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Electrical conductivity and self-temperature-control heating properties of carbon nanotubes filled polyethylene films

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ABSTRACT

Electrical properties of polyethylene and carbon nanotube composite films were investigated, when the composite films were set in heating box or under electric field at constant voltage. The composite films were prepared by gelation/crystallization from dilute solution. The mixture of ultra-high molecular weight polyethylene (UHMWPE) and branched low molecular weight polyethylene (LMWPE) was used as matrix, and multi-walled carbon nanotubes (MWNTs) were used as fillers. The filler content was chosen to be 10 wt% (ca. 5.25 vol%) which is a relatively higher loading than the percolation threshold to ensure to act as heating element in plane heater of composite film. The focus was concentrated on the temperature dependences of electric conductivity by external heating and by exothermic effect concerning self-temperature-control heating properties which were measured for the three kinds of UHMWPE–LMWPE composites with the same content of MWNTs in the composites. When a certain voltage was applied to the composite, the surface temperature of film reaches the equilibrium value within less than 100 s. The maximum surface temperature as the equilibrium state of the resultant composite film can be easily controlled by adjusting the composite ratio represented as UHMWPE/LMWPE. The high efficiency of heating and wide adjustability of stable temperature suggested its good application in high efficient plane heater.

1. Introduction

The development of polymers with high electrical conductivity has opened up the possibility of new applications for polymers. Conducting polymers can be obtained in two ways: by producing a polymer that is intrinsically conducting or can be made so by doping [1,2] and by loading an electrically insulating matrix with conductive fillers [3–13]. Carbon black [3–6], carbon fiber [7–9], graphite [10] and carbon nanotube [11–13] are commonly used as a component of conductive and reinforcement polymer composites. Conductive polymer composites can act as plane heater with a larger heating area as well as higher thermal efficiency compared with nichrome wire heater [10,14–17]. At the same time, polymer's positive temperature coefficient (PTC) of conductivity of the polymer composite ensures the safety and practice.

In these years, the composites of carbon nanotube and insulating polymer have been widely investigated in terms of their low percolation threshold for conductive material and reinforced polymeric composite and their applications as temperature or current sensors, flooring materials to dissipate static electric charge, antistatic coating and electromagnetic radiation shielding. But to the best of our knowledge, no experimental work has been reported in the literature on the self-heating properties of polymer–carbon nanotube composites and its application as plane heater. In this research, we approached to fabricate thin polyethylene and multi-walled carbon nanotubes (MWNTs) composite film as plane heater. To improve the thermal stability at high temperature and a uniform dispersion of MWNTs in polyethylene matrix, we used ultra-high molecular weight polyethylene (UHMWPE) and/or mixture of UHMWPE and branched low molecular weight polyethylene (LMWPE) as matrix. Dispersion of carbon nanotubes has been a critical issue for producing polymeric composite due to its high aspect ratio and entanglement and easy aggregating. It is impossible for fabricating uniform UHMWPE–MWNTs blend films using conventional melting and mixing method due to the extremely high viscosity of UHMWPE. Our previous research proved that the gelation technology is very effective to make the carbon nanotubes dispersed in UHMWPE solution using decalin as solvent [18]. We also produced a series of

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polyethylene composite films filled with several kinds of carbon fillers including carbon black, short carbon fibers and carbon nanotubes using the mixture of UHMWPE and LMWPE as matrix prepared by gelation/crystallization techniques [19–23]. Through the results from the studies on these kinds of composites, we can find the relatively easy to disperse the fillers into the matrix and get a uniform dispersed composite using gelation/crystallization technology. At the same time UHMWPE with the high viscosity and disentangled fibrils is helpful for fabricating composite films with good form stability at high temperature.

This paper is focused on research of the electrical conductivity of carbon nanotubes filled polyethylene gel composites film and the application possibility of this kind materials as self-temperature-control heating properties as plane heater.

2. Experimental section

The samples were prepared by using UHMWPE (Hercules 19000/90189) with an average viscosity molecular weight of 6.3×10^6, LMWPE (Sumikathene G201) with an average viscosity molecular weight of 4.13×10^4, and multi-walled carbon nanotubes (MWNTs) (supplied by Nikkiso Co. Ltd.). The average filament diameter of MWNT is about 30 nm and the average length is about 10–20 μm. The SEM image of the nanotubes used here is shown in Fig. 1.

The UHMWPE/LMWPE blend ratios chosen were 1/0, 1/1 and 1/2 by weight. The specimens were termed as 1/0, 1/1 and 1/2 composites. The concentration of MWNTs was fixed to 10 wt% (corresponding to be 5.25 vol%) which is much higher than the percolation threshold reported [12,13].

Decalin was used as solvent. MWNTs were firstly sonicated for 10 h in decalin solution. LMWPE and UHMWPE were added into the solution containing MWNTs and the mixture was well blended at 150 °C under strongly mechanical stirring and the well-blended polymer/solvent mixture kept at 150 °C for 30 min under nitrogen. The concentration of UHMWPE against decalin was fixed at 0.5 g/100 ml. The detailed preparation method can be found in the previous article [18]. The dried gel film was used for analysis after being pressed at 210 °C for 10 min under 20 MPa pressure. The thickness of samples is ca. 0.1–0.3 mm.

The thermal property of the sample was measured at a heating rate of 5 °C/min by differential scanning calorimetry (DSC 6200, SII Exstar 6000) from 20 to 160 °C in N_2 atmosphere. The weight of sample piece was ca. 5 mg.

