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Electrical and mechanical properties of iodine-doped highly elongated ultrahigh molecular weight polyethylene films filled with multiwalled carbon nanotubes

Yuezhen Bin,[1] Qingyun Chen,[1] Kohji Tashiro,[2] and Masaru Matsuo[1,*]
[1]*Graduate School of Humanities and Sciences, Nara Women's University, Nara 630-8263, Japan*
[2]*Department of Future Industry-Oriented Basic Science and Materials, Toyota Technological Institute, Tempaku, Nagoya 468-8511, Japan*

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Highly elongated ultrahigh molecular weight polyethylene (UHMWPE) films filled with multiwalled carbon nanotubes (MWNTs) were prepared by gelation and/or crystallization from solution, and the resultant films were elongated up to 50-fold. The drawn specimens were doped by iodine successfully. Electrical conductivity of the drawn MWNT-UHMWPE films increased sharply with increasing volume fraction of MWNTs beyond the percolation threshold since conductive paths began to form. This was due to a drastic increase of mutual contact possibility of MWNTs. The higher aspect ratio of MWNTs than carbon fibers provided higher t value denoting universal critical exponent by a scaling law, since the percolation threshold of the conductivity against MWNT content was lower than that against carbon fiber content. Iodine doping especially enhanced a drastic increase in electrical conductivity, but the trend of the conductivity versus the volume fraction of MWNTs was hardly affected by iodine doping. The mechanism responsible for the conductivity increase was analyzed mainly by Raman spectroscopy in terms of bond polarization. The doped iodine existed mainly as I_5^-, which formed the charge transfer complex. It may be expected that the I_5^-, provided an increase in charge carriers linked to the MWNTs and could be taken as bridge for the adjacent or nearly MWNTs. Incidentally, the storage modulus of the iodine-doped composite with 4.16 vol % at 20 °C was slightly higher than 25 GPa, and the corresponding electrical conductivity was approximately 0.1 S/cm, which indicated development of materials with high electrical conductivity and high mechanical property.

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I. INTRODUCTION

As technology and science advance, there is an increasing demand for the development of materials with good mechanical and electrical properties. Many efforts have been made to produce carbon nanotubes reinforced polymer composite[1–4] and to improve the properties of polymer.[5–8] The elongation of polymer film has been studied[9,10] in terms of promotion of its mechanical properties by improving degree of molecular chain orientation. On the other hand, iodine doping has been studied to improve the electrical conductivity in several polymers.[11–15] Doped polypropylene (PP) with iodine has been observed to increase its conductivity due to the formation of charge transfer complex.[15] Iodine doping of the ion-implanted polyethylene resulted in the immediate and provided drastic increase of the sheet conductivity by 3–4 orders.[16] Furthermore, carbon nanotubes can be doped by suitable donor or acceptor dopants[17–19] and the doping facilitates the charge transfer between dopants and tubes.

We have prepared the composite films of ultrahigh molecular weight polyethylene (UHMWPE) with multiwalled carbon nanotubes (MWNTs) by gelation and/or crystallization.[20] The resultant MWNTs-UHMWPE film could be elongated up over 100-fold. The coorientation of UHMWPE and MWNTs assured the elongated film possessing high mechanical properties. However, there are no reports, to the best of our knowledge, on the effect of doping on the electrical and mechanical properties of MWNTs and PE composites. In order to improve the electrical conductivity of the composites, the iodine doping was carried out for the highly oriented MWNT-UHMWPE films in this research. With this significant lack of information, this research sheds some light onto this future-promised but presently limited-data area. Structure and property changes induced by iodine doping have been investigated by Raman scattering and differential scanning calorimetry techniques, and measurements of mechanical and electrical properties were carried out.

