

Conductive network formation in the melt of carbon nanotube thermoplastic polyurethane composite

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Abstract

This research presents the effect of conductive network formation in the melt (dynamic percolation) to the conductivity of the composite for a multi-walled carbon nanotube/thermoplastic polyurethane composite system. An extremely low percolation threshold

0.13 wt.% was achieved in the melt processed composite film samples, whereas a much higher CNT concentration (3~4 wt.%) is needed to form a conductive network for the composite strands directly extruded from the melt. This is explained by the dynamic percolation behaviour of the CNT network in the melt. The temperature and CNT concentration needed to activate dynamic percolation in this composite was studied by measuring the conductivity temperature dependence of the extruded strand, in an attempt to give an estimation of processing conditions needed for optimized final product fabrication.

Introduction

The idea of using carbon nanotubes (CNT) as conductive filler to improve the electrical properties of polymer composites has drawn great attention both from industry and academia. Due to its high aspect ratio, it promises a very low percolation threshold as a conductive filler, which means the composite will have an improved electrical property without other properties (mechanical, etc) compromised.

Many polymers have been studied as a matrix for CNT conductive polymer composite, and very low percolation thresholds have been achieved with some of the system. Percolation thresholds extremely low (< 0.01 wt%) were achieved when epoxy is used as matrix.[1-3] A surfactant assist dispersion of the CNT in combination with latex technique was used to produce the conductive composites, and the percolation threshold is well below 0.1 wt%.[4-6] For most of the melt processed CNT composites, the percolation threshold is above 1 wt%. [7, 8] Several bi-component blend systems with a interconnected network of the two phase have been studied, and the percolation threshold can be decreased by a factor of 2~3, yielding a percolation threshold with equivalent CNT loading below 1%.[9, 10] It is been noticed that the very low percolation

thresholds are always achieved with a low viscosity system [11], while with the melt process where the viscosity is very high, the percolation threshold is relatively high.

The low percolation threshold has commonly been attributed to the high aspect ratio and a good dispersion of the CNT according to the percolation theory. However, the percolation theory is a statistic model, and the dynamics of the network formation is not considered in the model. During processing the composite is in the state of melt, solution, or liquid as in the case of epoxy, and flow or shearing which is necessary for the dispersion of the CNT are applied to the composite. Flow or shearing can disturb the formation of a conductive network. At the same time, the conductive filler tends to re-agglomerate[12-14], which will induce a time dependent network reformation process, and decide the conductivity of the final product. This is called dynamic percolation [15] by some researchers. This phenomenon has been noticed first for the carbon black conductive polymer composite system[15], the kinetics of colloid particle coagulation was used to describe the network formation process. The effect of temperature on the network formation has been attributed to the viscosity change at different temperatures [15]. A similar phenomenon is also observed for CNT polymer composite systems, where epoxy [11], polypropylene [16], and polycarbonate [17] were used as matrix. Alig et. al. proposed a model using electrical percolation approach combined with a cluster aggregation model to describe the time dependence of the network reformation process after shearing. [17]

In this research, a multi-walled carbon nanotube and thermoplastic polyurethane system is used to study the dynamic percolation behaviour of the CNT conductive polymer composite, in an attempt to understand the relationship between the processing and the dynamic percolation behaviour, in order to reduce the percolation threshold and to improve the conductivity in the final composite product. The conductivity of hot pressed film was compared with the ones of the

extruded strand. While a percolation threshold as low as 0.13 wt.% was achieved for the hot-presses film, 5 wt.% CNT is needed to introduce a good level of conductivity to the extruded strand. A lab designed experiment is used to study the effect of the temperature and filler concentration to the dynamic percolation behaviour.

Experiments

The multiwalled carbon nanotubes used are supplied by Nanocyl, Belgium (Product No. C7000). The Polyurethane used is supplied by Estane, (Product No. X4280). A desired amount of carbon nanotubes are mixed with the polyurethane at 190 °C under nitrogen environment for 4 min at 50 rpm using a DSM Xplore 15ml mini extruder. After the mixing is finished, the screw speed is set to 5 rpm and kept for 1min. At the same time the temperature of the mini extruder was set to a desired extrusion temperature and allowed to stabilise within the 1 min. Then the composite strand is extruded with a typical diameter of about 3mm. Two sets of composites with CNT concentration ranging from 1 wt.% to 5 wt.% are produced with extrusion temperatures of 190 °C and 210 °C. Another set of composites with concentration from 0.2 wt.% to 1 wt.% are mixed with the same condition, extruded at 190 °C and cut into pellets. Then the pellets are fabricated into film by hot pressing at 210°C for 7 min, for comparison.

The conductivities of all samples are measured by a simple two point measurement with a combination of a picoameter (Keithley 6485), and a voltage source (Agilent 6614C). The conductivity of the extruded strand is measured on composite rod cut from the extruded strand with a length about 10mm, and a typical diameter of about 3mm. Silver epoxy is used as electrodes. The conductivity of the film is measured on a strip with the dimension of 0.1mm×10mm×30mm.