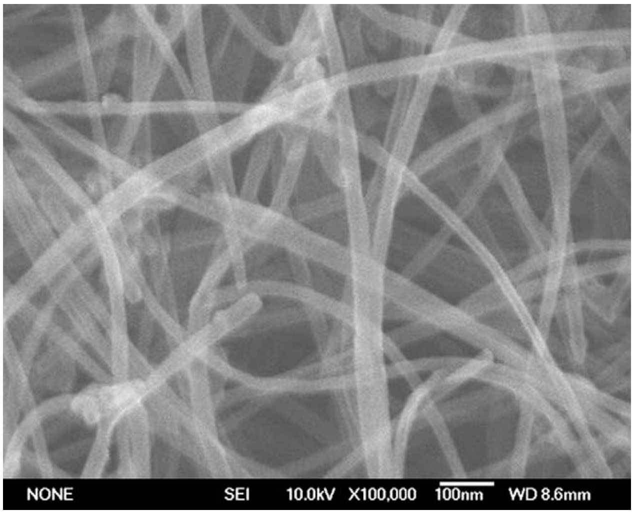

Fig. 1. SEM image of MWNTs.

The electrical conductivity of composite films and its self-heating properties were estimated with two homemade measurement systems as shown in Fig. 2. The electrical conductivity was measured by resistance measuring device (HR-100, Iwamoto Seisakusho) using a digital multimeter (Advantest R6441A Digital Multimeter). To prepare test specimens, the composite material was cut into strips of 20 mm in length and 10 mm in width. The specimen length clamped between copper metal jaws was 5 mm at each end. The measurement system is shown in Fig. 2(a). The thermoelectric properties of composite films were measured on computer-controlled equipment by gripping the samples between two copper jaws. The measuring system was designed as shown in Fig. 2(b). The test piece was cut from the films with 40 mm in length and 10 mm in width. The sample length clamped between the copper jaws was 20 mm. A fine thermocouple was attached on the center of sample surface. Time dependence of surface temperature and electric current of test pieces were detected under different applied voltages by using above system. The electrical resistivity of those composites with resistivity lower than 10^2 Ω cm was detected by four probes measuring system (Loresta-GP MCP-T600, Mitsubishi Chemical Co.).

3. Results and discussion

Fig. 3 shows DSC curves of the composite films with or without fillers. Three columns correspond to three series of samples which are the original (dry gel) UHMWPE–LMWPE composites without MWNTs, the original UHMWPE–LMWPE composite with 10 wt% MWNTs and the composite films pressed at 210 °C and then quenched to room temperature respectively. For the blend films with UHMWPE–LMWPE as matrix, two endothermic peaks can be observed for the samples with and without MWNTs. The peaks at higher and lower temperature sides are assigned with the melting points of UHMWPE and LMWPE crystallites, respectively, indicating that UHMWPE and LMWPE chains crystallize independently and the phase separation occur. In column (a), the endothermic peak of UHMWPE for the composite without MWNT shifts to higher temperature and becomes smaller with increasing LMWPE content. Comparing column (b) with column (a), there is no obvious deference for thermal behavior between the composite films. Column (c) reveals that the heat of fusion and melting of polyethylene are influenced by pressing at 210 °C, and then the melting point of UHMWPE crystallite shifts to lower temperature and the endothermic peak becomes smaller. The detailed results were estimated by the DSC curves, which are summarized in Table 1. As listed in Table 1, melting point (T_m), heat of fusion (Δh_f), and crystallinity (X_c) of UHMWPE and LWMPE crystallite are listed separately based on the contribution of each component. Each heat of fusion is calculated by the relationship: $(\Delta h_f) =$ observed value/content of UHMWPE (or LMWPE) based on individual peak concerning LMWPE and UHMWPE crystallites. X_c is calculated as $\Delta h_f/(\Delta h_{f\text{-}PE})$, by assuming the heat of fusion for 100% crystalline polyethylene ($\Delta h_{f\text{-}PE}$) to be 280.5 J/g [24].

It is noticed that the crystallinity of UHMWPE slightly decreased due to the addition of LWMPE, while that of LMWPE increased. This suggests that the stability of UHMWPE crystallites becomes worse with increasing LMWPE content. But the crystallinities of UHMWPE and LMWPE components in the blend samples increase slightly rather than decrease by filling MWNTs in the matrix indicating that the addition of MWNTs does not influence the growth of UHMWPE and LMWPE crystallites during slow evaporation of the solvent. However, the crystallinities of both components of UHMWPE and

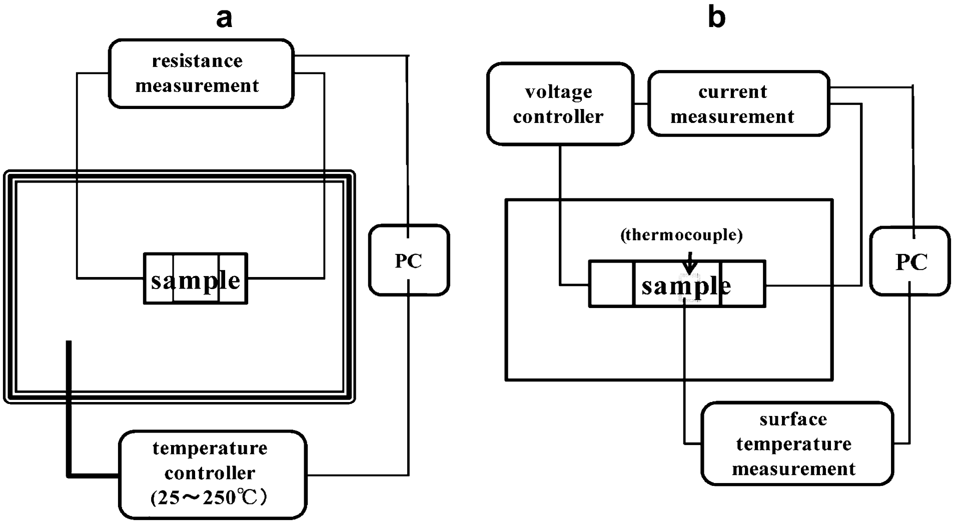

Fig. 2. Measurement system of electrical conductivity (a) and self-heating properties (b) of composite films.

