Development of Highly Oriented Polyethylene Filled with Aligned Carbon Nanotubes by Gelation/Crystallization from Solutions

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ABSTRACT: Multiwalled carbon nanotubes (MWNTs) and ultrahigh molecular weight polyethylene (UHMWPE) composites were prepared by gelation/crystallization from solution. The dried composites of MWNTs−UHMWPE with 15 wt % of MWNTs would be elongated up to more than 100-fold ($\lambda = 100$). The electric conductivity was 10^{-3} S/cm termed as conductive materials, and the Young's modulus reached 58 GPa at room temperature. The composites possess extraordinary stability in electric conductivity during many repeated heating cycles from room temperature to 150 °C. Scanning electron microscopy revealed that MWNTs with continuous networks are oriented predominantly parallel to the stretching direction. Such characteristic alignment of MWNTs was found to play an important role in forming effective conductive paths in the highly oriented composites.

1. Introduction

Carbon nanotubes (CNTs) are long and slender fibers where the walls of the tubes are hexagonal carbon (graphite structure) and often capped at each end. It has attracted great interest from all over the world since the moment it appeared. CNTs possess superior mechanical, thermal, and electrical properties:[1−3] high elastic modulus greater than 1 TPa (that of diamond is 1.2 TPa), thermally stable up to 2800 °C in a vacuum, thermal conductivity about twice as high as that of diamond, electric-current-carrying capacity 1000 times higher than that of copper wires. Judging from the unique electronic properties and thermal conductivity, CNTs offer tremendous opportunities for development of a new fundamental material system. In particular, the exceptional mechanical properties of CNTs with low density offer scope for the development of nanotube-reinforced composite materials.

Many efforts have been made in development of nanotube-reinforced composite materials. Shaffer et al.[4] processed CNTs/poly(vinyl alcohol) composites. From the theory developed for short-fiber compsites, nanotubes' elastic modulus of 150 MPa was obtained from their experimental data. This value, however, is well below the value reported for the isolated CNTs. Qian et al. characterized CNTs/polystyrene composites. They achieved 36−42% increase in the elastic stiffness and a 25% increase in the tensile strength.[5] The study of Jia et al. showed that CNTs can be initiated by a free-radical initiator to open their π bonds to form a C−C bond between CNTs and the matrixs.[6] Lordi and Yao suggested that the strength of interface may result from molecular-level entanglement of the two phases and forced long-range ordering of the polymer.[7]

There are several previous reports on fabricating aligned CNTs. Ajayan et al.[8] fabricated a composite with CNTs randomly dispersed inside an epoxy matrix and found that slicing the composite caused partial alignment of the CNTs on the cut surface. De Heer et al. fabricated aligned CNTs films by drawing a nanotube suspension through a micropore filter.[9] Wang et al. synthesized multiwalled carbon nanotubes (MWNTs) by arc discharge and observed arrays of parallel bundles by the electron microscopy.[10] Terrones et al. produced aligned MWNTs on a patterned substrate by pyrolysis.[11] Jin et al.[12] pointed out that aligned nanotube composites could be obtained by mechanical stretching of the composite, and X-ray diffraction was used to determine the orientation and degree of the alignment. Bower et al.[13] further investigated the deformation of carbon nanotubes in these aligned films. Haggenmueller and co-workers showed that melt spinning of single-wall nanotubes can also be used to create a well-aligned nanotube composite.[14]

All above the reports have focused on the reinforced composite by filling CNTs. However, the Young's modulus and tensile strength were improved only several tens of percent. At the same time, they did not investigate the electric properties in detail at all. As is well-known, the polymers in their pure state are excellent electrical insulators. Carbon or metal particles have been often used as fillers to modify the polymer as semiconductors or conductors. In the present work, we tried to develop a kind of electrical conductive material with high mechanical properties by filling MWNTs into ultrahigh molecular weight polyethylene (UHMWPE) composites.

MWNTs and UHMWPE composites were prepared by gelation/crystallization technique using decalin as solvent. The gelation/crystallization is well-known as a powerful technique to prepare UHMWPE film with the greatest drawability up to 400-fold.[15−18] At the same time, the gelation method was proven to be a more effective rather than the kneading method to disperse carbon fillers or particles in the polymer matrix, especially for the polymer with high melting viscosity. Even though the kneading method has been widely used to prepare polymer-based composites with conductive fillers, but UHMWPE-based composites cannot be prepared by kneading because of its high viscosity. The maximum contents of carbon black (CB) particles are about 60 wt % for preparing the composites with low-density polyethylene based on the kneading method. On the other hand, the gelation/crystallization method can

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provide UHMWPE-based composites with 90 wt % content of CB and carbon fibers (CF) particles.[20] The high viscosity of solution is helpful to provide a shear stress and make the filler disperse uniformly.