The measurement mechanism of the conductivity temperature dependence is shown in Fig. 1. The test device was placed on a heating source, with a thermo couple next to it to monitor the temperature. Heat transport compound was applied between the test device, the thermo couple, and the heating source to ensure the heat transfer. As illustrated in Fig. 1 the test device is CNT composite rod sealed in Kapton film and silver epoxy. This capsule will maintain the strength, shape and volume of the test device when it's being heated to elevated temperatures. The conductance was again measured by a combination of a picoameter (Keithley 6485), and a voltage source (Agilent 6614C). The voltage applied to the sample is 1 V. The voltage is applied for 1 second, and then removed for 1 second, to avoid electric field induced CNT alignment and network formation [18]. The corresponding current and temperature are recorded during a continuous temperature scan. Three samples are tested for composite strand extruded at 190 °C with different CNT concentrations.

Results and Discussion

Figure 2 shows the conductivity of the low CNT concentration films and strand extruded at 190 °C and 210 °C. The conductivity of the films shows typical percolation behaviour, which is commonly described by the percolation theory [19], which is written as,

$$\sigma = \sigma_0 (p - p_c)^t \quad (1)$$

Where p_c is the percolation threshold and t is the exponent, which depends on the dimensionality of the composite. Fitting the film conductivity data with Eq (1) yields a percolation threshold of $0.13\% \pm 0.05\%$ which is very low compare with literature of melt-processed samples. [7, 8] The exponent t is 4.62 from the fitting. This value is much bigger than the theoretical value for the

three dimensional network. The high exponent value can be attributed a tunnelling percolation network [20]. In the case of tunnelling percolation network, such a large exponent indicates a broad distribution of the tunnelling resistance, hence a broad distribution of the inter particle distance [20].

Obviously from Fig. 2, the conductivity of the extruded strand needs a much higher CNT loading to form a conductive network, and the composite strands have a much lower conductivity level. Normally a higher percolation threshold is attributed to a poor dispersion of the conductive fillers. However in this case, for 1% CNT composite, the dispersion state should be exactly the same as the one in the film, since the same mixing condition was applied. The fact that the difference between the conductivity between the film and the extruded strand of 1% CNT composite is almost 10 magnitudes indicates that the conductive network in the film state and the strand state are totally different. Unambiguously, a dynamic percolation is activated during the hot pressing. When the film is produced the melt stayed at 210°C for 7 min, which allow the CNT to form a highly conductive network, yielding an exceptionally low percolation threshold for melt processed composite. While the 210°C extruded strand is only heated to 210 °C before the extrusion, it seems that the network could not be improved by the dynamic percolation at this condition, and the conductivity of the 1% CNT composite shows no difference with the 190 °C extruded one. It is also worth to note that during the extrusion, the melt is constantly under shearing induced by the screw or flowing of the melt in the die. Shearing is proved to destroy the conductive network in the melt, and the network is recoverable in the melt after the shearing is removed[16, 17].

It is also very interesting that in Fig. 2, when the CNT concentration is no less than 3%, there is obvious difference between the conductivity of samples extruded at 190 °C and 210 °C. The

conductivities of the 210 °C extruded samples are about one magnitude higher than the 190 °C extruded ones. Considering that the mixing condition of the composites is exactly the same, the same state of dispersion should be expected when the loading of the CNT is the same. Hence the difference in the conductivity of the composites with the same CNT concentration can only be attributed to dynamic percolation mentioned above. This result also indicates that the conductivity of a CNT composite can be improved by increasing the processing temperature.

The conductivity concentration plot of the extruded strand does not show typical percolation behaviour, indicating that the network formation of the strand is not dominated by the statistic percolation theory. Since the interparticle distance of a randomly dispersed spherical particle system is proportional to $p^{-1/3}$, where p is the volume fraction of the filler, assuming the conduction mechanism of the system is dominated by electron tunnelling between the spherical particles, the conductivity can be written as[21]

$$\sigma \propto p^{-1/3} \quad (2)$$

Eq.2 is often used as a first indication that the conductivity is dominated by tunnelling effect [11, 21, 22]. If we assume that the CNT agglomerations can be considered as near spheres, the resistance is dominated by the inter agglomeration distance, and the weight fraction can be used as volume fraction when the loading is very low, a linear relationship should be expected in Fig. 3. However, this is only true when the CNT loading is no higher than 3 wt.% for 190 °C extruded samples and 2% for 210 °C extruded samples, as indicated by the dash dot line in Fig. 3. After that the conductivity deviates from the indicated line and increases rapidly. It seems that at 190 °C during extrusion, 4 wt.% CNT is needed to activate the dynamic percolation process, and at 210 °C only 3 wt.% CNT is needed to activate this process. All the results above show that under

certain extrusion conditions, and certain temperatures, a certain CNT concentration is needed to activate the dynamic percolation, and improve the conductivity of the extruded composite.

To further study the effect of CNT concentration and temperature to the dynamic percolation in the melt, the temperature dependence of the composite conductivity is studied. A temperature scan is made from room temperature up to 240 °C, and the temperature and conductivity are recorded to observe the dynamic percolation behaviour of the composite. Figure 4 (a) shows the heating profile of the temperature scan, which is the same for all the samples. Figure 4 (b) shows a conductivity versus temperature curve of a 3 wt.% CNT composite strand as an example. A sharp conductivity increase of the composite was observed between 150 °C and 225 °C as expected. To quantify the transition point of the dynamic percolation, figure 4 (b) was re-plotted into Figure 4 (c), and then the curve was differentiated, yielding figure 4 (d), where an onset temperature and a peak temperature can be subtracted.