LMWPE decreased significantly for all the samples pressed at high temperature and subsequently quenched at room temperature. The heat-treatment is thought to provide a drastic increase in the amorphous region under the heat pressing and cooling presses. In spite of independent crystallization of LMWPE and UHMWPE chains, the molecular chains of LMWPE and UHMWPE are thought to entangle each other in amorphous region.

The electrical resistance was measured for the pressed 1/0, 1/1 and 1/2 composites with 10 wt% MWNT content by four probes measurement at first. The electrical conductivities calculated for the 1/0, 1/1 and 1/2 composites are 0.107, 0.015 and 0.007 s/cm, respectively. The temperature dependence of electrical conductivity was then measured with two terminal method using the measuring system as shown in Fig. 1(a), in which the composite was heated at a heating rate of 5 °C/min. The weak voltage (or current 0.1–1 mA) was applied in order to avoid the influence of self-heating of the samples. Fig. 4 shows the results of the temperature dependence of electrical conductivity for 1/0, 1/1 and 1/2 samples measured in the range of 25–220 °C. The measurements were carried out for three cycles by using the same specimen. The common phenomenon for three samples observed in the first run is that the conductivity increases slowly and has a small jump-down near to the melting point of dry gel matrix, and then increases again till to the 220 °C. The electrical conductivity under the second and third runs becomes more stable compared with the first heating. For the 1/2 composite, the small jump-down occurred at temperature range (101–102 °C) close to the melting points of melt-crystallized LMWPE matrix after the first run, while, for the 1/1 composite, the small jump-down occurred at ca. 130 °C, indicating the melting of the melt-crystallized UHMWPE matrix.

The electrical conductivity obtained slightly decreased after the jump-down and tended to increase again. The jump-down is surely associated with the thermal expansion of polymer during the melting of crystallites. The thermal expansion theory is usually used for explaining the PTC effect of polymer-conductive filler composite. However, in the present composite systems, the thermal expansion of polyethylene only led to a slight increase in electrical resistivity but not enough to break the conductive networks formed by MWNTs, since the MWNT content 10 wt% is much higher than the percolation threshold [12]. In the temperature range beyond the melting points of both of UHMWPE and LMWPE components, the conductivity increases further, and shows

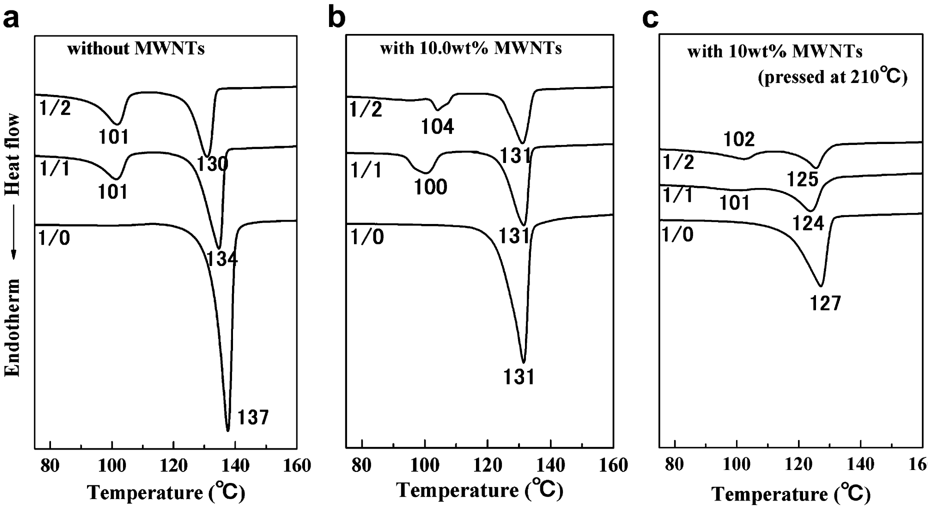

Fig. 3. DSC curves of UHMWPE–LMWPE–MWNT composite films.

Table 1
Analysis of DSC profiles for the UHMWPE–LMWPE–MWNT composite films.

	UHMWPE/ LMWPE	LMWPE			UHMWPE		
		T_m(°C)	Δh_f(J/g)	X_c (%)	T_m(°C)	Δh_f(J/g)	X_c (%)
MWNTs = 0%	1/0	–	–	–	137	222.0	79.1
	1/1	101	38.0	27.1	134	103.0	73.4
	1/2	101	60.2	32.2	130	65.5	70.1
MWNTs = 10 wt%	1/0	–	–	–	131	20.3	80.4
	1/1	100	28.7	22.7	131	97.4	77.2
	1/2	104	39.1	22.8	131	60.6	72.5
MWNTs = 10 wt% pressed	1/0	–	–	–	127	144.0	57.0
	1/1	101	5.8	4.7	124	47.8	37.9
	1/2	102	16.7	9.7	125	26.4	31.6