II. EXPERIMENT

UHMWPE (Hercules 19000/90189) with an average viscosity molecular weight ($\bar{M}_v = 6\,000\,000$) was produced by Mitsui Chemical Co., Ltd. The MWNTs named hyperion graphite fibrils were produced by Hyperion with a diameter (D) of 10–20 nm, a length (L) of 10–20 μm, and an aspect ratio (L/D) of $(1-2)\times 10^3$. The BET surface area was 250 m^2/g, and the di-butylphthalate (DBP) adsorption was 400–500 cm^3/100 g. The density was 2.0 g/cm^3. Figure 1 shows a transmission electron microscope (TEM) image and the Raman spectrum observed with an excitation laser wavelength of 488 nm. Image (a) indicated that the MWNTs possessed high purity and uniform diameter distribution. In Raman spectrum (b), however, the peak of the Raman-allowed phonon mode, at 1582 cm^{-1}, was not very sharp, and the intensity of the peak at 1345 cm^{-1} was high which appeared through the disorder-induced phonon mode.[21] It indicated that the present MWNTs had a low degree of graphitization.

The composite films were prepared by gelation and/or crystallization from decalin dilute solutions. The dry gel films were ultradrawn at 135–140 °C. The details were reported in our previous paper.[20] The drawn films were set in a

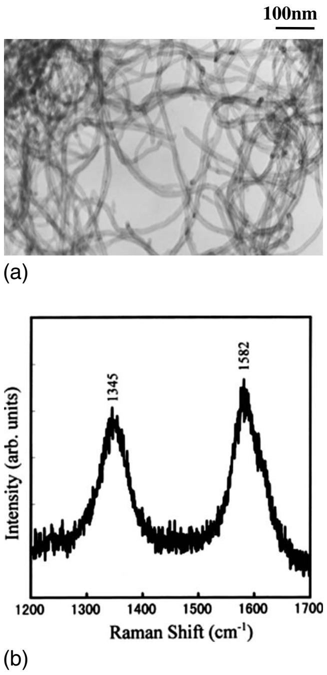

FIG. 1. (a) TEM image and (b) Raman spectrum of MWNTs.

desiccator containing iodine crystal. After being degassed, the desiccator was heated to 80 °C at the heating rate of 5 °C/min and saturated by iodine vapor. The samples were set in the saturated iodine vapor at 80 °C for 6 h. After then, the samples were picked out and washed by ethanol until the solvent was colorless and then vacuum dried for 24 h. The electrical conductivity was measured soon after vacuum drying.

Electrical conductivity of the drawn films was measured in the stretching direction by high resistance measuring device (HR-100) produced by Iwamoto Seisakusho Co., Ltd. at room temperature or in the temperature range from 20 to 220 °C in air, in which the heating rate was 5 °C/min. To prepare test specimens, the composite material was cut into strips of 20 mm length and 5 mm width. The specimen length clamped between copper metal jaws was 5 mm at the each end, in which silver paste was used to ensure complete contact between film surfaces and copper jaws. The specimens with electric conductivity $<10^{-6}\ \Omega^{-1}\,\mathrm{cm}^{-1}$ were measured with the Hewlett 4339B (Hewlett Packard Co., Ltd., Japan) by applying 10 V_{dc}, while those with the conductivity $>10^{-6}\ \Omega^{-1}\,\mathrm{cm}^{-1}$ were measured under the constant current of 0.1–1 mA by the Advantest R6441A digital multimeter furnished by Advantest Co., Ltd., Japan.

Thermal property of the blend film was estimated by differential scanning calorimetry (DSC) (DSC6200, SII Exstar 6000) from 20 to 180 °C in the N_2 atmosphere. The scanning speed was 5 °C/min.

The temperature dependence of the dynamic tensile modulus was estimated with a viscoelastic spectrometer purchased from Iwamoto Machine Co., Ltd. at a fixed frequency of 10 Hz over the temperature range from −150 to 160 °C.

Polarized Raman spectra were measured with a JASCO NRS-2100 laser Raman spectrophotometer. The 90° scattering was collected, where the incident laser was an Ar ion laser with a wavelength of 514.5 nm.