Before the dynamic percolation transition, the conductive network can be considered as static at all temperatures. Hence the temperature dependence before the transition point can be attributed to the temperature dependence induced by tunnelling resistance. Sheng's fluctuation induced tunnelling model is commonly used to describe the conductive mechanism of the CNT composites [23, 24]. At high temperature, the model becomes a thermal activation with activation energy ΔE [25], and can be written as

$$\ln \sigma \propto -\Delta E / T \quad (3)$$

Where ΔE is the activation energy and T is the absolute temperature. A linear regime in Figure 4 (c) and a constant regime in Figure 4 (d) can be observed as predicted by the model (Eq. (3)), indicating that the conduction mechanism of the composite at this temperature range can be described by Eq. (3).

A peak is clearly shown in the differentiated curve in figure 4 (d). The Lorentzian function is used to fit the peak. Then the onset of the peak was determined from the fitted curve. This onset is considered to correspond to the starting temperature of the dynamic percolation transition. A peak value can also be subtracted from the fitting. It represents the temperature where the conductivity has the biggest increasing rate against the temperature, which is also of great interest to this research. However, the dynamic percolation is not only related to the temperature, but also a time dependent process as proved in other reports[15-17]. The peak values may vary with different heating profiles. While before the transition, the conductive network remains the same and the conductivity temperature dependence is dominated by the hopping effect, which is a time independent relationship. So ideally, the onset of the peak should be a value independent of heating profile.

Figure 5 (a) shows the temperature dependence of composites with various CNT concentrations. It is obvious that with increasing CNT concentration in the composite, the transition points are shifted to lower temperatures. It can be shown more clearly in Figure 5 (b) that the curves are shifted to lower temperatures with increasing CNT concentration. This is consistent with the analysis from the simple conductivity measurement. At the same time, the amplitude of the transition decreases with increasing CNT concentration. This might be because when the CNT concentration is high enough, the dynamic percolation has already been activated during the extrusion condition, and the network is more resistant to outer stimuli [26].

The temperatures of the onset and the peak subtracted from the fitted curve in Figure 5 (b) are shown in Figure 6 (a) and (b) respectively. They appeared to show a similar trend, that the transition points are decreased with an increasing CNT concentration, but after 3 wt.% both the onset and the peak almost remain the same, which also can be observed in Figure 5 (b). This may

be because at low temperature the mobility of the polymer chains is very low, and the CNT can not form the network. So although increasing CNT concentration can decrease the temperature needed for the dynamic percolation process, this effect is limited by the mobility of the polymer chains.

From the simple conductivity analysis in Figure 3, it seems that the dynamic percolation is activated when the CNT loading is higher than 3 wt.% when the composite is extruded at 190 °C and higher than 2 wt.% when the composite is extruded at 210 °C. As shown in Figure 6 (a), when the CNT loading is higher than 1%, the onset temperatures are lower than 210 °C and when the CNT loading is higher than 2%, the onset temperatures are lower than 190 °C. When the onset temperature is lower than the extrusion temperature, the dynamic percolation process should be expected. This result is slightly deviated from the simple conductivity analysis (Table 1). This may be because that apart from the temperature other conditions are very different between the temperature dependence measurement and the extrusion. Due to the shearing and flow induced by the extrusion, a higher CNT content or a higher temperature is needed to maintain the conductive network. Also, as mentioned above, the dynamic percolation is a time dependent process, the very short residence time during the extrusion process limits the effect of network formation. When the same analysis is applied to Figure 6 (b), which shows the peak temperature, the results are more close to the simple conductivity measurement as shown in Table 1. Although the effect of heating profile on the peak temperature is still not clear, it seems that in the current system, the peak temperature is more important for the determination of the processing temperature and composite composition needed for conductive composite processing, especially when the residence time of the polymer is very short during the processing.

Conclusion

The dynamic percolation behaviour of a MWNT/thermoplastic polyurethane composite is studied. A statistic percolation behaviour is observed in hot-pressed film samples with a percolation threshold as low as 0.13 wt.%, while the conductivity of the extruded strand shows a hopping dominated behaviour at low concentrations and a dynamic percolation dominated behaviour at high concentrations. A temperature dependent resistance measurement is proposed to study the effect of temperature and filler concentration to the dynamic percolation process. It is shown that a higher temperature can reduce the filler concentration required to activate the process, while a higher filler concentration can lower the critical temperature for dynamic percolation. Meanwhile, shearing of the melt seems to increase both parameters, which means that shearing is not preferable during processing. Although high shear is essential for the dispersion of the CNTs in the composite, the composite melt should be given enough time and temperature under low shear for formation of the conductive network.