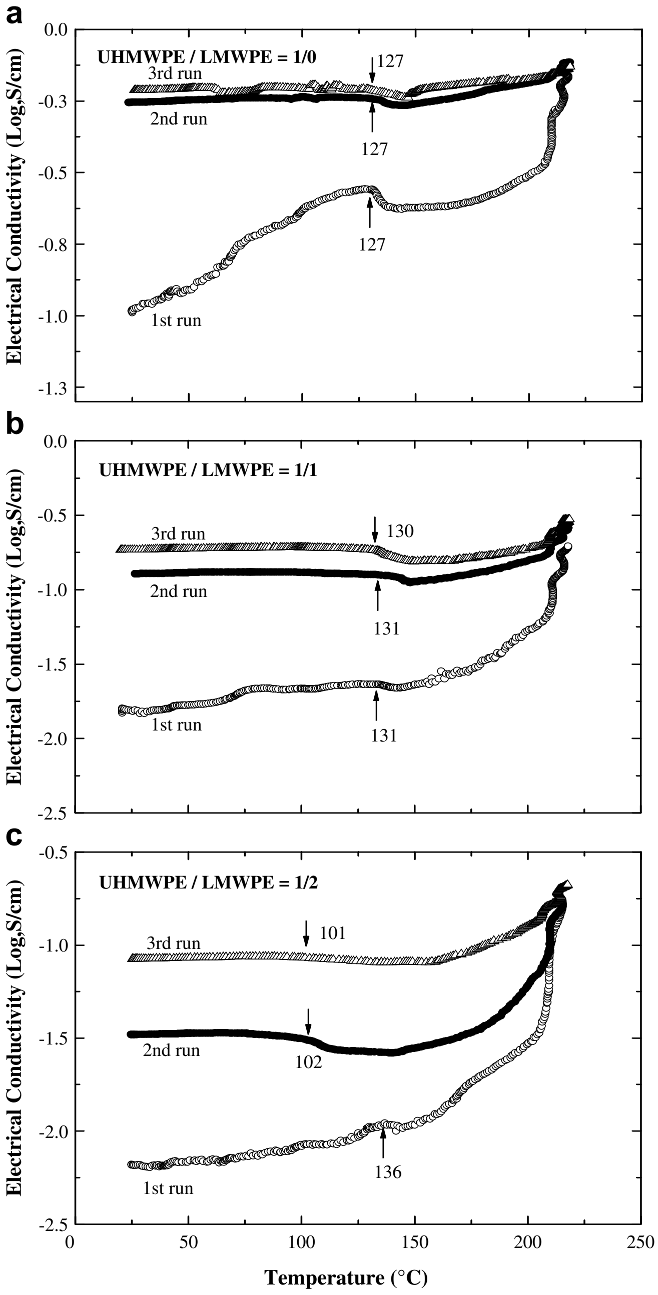

Fig. 4. Temperature dependence of electrical conductivities measured under heating press from 25 to 220 °C. A sample was measured for 3 heating cycles.

a drastic increase at temperature near to 200 °C. The higher the UHMWPE content is, the less the increase in conductivity at elevated temperature. Such thermal behavior of the UHMWPE–LMWPE–MWNT composite is considered to be due to the fact that the considerable mobility of UHMWPE and LMWPE chains beyond the melting point causes the active movement and the rearrangement of MWNTs, and then provides more contacting points among MWNTs. However the thermal expansion of matrix is not significant enough to cause the separation of the contacted MWNTs due to the extremely high viscosity of UHMWPE, so the conductive paths for charge transportation are maintained. Hence it is evident that the hopping conduction surely influences the conductivity at high temperature. The temperature dependence of conductivity for the composite in the second and third cycle showed a similar behavior as the first run, but the values became more stable and high level compared with the first run indicating that the connection between MWNTs becomes tighter after the first heating cycle. This behavior can be explained through SEM images observed for the original sample and the compared sample after being detected the electrical resistivity. Fig. 5 shows an example of SEM images observed for the cross-section of 1/2 samples cracked under N_2 liquid, in which the pictures (a) and (b) are original pressed film and (c) and (d) are the samples after three heating cycles, (b) and (d) are the magnification of (a) and (c) respectively. We can see that the MWNTs entangled each other or form entanglements with polyethylene fibrils, and most of nanotubes are covered by a thick polymer layer in the original state. On the other hand, photos (c) and (d) indicated that the carbon nanotubes entangle each other and percolate the polymer matrix and then the polymer layers on the surfaces of carbon nanotubes are very thin after heating.

The heating under being clamped between two jams results to different structure (as (c) and (d)) compared to the original sample in (a) and (b) which the whole sample was heat pressed at 210 °C and then quenching to room temperature. This morphology shown in photos (c) and (d) ensures more contact points of nanotubes and thus high conductivity in the second and third runs, and the conductivity becomes more and more stable as heating cycle increase. A similar phenomenon was confirmed from our previous papers where the pure UHMWPE was used as matrix [12,18,22].

Based on the results in Fig. 4, the conductivity values of samples in the original state at room temperature or those of samples after cooling down to the room temperature are depicted in Fig. 6. We can notice that the conductivity at room temperature becomes lower as LMWPE content increases. The same tendency is also confirmed for the sample after two and three heating cycles. However, this phenomenon is different for other LMWPE–UHMWPE blends with carbon black and short carbon fibers as fillers. In those cases [9,19,23], the conductivity of LMWPE–UHMWPE-filler composites containing the same content of conductive fillers increased with increasing LWMPE content. It suggests that those conductive fillers (carbon black and short carbon fibers) prefer to be located in the LWMPE domains. As increasing LMWPE content, LWMPE formed continuous phase and the fillers tended to form conductive chains easily in LMWPE domains. Different from the carbon black or short carbon fibers, the MWNTs form network structures and then the location selectivity and the mobility in matrix are greatly restricted compared with other small particles or fillers with a low aspect ratio, even though the distribution of MWNTs is somewhat non-uniform in UHMWPE and LMWPE domains. After the heat treatment, the conductivities of all the samples increased and the influence of the blend ratio became inconspicuous, but the conductivity values still decrease with increasing LWMPE content.

As shown in Fig. 5(a) and (b), the networks of MWNTs are relatively uniformly dispersed in the matrix and they formed some