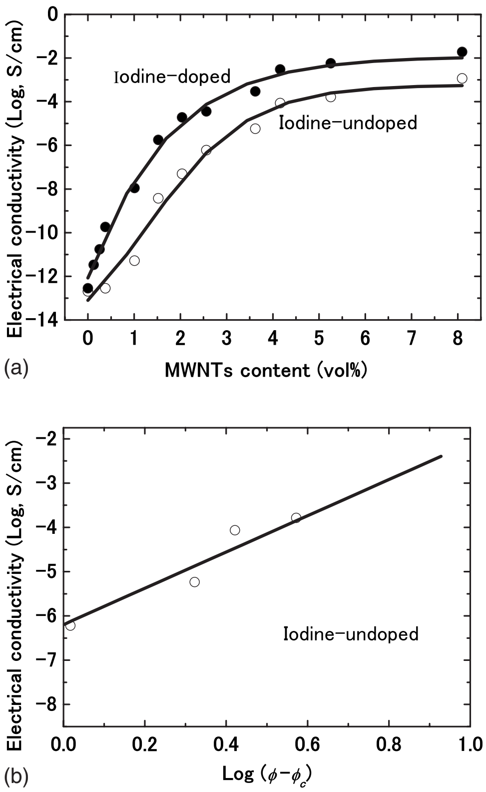

FIG. 2. (a) Electrical conductivity versus volume fraction of MWNTs. (b) Log-log plot of the conductivity against $\Phi-\Phi_c$ with $\Phi_c=1.52$ vol % according to Eq. (1).

III. RESULTS AND DISCUSSION

Figure 2 shows the electrical conductivity of the MWNT-UHMWPE films as a function of the MWNT content, which were prepared by drawing the original films to 50-fold. The value of the electrical conductivity of the drawn films increased 9 orders of magnitude from 10^{-13} to 10^{-4} S/cm, with increasing the content of MWNTs, and tended to level off around 4.16 vol % MWNTs. This indicates a typical percolation transition behavior. In Fig. 2(a), it is clearly seen that the conductivity of iodine-doped MWNT-UHMWPE films was improved 1 to 4 orders of magnitude compared with the undoped films, but the trend of the conductivity versus the volume fraction of MWNTs was hardly affected by iodine doping. Further, it is found that the conductivity of neat UHMWPE did not change by iodine doping. This tendency is different from the result by Lewis and Taylor reported for undrawn low molecular weight polyethylene films.[16]

According to classical percolation theory,[22] the conductivity of composite film as a function of conductive filler can be described by a scaling law of the form

$$\sigma=\sigma_0(\Phi-\Phi_c)^t, \tag{1}$$

where Φ is the volume fraction of the filler, Φ_c is the percolation threshold, σ_0 is the conductivity of the filler, and

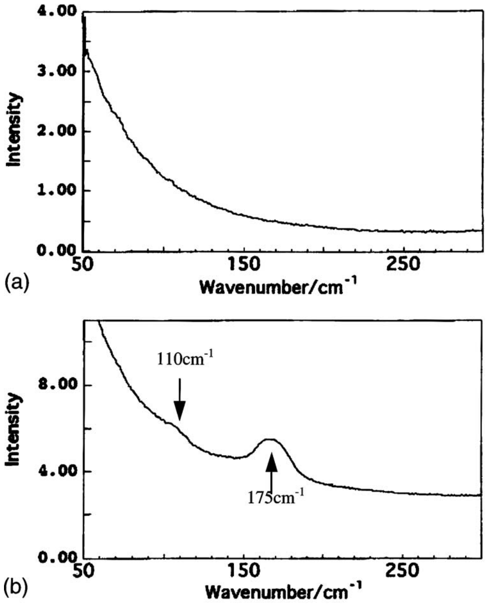

FIG. 3. Raman spectra of the iodine-doped composite films with 1.52 vol % MWNTs using a 514.5 nm excitation: (a) pristine and (b) 2 months after doping.

$t(>0)$ is the universal critical exponent characterizing the relationship between σ and Φ. This equation is valid when $\Phi > \Phi_c$ and $(\Phi - \Phi_c)$ is small. As the volume fraction increases beyond the percolation threshold, the conductivity increases sharply as conductive paths begin to form. For the present drawn films, the conductivity of pristine films is plotted logarithmically, as shown in Fig. 2(b). Fitting the observed data according to Eq. (1) gives the parameters $\Phi_c = 1.52$ vol % (3 wt %) and $t = 4.09$. Many authors had verified the scaling law on carbon-nanotube (CNT)-polymer composite.[23–25] Various values between 8 wt % (Ref. 23) and 0.0025 wt % (Ref. 25) had been reported as the percolation threshold for the CNT-filled polymer composite. Many factors such as distribution of CNTs, CNT-matrix interaction, and processing technique were thought to influence the percolation threshold significantly. On the other hand, the t value obtained in this research is higher than very high t values, 3.1 (Ref. 26) and 3.3 (Ref. 27), reported for carbon fiber. The reason may be the high aspect ratio of the MWNTs as described in Experiment, which is helpful to develop the conductive paths due to easy formation of cross-linking structure.