Normally the processing temperature is limited, due to degradation of the polymer at high temperature. The concentration of the filler is also limited for economic reasons, and other requirements on the composite property. The temperature dependence measurement proposed here can be used to estimate the processing temperature and composite composition, to find a balance between these two parameters. This research also demonstrated that the dynamic percolation behaviour of the conductive polymer composite can be harnessed and used to lower the percolation threshold and improve the conductivity of the final product.

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Table 1

concentration	1 wt. %	2 wt. %	3 wt. %	5 wt. %
Onset T (°C)	217	197	171	161
Peak T (°C)	227	209	184	182
σ analysis T (°C)	>210	>210	>190 <210	<190

Table 1

Temperature to activate the dynamic percolation of composites with different CNT concentration.

Figure 1

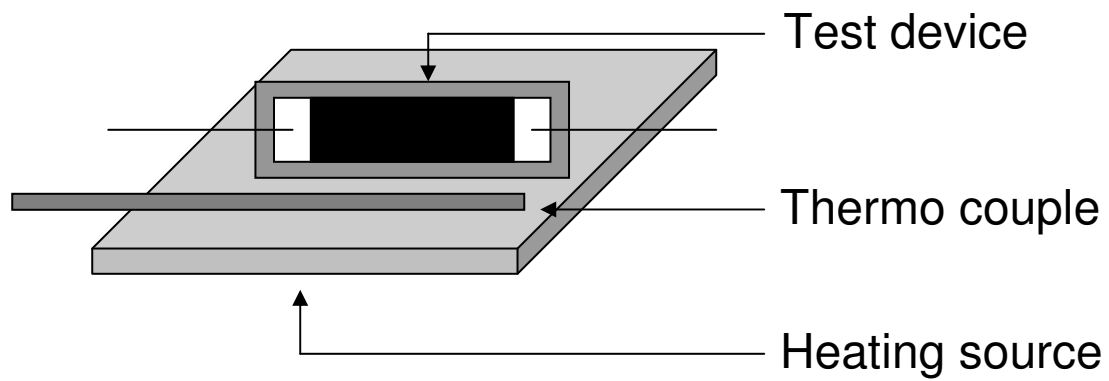


Figure 2

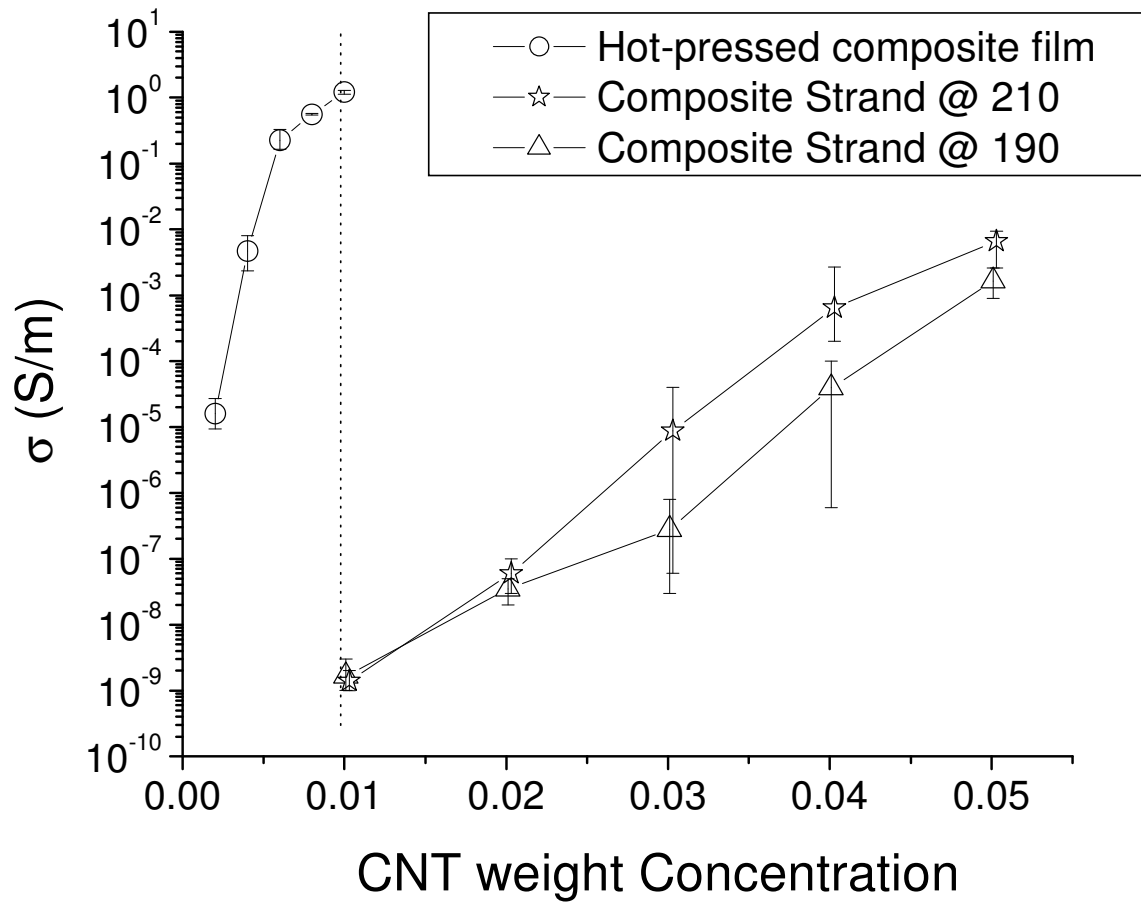


Figure 3

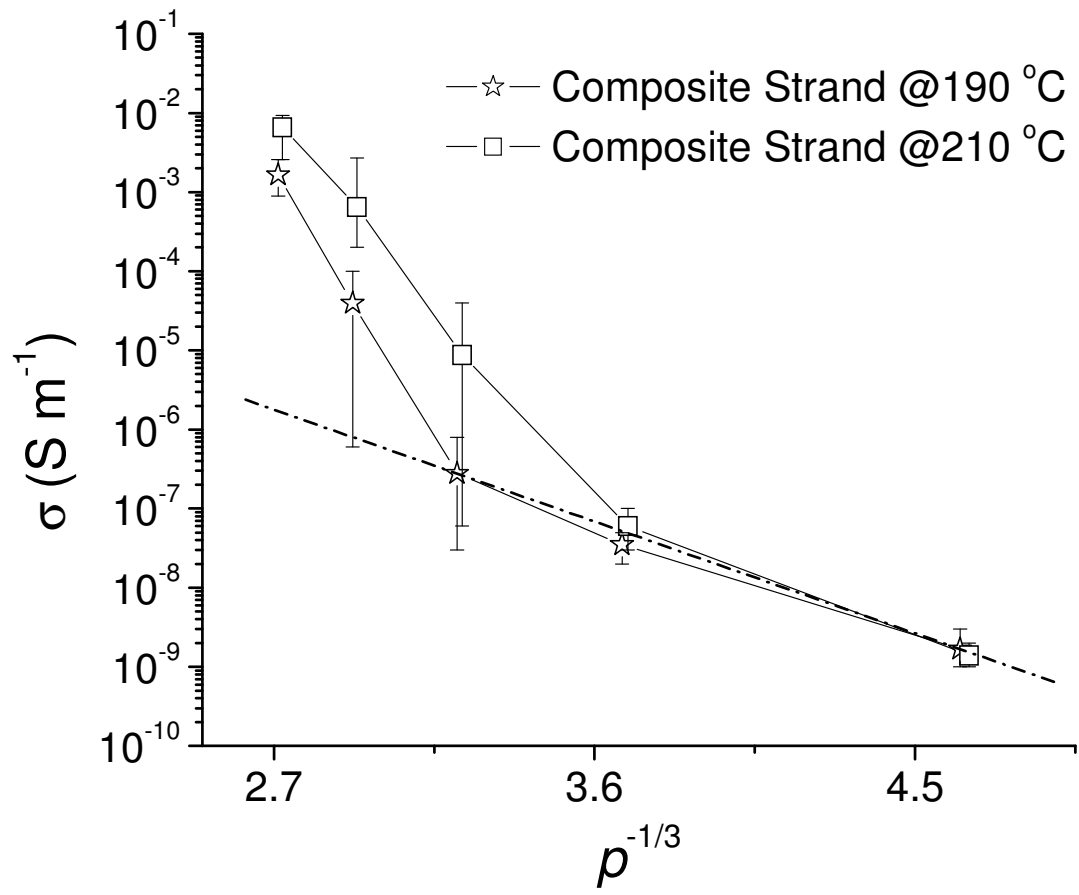
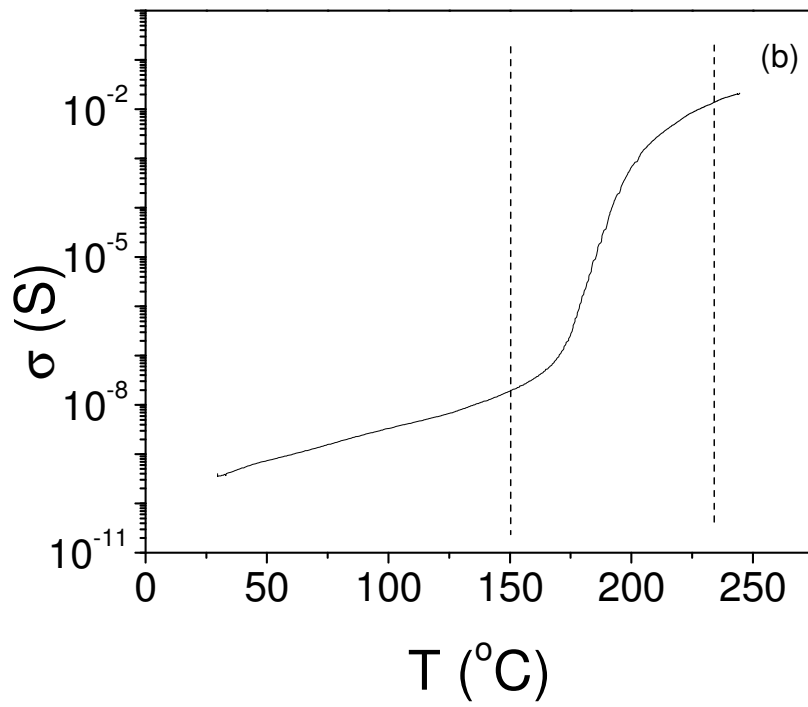
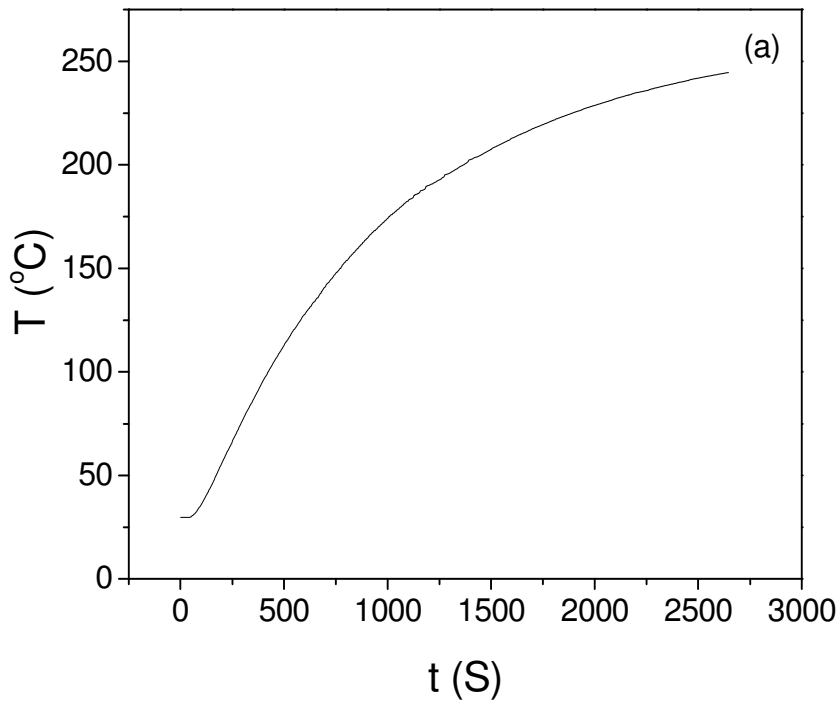