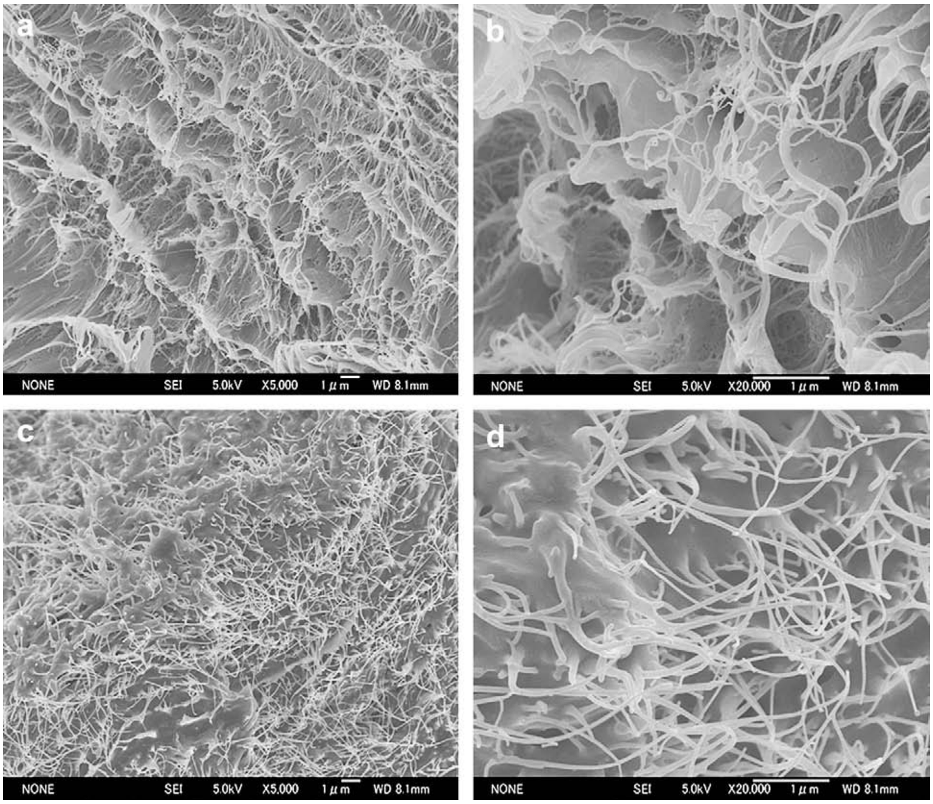

Fig. 5. SEM images of the cross-section of composite film with UHMWPE/LMWPE = 1/2 and the 10 wt% MWNTs, (a) and (b) are for original pressed film, (c) and (d) are for the film after 3 heating cycles.

entanglements each other or with UHMWPE fibrils. In the composite, the UHMWPE and LMWPE domains couldn't be differentiated under SEM. Hence LMWPE with low viscosity is thought to flow into the networks of MWNTs and the entangled structure of MWNTs and UHMWPE fibrils during pressing and crystallization, and form small crystal domain which couldn't be observed under SEM but confirmed by DSC. The preferential dispersion of MWNTs in LMWPE domains was not observed, which was different from other multi-phase polymer and conductive filler composites [19,23,25].

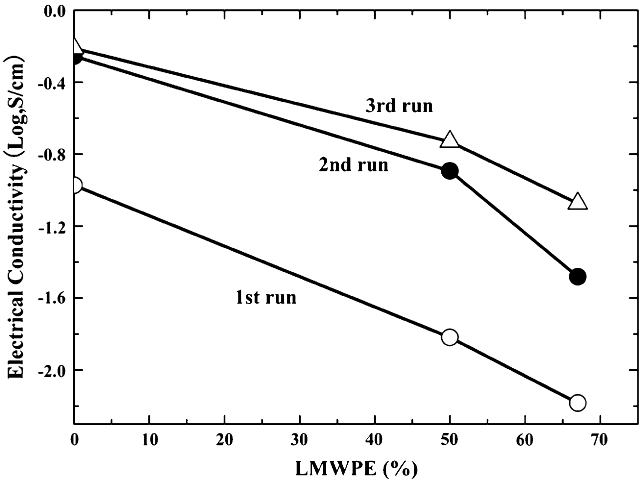

Fig. 6. Electrical conductivities of composite films at room temperature at different cycles.

Many researches have dealt with the PTC effects and the percolation theory of carbon nanotube-filled polymers. A lot of efforts have been done to make a uniform dispersion of carbon nanotubes in polymers including chemical and physical treatments on carbon nanotubes. These efforts aimed to lower load of carbon nanotubes and get a high electrical conductivity or high mechanical properties. A large number of experimental results reveal that the carbon nanotubes have an absolutely low percolation threshold compared with carbon black and carbon fiber or graphite carbon [26–29]. The percolation threshold could be less than 0.1 vol%. The limit value of percolation threshold has not been obtained till now, since it is almost impossible to disperse the carbon nanotubes in matrix perfectly with total disentanglement of the bundles or networks of nanotubes.

To our best knowledge, there is no report on the self-control heating properties of carbon nanotube-filled polymer composites. Here we firstly prepared the thin composite gel films with a high load of MWNT (10 wt%) and investigated the self-heating properties of polyethylene–MWNT composite films.

At first, the investigation was done for the change of current and surface temperature under different applied voltages with the measurement system as shown in Fig. 2(b). Fig. 7 shows voltage dependence of the current and surface temperature of composite films with the different composite ratio of UHMWPE/LMWPE. The applied voltage changed from 1 V to 30 V with the interval of 1 V, and the sample was measured for 150 s at one step. From Fig. 7(a), it is seen that the current (I)–voltage (V) exhibits a linear correlation and shows a positive slope, indicating Ohmic behavior in the whole applied voltage range for the 1/2 composite. But for the 1/0 and 1/1 composite, the I–V curves show unusual Ohmic behavior in the high-applied voltage range, especially for the 1/0 samples. The electric current flows through the direct contact of carbon