To better understand an increase in the conductivity and study the mechanism, the Raman spectra were measured after washing the composites by ethanol. Figure 3 shows the spectra of iodine measured for the elongated composite films with 1.52 vol % MWNTs, namely, (a) pristine and (b) the iodine-doped MWNT-UHMWPE film stored in desiccator for 2 months. As shown in Fig. 3(b), the strong and broad peak at 175 cm^{-1} and a very weak peak at 110 cm^{-1} were observed. These peaks were assigned, respectively, to the I_5^- and I_3^- polyiodine chains, similarly to the cases of the iodine-doped single-walled carbon nanotubes.[28] Raman peak at 215 cm^{-1}, which is due to the existence of neutral or dissociative molecular iodine (I_2^0),[29] is not observed. This indicates that no excessive iodine existed in the sample after being washed with ethanol and vacuum drying. Considering the low intensity of I_3^-, the increase in the electrical conductivity is assumed mainly due to the I_5^- which acts as the charge carriers to form the charge transfer complex. In spite of the washing, the existence of the I_5^- and I_3^- peaks is interesting phenomenon different from the result by Michel *et al.*[18] This indicates strong interaction between iodine and networks of MWNTs and UHMWPE chains. The quantitative estimation for doping concentration, however, still remains unresolved problem.

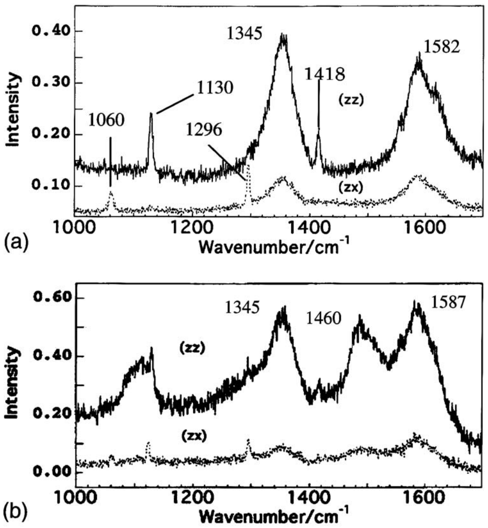

FIG. 4. Raman spectra of the composite films with 1.52 vol % MWNT doped iodine measured using a 514.5 nm excitation: (a) pristine and (b) 2 months after doping.

In Fig. 4, Raman spectra of (a) pristine and (b) the iodine-doped MWNT-UHMWPE film kept in desiccator for 2 months are shown, where the (ZZ) and (ZX) polarization components are presented. In this figure, the Z axis is the drawn axis and the X axis is perpendicular to Z axis. As for the D mode (1345 cm^{-1}) and G mode (1582 cm^{-1}) of MWNTs, the intensity of (ZX) component is much lower than that of the (ZZ) component, suggesting that most of MWNTs in the films are oriented along the chain axis. For the pristine sample, the peaks at 1060, 1296, 1130, and 1418 cm^{-1} correspond to polyethylene. The band assignments are listed in Table I.[30] When the films were doped with iodine, the peak at 1130 cm^{-1} due to the C-C stretching mode became broader, and a new peak appeared at about 1460 cm^{-1}, being attributed to the CH_2 bending mode belonging to the amorphous phase. Iodine, a highly electronegation, could interact with the UHMWPE lattice and produce the distortions and stresses within the crystallites, thereby led to structural modifications. This phenomenon was also found in other polymers, such as PP[31] and low density polyethylene.[32]

The peaks at 1345 and 1582 cm^{-1} are assigned to the D mode and G mode of MWNTs (shown in Fig. 1), respectively. Comparing Figs. 4(a) and 4(b), it is found that G mode upshifted 5 cm^{-1} after iodine doping. This result is in agreement with the study by Cambedouzou *et al.*[33] The outer

TABLE I. Assignments of the Raman bands of polyethylene. Note that *C*, crystalline; *A*, amorphous; υ, stretching (s, symmetric; as, asymmetric); ρ, rocking; δ, bending; τ, twisting; and ω, wagging.

