. We believe that two main reasons might explain such differences: (i) the amount of nanotubes is greater in our experiments and (ii) it also possible that the systems studied in Ref. [9] have experienced a thermal treatment during their preparation which induced some crystallization of the PVA. This could explain the absence of large resistivity variations as in our case. Differences could also arise from contributions of surfactant residues present in the fibers. Such residues could affect the thermal behavior of the polymer. This is the topic of current studies. Nevertheless, we believe that the surfactant itself does not substantially contribute to the conductivity of the fibers. Indeed, the conductivity of PVA systems with small fractions of SDS was not measurable with the presently used equipments. This means that the contribution of surfactant residues is negligible compared to the contribution of the nanotubes. This is due to the small mobility of ions in the polymer and the absence of dissociated species.

The values of ρ_o, the resistivity of thermally annealed washed and thermally annealed unwashed fibers at room temperature, respectively, are 2.85×10^{-4} and 1.52×10^{-3} Ω m. The resistivity of unwashed fibers is lower because of the smaller fraction of nanotubes (11 wt%) compared to the fraction of nanotubes in washed fibers (23 wt%). Surprisingly, and also somehow fortuitously, these values are close to the resistivity of pure single walled nanotube fibers spun by a similar process but without polymer as binding agent [19]. One could expect that composite fibers should be far more resistive than pure nanotube fibers [7]. However, a direct comparison has to be considered with some caution. Indeed, pure nanotube fibers studied in Ref. [19] have been spun with single walled nanotubes. In contrast with multiwalled nanotubes, single walled nanotubes contain a significant fraction of semi-conducting tubes and impurities. In addition, their smaller diameter yields smaller intertube contacts which can therefore strongly limit the conductivity of the fibers. The larger diameter of multiwalled nanotubes and their metallic behavior can explain why, even in the presence of insulating polymer, the conductivity of composite fibers can compare with that of pure single walled nanotube fibers.

By investigating the conductivity of thermally annealed nanotube fibers as a function of the temperature we can even go towards deeper comparisons with pure nanotube fibers. Indeed, the fibers we presently study behave like classical nanotube composites at high temperature, that is, like effective semiconductors with a resistivity that varies as $\rho = \rho_0 e^{(E_0/2kT)}$, where E_0 is directly related to the activation barrier for the conductivity by fluctuation induced tunneling at the intertube contacts [25]. Exponential fits shown in Figs. 7 and 8 allow us to deduce that $E_0 = 56$ meV for unwashed fibers and that $E_0 = 8.5$ meV for washed fibers. These values compare well with those found for pure single walled nanotube fibers. The latter indeed vary from 10 to 50 meV [19]. Interestingly we note that the activation energy is greater for unwashed fibers. This can be understood by considering that the fraction

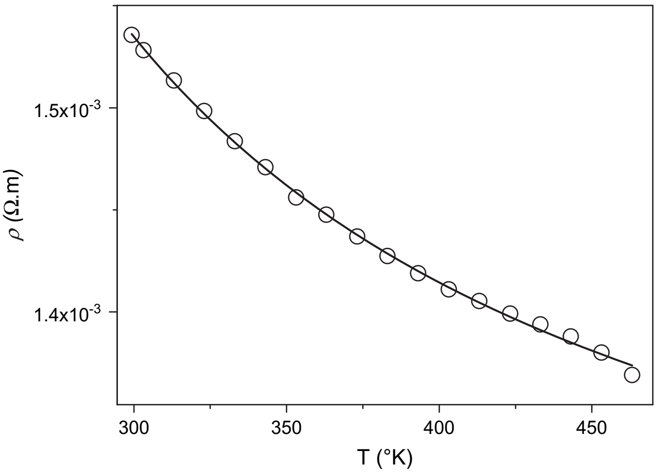

Fig. 7. Resistivity of annealed and unwashed nanotube fibers as a function of temperature. The experimental data (circles) are fitted with an exponential decay (line). We deduce from the fit that $E_0 = 56$ meV.

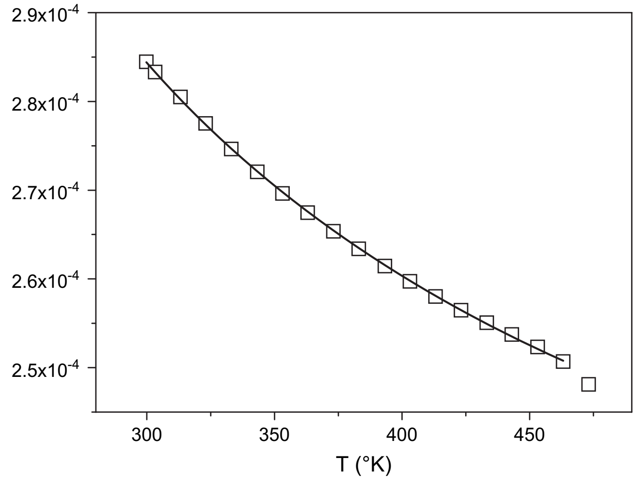

Fig. 8. Resistivity of annealed and washed nanotube fibers as a function of temperature. The experimental data (squares) are fitted with an exponential decay (line). We deduce from the fit that $E_0 = 8.5$ meV.

of insulating polymer is greater in these systems. A greater fraction of polymer induces a larger average separation between the nanotubes and more resistive intertube contacts.

4. Conclusion

In conclusion, we have studied the resistivity of composite nanotube fibers made of PVA and multiwalled carbon nanotubes. Raw fibers which contain a large fraction of amorphous polymer exhibit a behavior which is dominated by the thermal properties of the polymer. A strong decrease of the resistivity is observed in the vicinity of the glass transition temperature of the PVA. This effect is more pronounced when the fraction of polymer is large. On the basis of X-ray diffraction experiments, it is believed that the main origin of this behavior is related to structural modifications as the mobility of the polymer chains increases at T_g. This mobility can allow some motion of the nanotubes which increases the quality and the density of nanotube contacts. When the polymer is crystallized upon thermal annealing, the conductivity of the composite fibers becomes more stable and does not exhibit any abrupt change in the vicinity of T_g. Instead, the conductive behavior is nonmetallic with fluctuation induced tunneling. The related barrier of this activated mechanism is greater when the fraction of polymer is large. We hope that the fundamental findings reported in this work could be useful for future technological developments of nanotube composite fibers in the fields of textiles and composite materials.

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