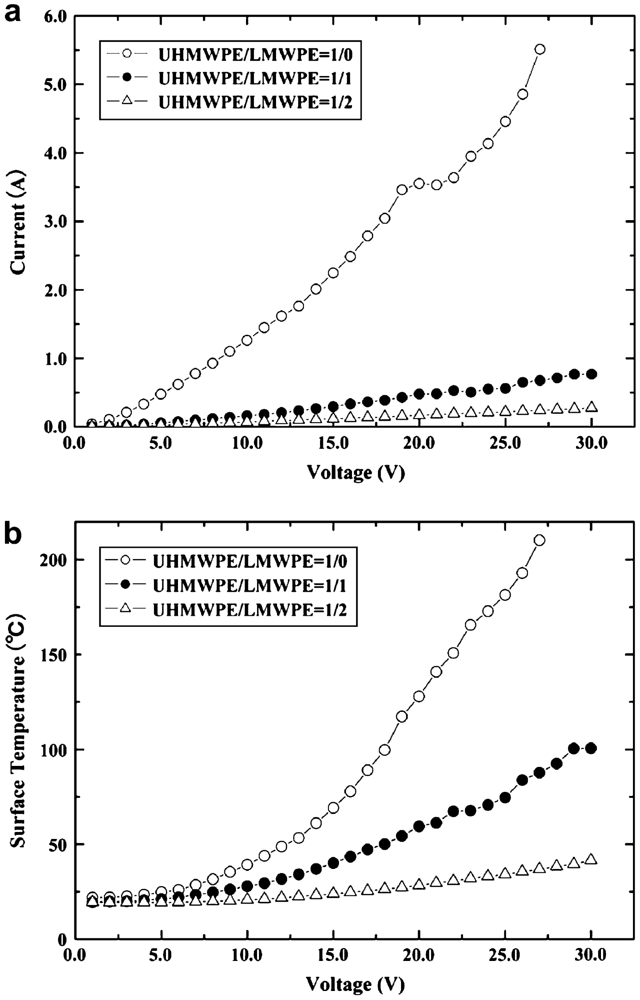

Fig. 7. The change of current and surface temperature under different supplied voltages.

nanotube networks under low supplied voltage. With increasing the supplied voltage, the current and temperature increase obviously during Joule heating. The Joule heating allows the execution of hopping, which led to an increasingly effective dimensionality and narrow width of the gaps among the conductive particles, thus the *I–V* curves deviate from the Ohmic behavior. The plateau in *I-V* curve of 1/0 sample is maybe due to that the temperature in the range of 18–21 V is near to the melting point of the matrix (127 °C). At the further increase in supplied voltage, melting of matrix surely influences the structure of the composite film and the slight movement and rearrangement of MWNT may occur. And this leads to the gap among the conductive particle becoming narrow and network structure becoming tight and electric current and temperature increase significantly.

From the surface temperature dependence on the supplied voltage as shown in Fig. 7(b), it is seen that at low supplied voltage ($V < 5$ V), the surface temperature was almost the same without any remarkable change. And then the surface temperature of films increases with increasing voltage. Interestingly, the temperature strongly depends upon the composition of matrix when the MWNTs content is the same. The temperature for the 1/0 composite is much higher than those of other two 1/1 and 1/2 composites, when the same voltage is supplied. For the 1/0 composition, the sample shape did not change macroscopically at the temperatures even beyond 200 °C. Such phenomenon as discussed before is due to the high viscosity of UHMWPE ensuring the thermal stability of the composite film.

For practical reasons, we focused on the temperature–time behavior as a function of applied power for the composite films under a relative high voltage (>5 V) based on the results as shown in Fig. 7. Fig. 8 shows time dependence of surface temperature (*T–t* curve) of composite films under different supplied voltages. The measurements were done for the three composites containing 10 wt% MWNTs. The supplied voltage was changed from 10 V to 30 V with a step of 5 V. Each sample was tested for 300 s at one step. The sample was cooled down to room temperature after one step of measurement to ensure that the starting point is at room temperature. The temperature was

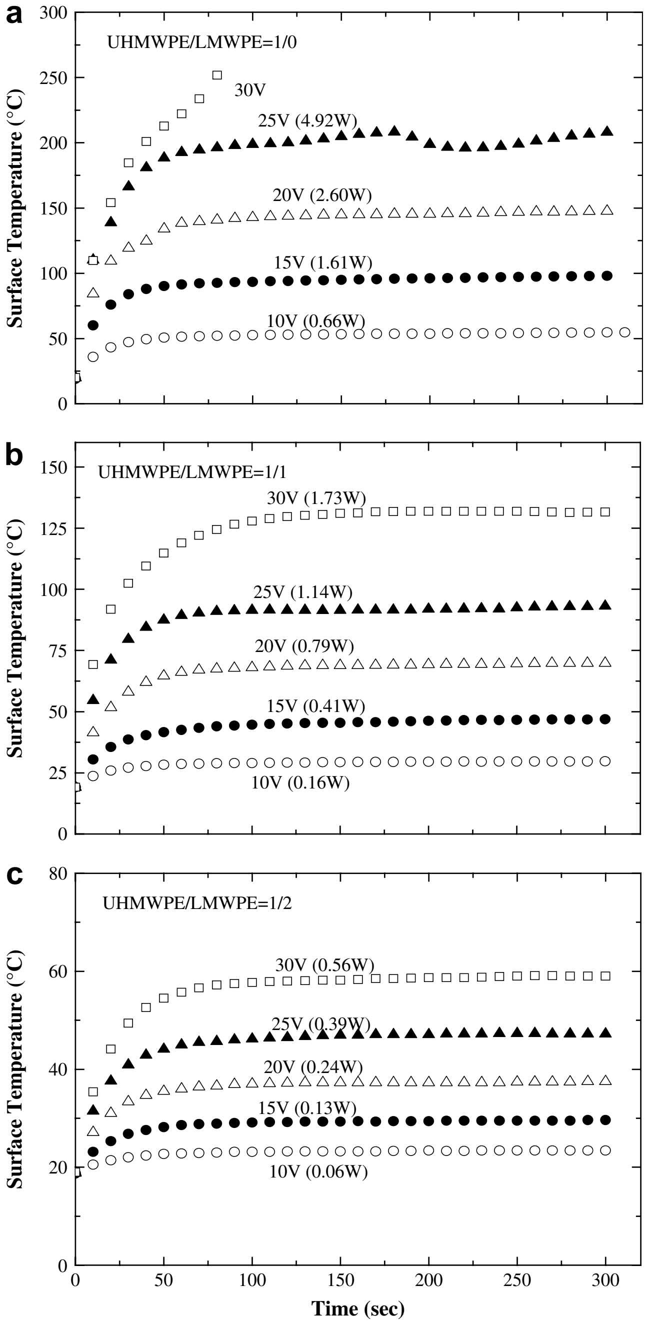

Fig. 8. Time dependence of surface temperature of composite films under different supplied voltage.

detected by the thermocouple attached on the surface at the center of composite films. We can notice that the center temperature of the films abruptly raised and tended to level off within less than 100 s.