Frequency (cm^{-1})	Phase	Mode	Symmetry
1060	*C* (*A*)	υ_{as}(C-C)	$B_{2g}+B_{3g}$
1080	*A*	υ(C-C)	
1130	*C* (*A*)	υ_s(C-C)	A_g+B_{1g}
1170	*C* (*A*)	$\rho(\mathrm{CH_2})$	A_g+B_{1g}
1296	*C*	$\tau(\mathrm{CH_2})$	$B_{2g}+B_{3g}$
1310	*A*		
1370	*C*	$\omega(\mathrm{CH_2})$	$B_{2g}+B_{3g}$
1418	*C*	$\delta(\mathrm{CH_2})$	A_g
1440	*A*	Fermi resonance	$B_{1g}+A_g$?
		+	
1460	*A*	Overtones?	A_g+B_{1g}?

tube vibrations are affected by the iodine doping. According to the reports by Michel *et al.*[18] and Zhou *et al.*,[17] the adsorption of iodine occurs on the surface of MWNTs. Therefore, the content of MWNTs and the crystallinity of UHMWPE could influence the concentration of doped iodine. It is plausible that the enhancement degree of the conductivity is different, as shown in Fig. 2.

The temperature dependence of the electrical conductivity is investigated for the pristine and doped MWNT-UHMWPE films drawn by 50-fold. The results for three heating cycles as the first, second, and third runs in the temperature range from 25 to 150 °C are shown in Figs. 5 and 6 for 1.52 and 4.16 vol % MWNTs, respectively. The repeated heat treatments were done at a constant length. For the films with 1.52 vol % MWNTs in Fig. 5, the electrical conductivity of the pristine film was irregular for three cycles, indicating that the charge transfer was not smooth at the percolation threshold Φ_c. In this case, the content of MWNTs was the key for the formation of conductive network. It is thought that the thermally induced hopping transport between disconnected (or weakly connected) parts of the network is unstable. After iodine doping, the conductivity became regular. The I_5^-, as charge carrier, can be taken as bridge for the adjacent or nearby MWNTs. For the first heating run, the conductivity suddenly increased near the melting point of UHMWPE. In the second and third runs, the conductivity was slightly higher than that of the first run. Furthermore, compared with the pristine film, the iodine-doped film shows that the stability against temperature is promoted for all the three heating runs. Beyond the fourth run, the route of the temperature dependence is confirmed to be similar to the third run route, which indicates more stable electrical properties by heating treatment.

For the films with 4.16 vol % MWNTs ensuring enough conductive paths, the conductivity of the pristine film increased slowly from 25 to 150 °C, as shown in Fig. 6(a). When the temperature was over 120 °C in the first run, there was also a sudden increase in the conductivity. However, for the second run, the conductivity was maintained constantly during the heating process up to 130 °C and tended to increase slightly at further high temperature. Accordingly, it is of interest to consider that the conductivity increases by heat treatment up to 150 °C. The conductivity of the pristine film obviously increased with temperature and the conductivity increased by an increase in heating cycles. According to the previous works,[34,35] the scanning electron microscopy (SEM) observations revealed that the MWNTs within the matrix of the original film (dry gel film) prepared in decalin were covered by UHMWPE, and their average diameters became much thicker than the original diameters of the MWNTs, indicating that most of the UHMWPE chains crystallized on the MWNT surface and acted as nuclear growth of UHMWPE under gelation process. However, when the original film was heated beyond the melting point of UHMWPE, the most of melted UHMWPE chains did not crystallized on the MWNT surface. SEM observation provided the dispersion of bare MWNTs in the UHMWPE matrix. The oriented crystallization for UHMWPE chains by the elongation of the original film at 135–140 °C did not occur mostly on the