Figure 4



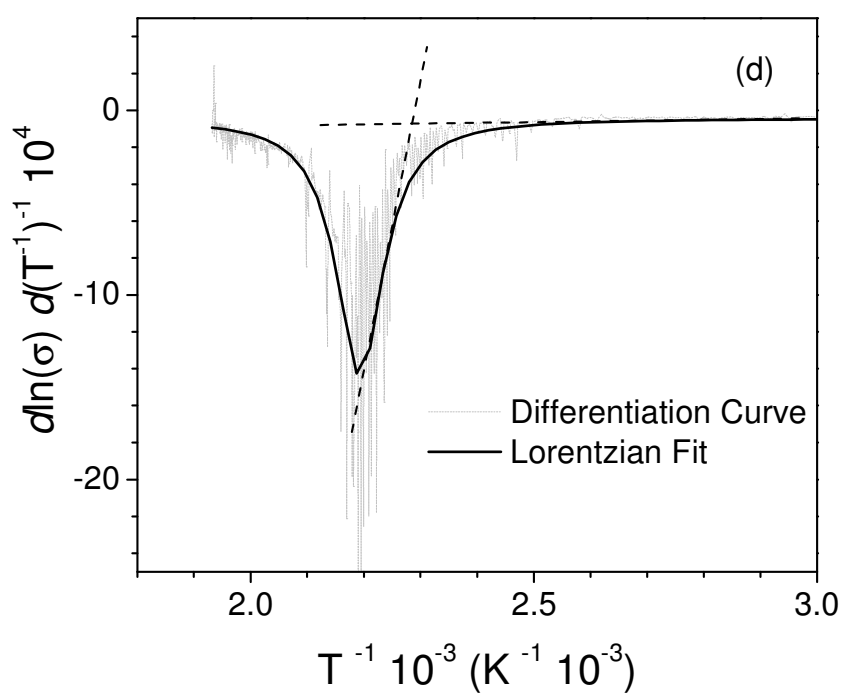
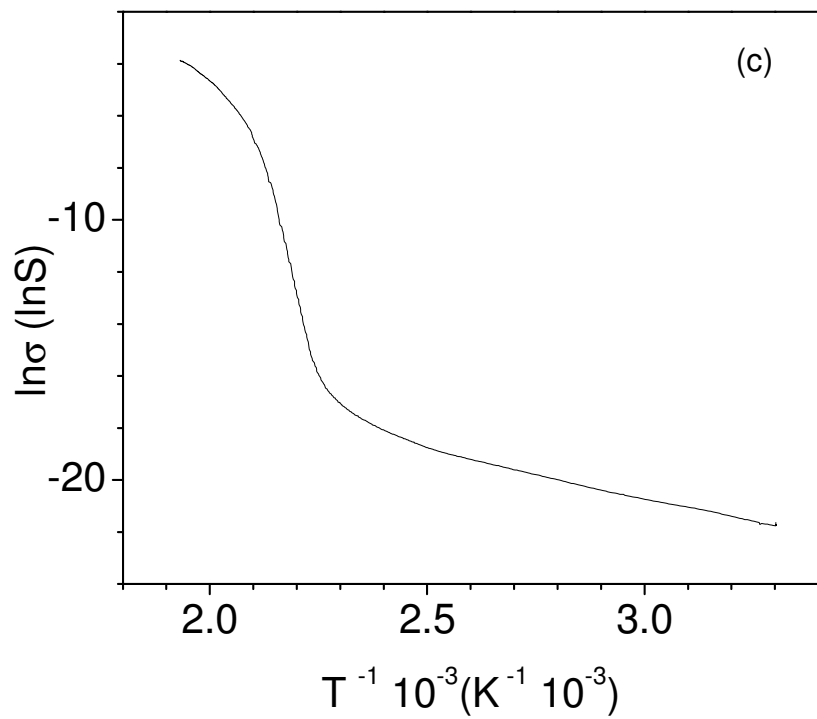