Here it should be noted that the stable temperature increases by Joule heating greatly depends on the composite ratio of UHMWPE/LMWPE containing the same content of MWNTs. The leveling-off temperature becomes higher with increasing UHMWPE content at the same applied voltage. Compared Fig. 8(a) with Table 1, the stable surface temperature of films is found to be much higher than the melting point of UHMWPE (127 °C) when the applied voltage is higher than 20 V for the 1/0 composite with 10 wt% MWNTs. The extremely high supplied voltage creates a large amount of Joule heating and provides the surface temperature of film very high even higher than 200 °C. The same phenomenon also can be observed for the 1/1 composite, as shown in Fig. 8(b). The stable surface temperature is higher than both of melting points of LMWPE (101 °C) and UHMWPE (124 °C) when the applied voltage was 30 V. Comparing the three composites, it is clear that the magnitude of maximum temperature for the 1/0 composite is higher than the other two composites, the 1/1 and 1/2 composites, under the same applied voltage. This observation clarifies that the UHMWPE improves the tidiness of carbon nanotube network structure and promotes the heating efficiency of composite film as plane heater. The quick heating and wide adjustability of temperature suggested its good application to high efficient plane heater. But exceeded high temperature must lead to disruption of the film structure due to the partly melting of polyethylene matrix when the time is long enough. For a practical application as plane heater, of course, the temperature should be controlled to be lower than the melting points of the matrix.

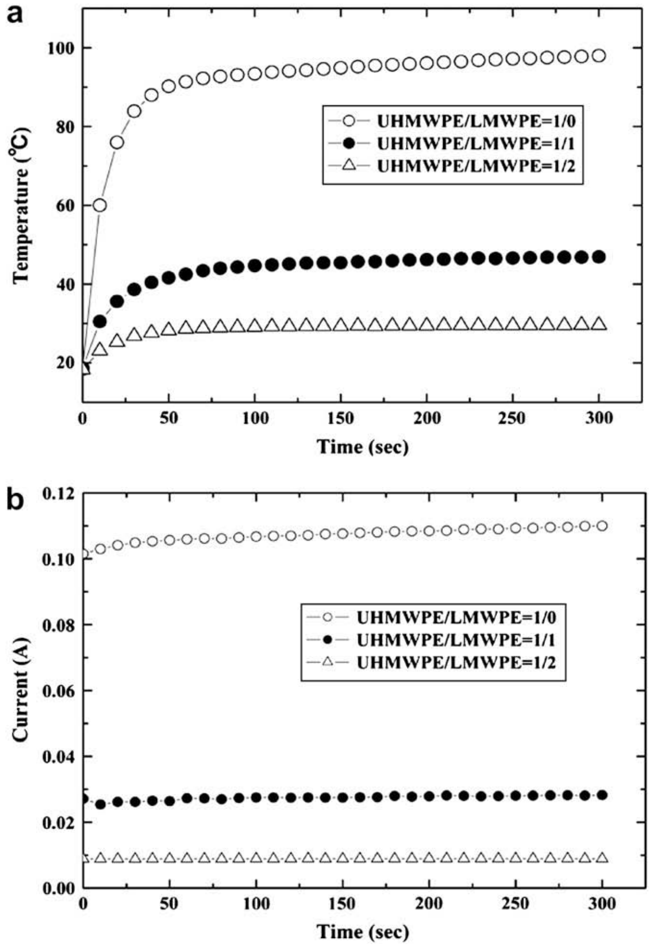

Fig. 9. Surface temperature and current dependence on time after switch-on at the supplied voltage of 15 V.

Table 2
Characteristic growth time constant T_{gs} at different applied voltage.

UHMWPE/LMWPE	Applied Voltage				
	10 V	15 V	20 V	25 V	30 V
1/0	13.83	12.61	13.34	15.75	-
1/1	14.16	16.96	16.87	14.86	15.96
1/2	15.71	16.03	15.44	15.47	17.97

To pursue more detailed analysis for the characteristic thermal properties, we introduce two parameters, characteristic time growth τ_g and efficiency of heat transfer h_r for the composite films. Fig. 9(a) and (b) presents temperature and current dependences on time, respectively, after switching-on at the applied voltage of 15 V. The results at 15 V in column (a) were quoted in Fig. 8 to make clear differences among *T*–*t* curves for the three kinds of composites. Judging from Fig. 8 and Fig. 9(a), the *T*–*t* curves can be divided into two stages: stage I as the temperature growth stage and stage II as the equilibrium stage (i.e. heat gain by working power is equal to heat loss by radiation and convection). In stage I, the characteristic growth time constant (τ_g) during applied power (i.e. temperature growth) calculated at $t = \tau_g$, can be expressed by an exponentially growth function as follows [30]:

$$\left(\frac{T(t) - T_r}{T_u - T_r}\right) = 1 - e^{\frac{-t}{\tau_g}} \tag{1}$$

where T_r and T_u are the initial and ultimate temperature, respectively. By fitting the data in the first stage of *T*–*t* curves ($t = 0$–70 s) in Fig. 9 with formula (1), the τ_g was calculated and listed in Table 2. τ_g is in the range of 12–18 s indicating very quick growth speed. The value of τ_g for the 1/1 and 1/2 composites show a little bit longer τ_g than that for the 1/0 composite because of the lower conductivity. The deviation of the values for the fitting results at high supplied voltage is attributed to the radiation effect of self-heating samples at high temperature.