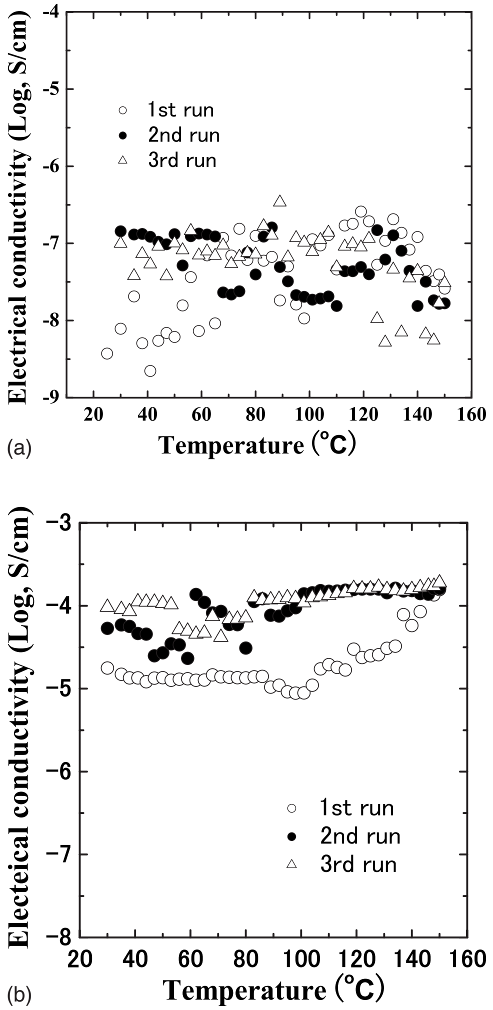

FIG. 5. Electrical conductivity for the films with 1.52 vol % MWNTs during three heating cycles: (a) pristine and (b) iodine doped.

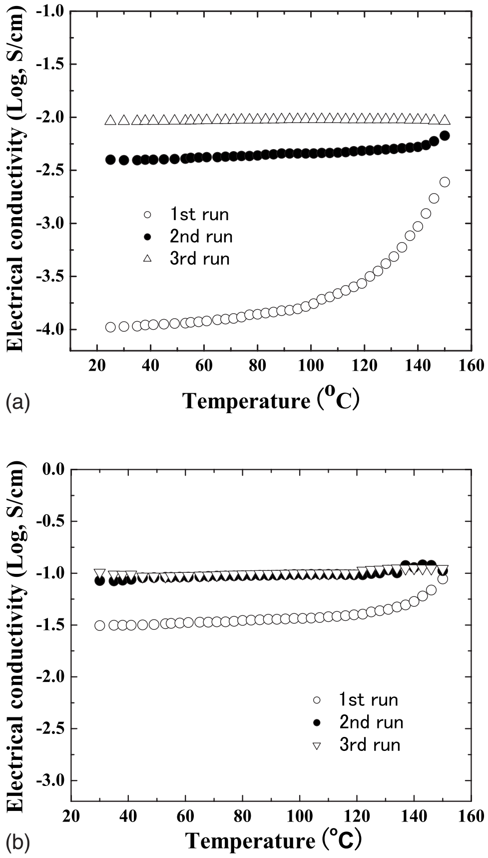

FIG. 6. Electrical conductivity for the films with 4.16 vol % MWNTs during three heating cycles: (a) pristine and (b) iodine doped.

surface of MWNTs. Accordingly, the conductivity (10^{-4} S/cm) of the drawn film with 4.16 vol % MWNTs before the first heating run, shown in Fig. 6, was confirmed to be much higher than conductivity (10^{-8} S/cm) (Refs. 20 and 35) of undrawn films with the same MWNT content. The increase in conductivity by an increase in heating cycles is probably thought to be due to the perfect melting of residual trace of UHMWPE on the surface of some of MWNTs. Namely, the increase in conductivity of the pristine film with increasing temperature is attributed to an increase of mutual contact possibility of MWNTs.

As shown in Fig. 6(b), the conductivity of the iodine-doped film is higher than that of the pristine film. The Raman spectra concerning the I_5^- show the same profiles as Fig. 3 for the films heat treated up to 150 °C. No weight loss was also confirmed by thermogravimetric analysis.[17] This indicates that the I_5^- localized on the outer layers of bare MWNTs and/or UHMWPE chains can be obviously maintained as charge transfer complex after the heat treatment and played an important role to ensure good electrical conductivity of the iodine-doped system because of an increase in charge carriers linked to the MWNTs. Namely, the I_5^- provided additional charge carriers to the UHMWPE-MWNT system and could be taken as bridge for the adjacent or nearly MWNTs.