Figure 5

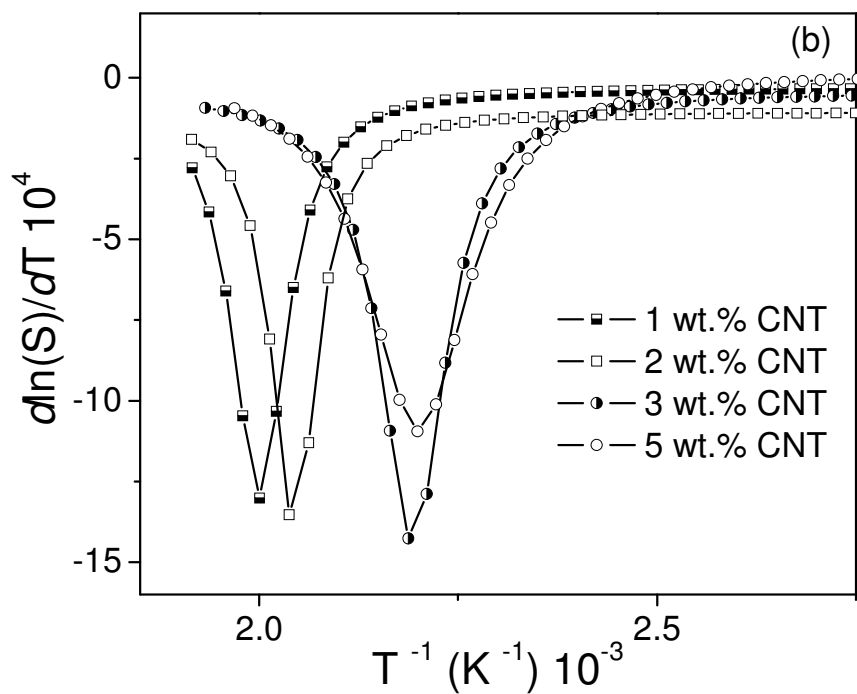
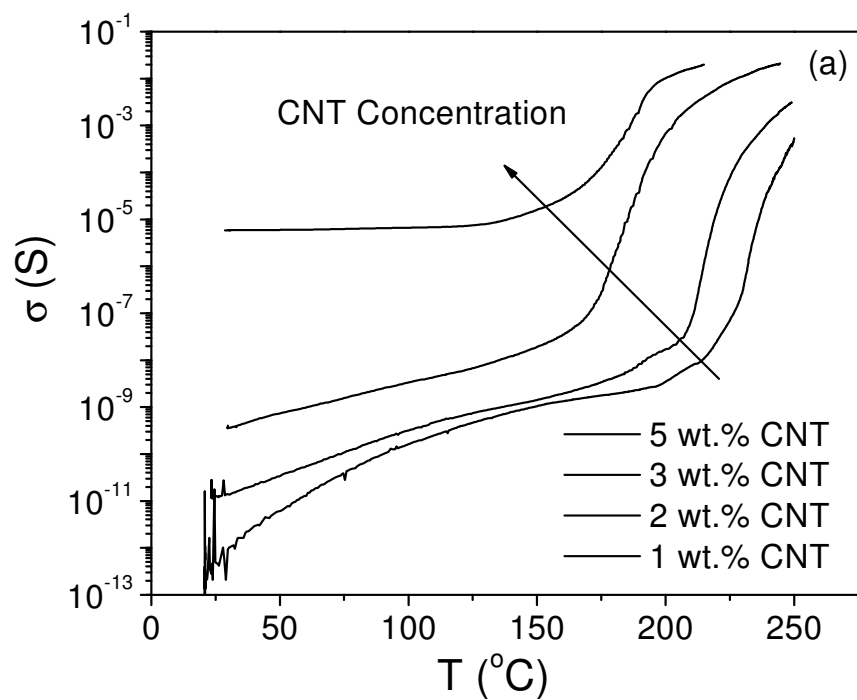