According to the conservation law of energy, the amount of heat transfer by radiation and convection (h_r) in stage II is given by:

$$h_r = \frac{I_c V_o}{T_m - T_0} \tag{2}$$

where V_0 is the initial applied voltage and I_c is the steady state current. The example *I*–*t* curves in Fig. 9(b) indicate that the change in current is very small and almost keeps a constant level. The results of h_r calculated for the three composites with 1/0, 1/1 and 1/2 containing 10 wt% MWNTs at different supplied voltages are listed in Table 3. It can be seen that the h_r decreases as LMWPE content increases, indicating the lower efficiency of heat transfer by effective radiation and convection. It is suggested that the UHMWPE fibrils improve the ordering and architecture of the composite where the composite become denser and more compact and carbon nanotube network structure become tighter, thus it improves the thermal stability and thermal conductivity of the composite.

Table 3
The amount of heat h_r (W/°C) transfer by radiation and convection when the sample is under the equilibrium stage.

UHMWPE/LMWPE	Applied Voltage		
	10 V	15 V	20 V
1/0	0.018	0.020	0.021
1/1	0.015	0.015	0.016
1/2	0.011	0.012	0.013

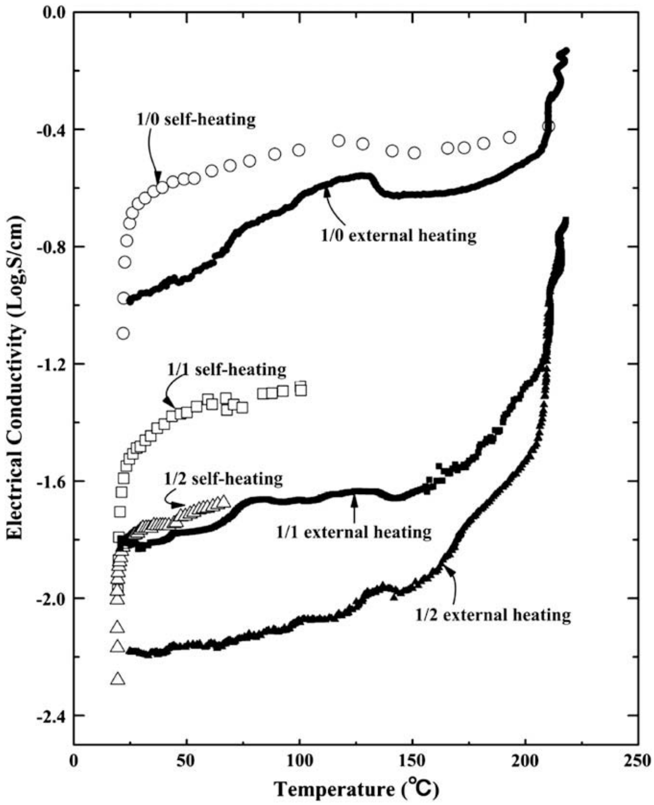

Fig. 10. Difference of electrical conductivity of the same composite films under external heating or self-heating conditions.

Fig. 10 shows temperature dependence of electrical conductivity of the three composite films by two methods, external heating and by self-heating effect under a certain applied electric field as shown in Fig. 2 (a) and (b) respectively. The increase in temperature by the latter method is due to self-heating of the composite itself and the plotted values were obtained by the results from the current–time and surface temperature–time at the applied voltage in the range of 5–25 V for the 1/0 composite and 5–30 V for the 1/1 and 1/2 composites. The measurement was limited by the applied voltage and current of the designed system. In the external heating, the electrical conductivity of sample under ambient changing temperature was obtained from the measurement systems (see Fig. 2(a)), in which the conductivity was calculated as $\sigma = (1/R)(d/A)$, where R is observed resistivity at a certain applied current, d is the distance between two jaws, and A is the cross-sectional area of the sample. The conductivity under self-heating process was calculated according to the following equation: $\sigma = (I/V)(d/A)$, where I is the electric current measured with the system as shown in Fig. 2 (b), V is the supplied voltage. From Fig. 10, the electrical conductivity calculated from self-heating system is higher than the value measured directly under environmental heating system. It is attributed to that the applied current in the external heating measurement in Fig. 2(a) is less than 1 mA and doesn't result to Joule heating. However the self-heating properties measurement in Fig. 2(b), the supplied voltage leads to strong heating effect and promoting the hopping of conductive particles thus result to high conductivity.

4. Conclusions

The UHMWPE–LMWPE–MWNT composite films were prepared by gelation/crystallization from dilute solution. The filler content was 10 wt% of MWNTs. The electrical conductivity, its temperature dependence and self-temperature-control heating properties of gel composite films were strongly dependent upon the UHMWPE/LMWPE ratios, the 1/0, 1/1, and 1/2, when MWNT content in the composites was the same. The temperature dependence of electrical conductivities measured from 25 to 220 °C shows that the conductivity increased slowly and had small jump-down near to the melting point matrix, and then increased again till to the 220 °C. The increase in conductivity of composite was obvious for the first run, but for the second and third run, the temperature dependence was less pronounced. The jump-down associated with the thermal expansion of polymer happened near melting points of matrix ca. 127 °C and ca. 100 °C corresponding to the melting points of UHMWPE and LWMPE respectively. The jump shifted to higher temperature as the heating cycles increased. However the thermal expansion of polyethylene only led to a little increase in electrical resistivity but not enough to break the conductive networks formed by MWNTs because the high content of MWNTs. The extremely high viscosity of UHMWPE at high temperature maintained the stability form of the composites. The higher was the UHMWPE content, the less was the increase in conductivity at elevated temperature.

The self-heating effect for MWNT-filled polyethylene dry gel films was firstly investigated. When a certain voltage was applied to the composite, the surface temperature of film reached the maximum and became stable at time shorter than 100 s. The maximum temperature of the resultant composite film could be controlled by adjusting the UHMWPE/LMWPE ratios in composite. The quick heating and wide adjustability of temperature suggested its good application to high efficient plane heater.

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