Here, it may be noted that the thermal expansion of UHMWPE at temperatures close to its melting point is not considerable enough to cause the separation of the contacted MWNTs, so the conductive paths for charge transportation are maintained. Namely, the conductivity under the second and third runs was extraordinarily stable. The conductivity for the MWNT-UHMWPE composite in the second heating cycle showed almost the constant values. This indicates that the cross linking between flexible MWNTs[20] becomes tighter than the thermal expansion of UHMWPE after the first heating run. Accordingly, the thermal behavior of MWNT-UHMWPE composites is different from that of carbon fiber-polyethylene composites taking positive thermal coefficient effect.[27]

Thermal property of the doped films drawn up to 50-fold was studied by DSC analysis. The crystallinities of the pristine and doped films during three heating runs were calculated and listed in Table II, where the crystallinity was calculated as the ratio of the observed Δh to Δh_f of a 100% crystalline polyethylene (245.3 J/g).[36] From Table II, it can be seen that the crystallinity before the first run is higher than those after the first and second heating runs. The values after the second run tend to be almost the same after the first run. In addition, the crystallinity of the pristine film (before the first heating run) with MWNTs contents less than 1.52 vol % was nearly equal to 98%, indicating the remarkable orientated crystallization of UHMWPE. However, the oriented MWNTs beyond the percolation threshold (1.52 vol %) obviously hampered the orientated crystallization, and an increase in crystallinity was quite less pronounced with increasing MWNT content. Furthermore, the crystallinity of the doped films was lower than that of the pristine films. This behavior was in agreement with the Raman analysis (Fig. 4).

Figures 7(a) and 7(b) show the temperature dependence of the storage modulus (E') and loss modulus (E'') measured for the pristine and doped MWNT-UHMWPE films with 1.52 and 4.16 vol % MWNTs, respectively. The storage modulus of the film with 1.52 vol % MWNTs was slightly higher than that of the film with 4.16 vol % MWNTs, indicating that an increase in MWNT networks hampered to pro-

TABLE II. Change of crystallinity X_C (%) of UHMWPE within the composite films with nondoping and doping at different heating runs.

MWNTs content (vol %)	Before first run		After first run		After second run	
	Nondoping	Doping	Nondoping	Doping	Nondoping	Doping
1.52	97.9	95.7	57.4	50.9	55.1	49.4
4.16	76.7	60.6	47.0	35.2	47.9	36.5