Figure 6

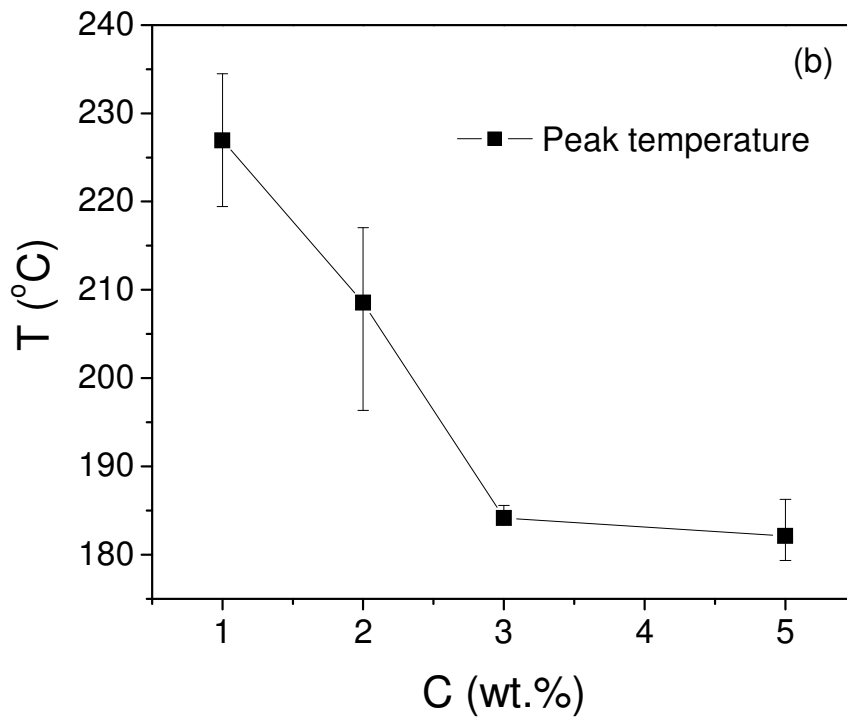
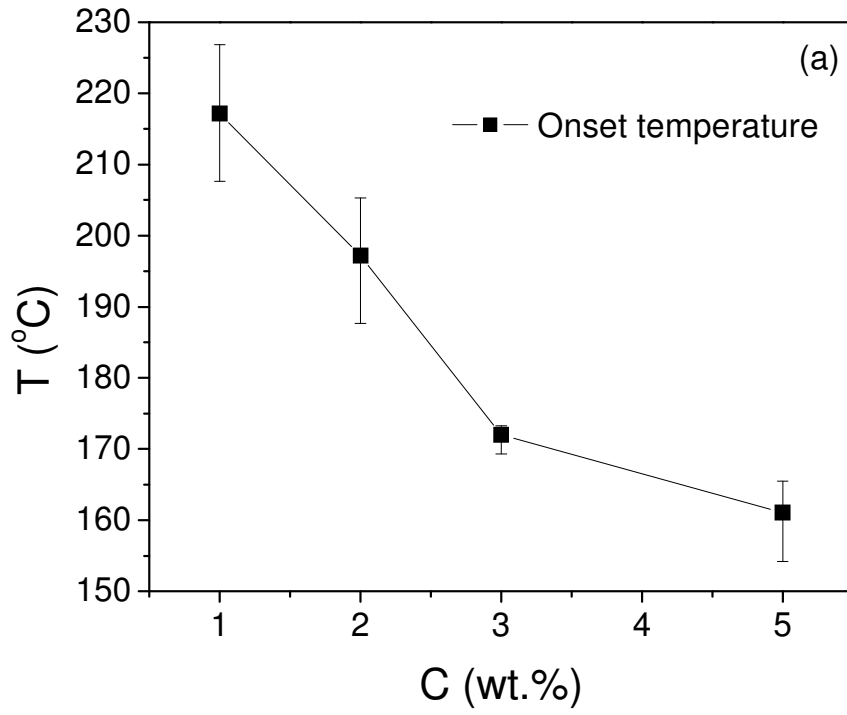


Figure Caption

Figure 1

Schematic illustration of the conductivity temperature dependence measurement. In the test device: black part, the CNT composite; white part, the silver epoxy electrode; grey part, Kapton film sealed with high temperature epoxy; black line, wires for connection with electrical measurement.

Figure 2

Conductivity versus CNT weight concentration for the hot-pressed film and strands extruded at 190 °C and 210 °C. Only the results for the film shows a percolation behaviour.

Figure 3

Logarithmic plot of conductivity of the extruded strands versus $p^{-1/3}$, a linear relationship can be consider as a first indication of a tunnelling transport mechanism.

Figure 4

The conductivity temperature dependence results of 3 wt.% CNT composite, as an example. (a) the heating profile of the temperature scan; (b) the logarithmic plot of conductivity versus temperature; (c) the plot of $\ln\sigma$ versus T^{-1} , where T is the absolute temperature. A linear regime was shown before the transition, indicating a hopping transport mechanism. (d) the grey line, differentiation of (c), solid black line, a Lorentzian fit of the differentiation.

Figure 5

(a) The logarithmic plot of conductivity versus temperature of CNT composite with different CNT loadings. A transition point is shown in each curve. (b) The Lorentzian fit of the differentiation curve of composite with different CNT concentration, where an accurate onset and peak temperature can be subtracted from each curve.

Figure 6

(a) Onset temperature versus CNT weight concentration. (b) Peak temperature versus CNT weight concentration.