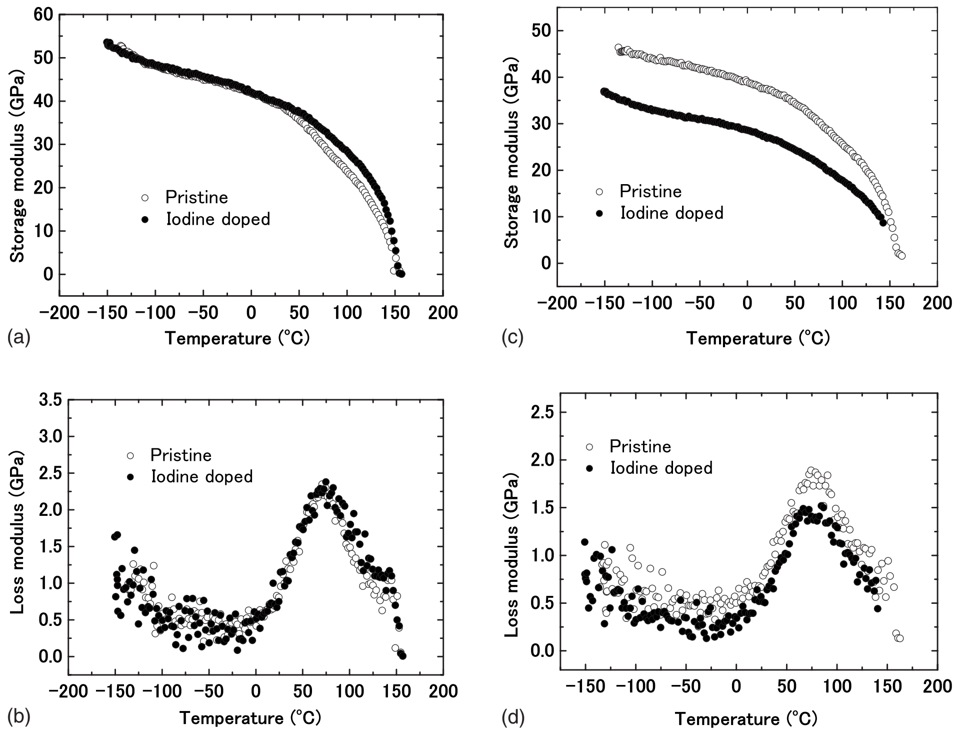

FIG. 7. Temperature dependence of storage and loss moduli of composite films at drawn ratio of 50-fold: (a), (b) with 1.52 vol % MWNTs and (c), (d) with 4.16 vol % MWNTs.

mote oriented crystallization of UHMWPE chains. For the films containing 1.52 vol % MWNTs, no significant change in E' after iodine doping was confirmed, and E' reached 42 GPa at 20 °C, while the E' of doped film with 4.16% MWNTs was maintained approximately 25 GPa at 20 °C. From Table II, it is known that by iodine doping, the decrease of crystallinity of the film with 1.52 vol % MWNTs was only 2.2% (from 97.9% to 95.7%), while that of the film with 4.16 vol % MWNTs was 16.7% (from 76.7% to 60.6%). Such drastic decrease could lead to the great decrease of the storage modulus by an increase in MWNT content. As for E'', the α-dispersion peak associated with crystal phase[37–39] showed no significant change indicating almost no change in activation energy of crystal dispersion. The β-dispersion peak associated with amorphous phase[39] was not observed indicating no significant macro-Brownian motion of oriented amorphous chains,[40] and then the drastic decrease of storage modulus did not occur around room temperature. Anyway, the iodine doping of the MWNT-UHMWPE films provided good stability of electrical conductivity without drastic decrease of the mechanical properties. This indicated that the iodine doping for drawn MWNT-UHMWPE film is potentially useful as the electronic or electrochemical devices which demand high mechanical properties.

IV. CONCLUSION

UHMWPE films filled with MWNTs were prepared by gelation and/or crystallization from solution and elongated up to 50-fold. The specimens were doped by iodine, and characteristics of the percolation of the films were investigated in terms of the effect of iodine doping on the electrical and mechanical properties of the MWNT-UHMWPE composite films. The electrical conductivity of the doped film was increased by 1 to 4 orders of magnitude. The percolation threshold of MWNTs was 1.52 vol %, while the conductivity tended to level off around 4.16 vol % MWNTs. The conductivity of composite film as a function of conductive filler can be described by a scaling law, and t value denoting universal critical exponent was 4.09, which was higher than the highest value, approximately 3.3, reported for carbon fibers. The conductivity was improved for pristine and doped films with increasing MWNT content because of an increase of mutual contact possibility of MWNTs. That is, the conductivity of film with 4.16 vol % MWNTs was much higher than that with 1.52 vol % MWNT. The conductivity increased by iodine doping, and this tendency was more considerable by heat treatment. Raman spectroscopy indicated that the doped iodine existed mainly as I_5^-, which formed the charge transfer complex. The I_5^- localized on the outer layers of bare MWNTs and/or UHMWPE chains played an important role to ensure further good electrical conductivity of the iodine-doped system. Namely, the I_5^- provided an increase in charge carriers linked to the MWNTs and could be taken as bridge for the adjacent or nearly MWNTs. The oriented crystallization of the films was less pronounced by an increase in MWNT content. Even so, the storage modulus of the iodine-doped film with 4.16 vol % MWNT was maintained approximately 25 GPa at 20 °C. Accordingly, iodine doping for drawn MWNT-UHMWPE film was confirmed to be one of the useful techniques to develop high modulus and high conductive materials.

*Corresponding author. FAX: (81) 742203462. m-matsuo@oc.nara-wu.ac.jp

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