In our experiment, MWNTs were dispersed uniformly in UHMWPE matrix and the composites show black in color with metal-like luster. The resultant MWNTs−UHMWPE composites can be elongated up to over 100-fold. Very slight decrease in electric conductivity was confirmed despite the high draw ratio such as 100-fold, and the value was kept beyond 10^{-3} S/cm. The corresponding Young's modulus reached 58 GPa at room temperature. Such extraordinary values have never been reported for conductive plastic tapes. The composites were confirmed possessing a great stability in electric conductivity during many repeated heating cycles from room temperature to 150 °C. In this paper, such interesting characteristics of the MWNTs−UHMWPE composites are discussed in terms of morphological aspects by using wide-angle X-ray diffraction (WAXD) and scanning electron microscopy (SEM).

2. Experimental Section

UHMWPE (Hercules 19000/90189) with an average viscosity molecular weight ($\bar{M}_v$ = 6 000 000) and fibrous type MWNTs were used as test specimens. MWNTs used in our experiment were furnished by Itochu Fine Chemical Corp. The MWNTs named Hyperion Graphite Fibrils were produced by Hyperion with a diameter of 10−20 nm, a length of 10−20 μm, and an L/D ratio of (1−2) × 10^3. The BET surface area is 250 M^2/g, and the DBP adsorption is 400−500 cm^3/100 g. The true density is 2.0 g/cm^3. Figure 1 shows a transmission electron microscope (TEM) image and the Raman spectrum at excitation laser wavelength of 488 nm. Image (a) indicates the MWNTs possess high purity and uniform diameter distribution. In Raman spectrum (b), however, the peak of the Raman-allowed phonon mode, E_{2g}, at about 1582 cm^{-1} is not very sharp, and the intensity of the peak at 1345 cm^{-1} is high which appears through the disorder-induced phonon mode due to the infinite size of crystals and defects.[19] It indicates the present MWNTs have a low degree of graphitization.

As comparing experiments, carbon black (CB) of Black Pearl 880 furnished by the Cabot Co. Ltd. was also used as raw materials. The average diameter of the CB particles is about 16 nm.

Uniform dispersion within the polymer matrix and improved nanotube-matrix wetting and adhesion have been critical issues in the processing of the nanocomposites. In preparing the composite of UHMWPE and MWNTs, great effort was given to disperse MWNTs into the UHMWPE solution uniformly, including pretreatment before mixing with UHMWPE and searching the optimum conditions such as the concentration of UHMWPE, etc. To make a homogeneous blend gel, MWNTs were first treated using ultrasonic in the decalin solvent more than 10 h at room temperature. Then UHMWPE was put in, and the mixture was stirred and heated with a mild heating rate up to 140 °C and maintained for 1 h at 140 °C. The concentration of UHMWPE was decided finally to be 1 g/100 mL decalin. This was the optimum concentration of UHMWPE to make CNTs well-distributed in solution and form a uniform gel film through a lot of experiments. The volume of solution was controlled to obtain the film with thickness of 700−800 μm. The hot homogenized solution was quenched by pouring it into a glass dish at room temperature, thus generating a gel. The solvent decalin was evaporated from their gel under ambient conditions. The composite film was cut into strips of length 30 mm and width 10 mm. The strip was clamped in a manual stretching device and stretched in a hot oven at 135 °C.

The electric conductivity for the drawn films was measured in the stretching direction by using a two-terminal method at room temperature or in the temperature range from 20 to 220 °C. The specimens of electric resistivity above 10^6 Ω·cm were measured by applying 10 V_{dc} of voltage, while those of low resistivity (<10^6 Ω·cm) were measured under the constant current of 0.1−1 mA. X-ray measurements were carried out by a 12 kW rotating-anode X-ray generator (Rigaku RAD-rA) with the monochromatic Cu Kα radiation (wavelength of 0.154 nm) was used. WAXD patterns were obtained with a flat camera. The temperature dependence of the dynamic tensile modulus was estimated with a viscoelastic spectrometer (VES-F) obtained from Iwamoto Machine Co., Ltd., at a fixed frequency of 10 Hz over the temperature range −150 to 300 °C.[18] The morphology was observed by SEM (TOPCON, ABT-150F).

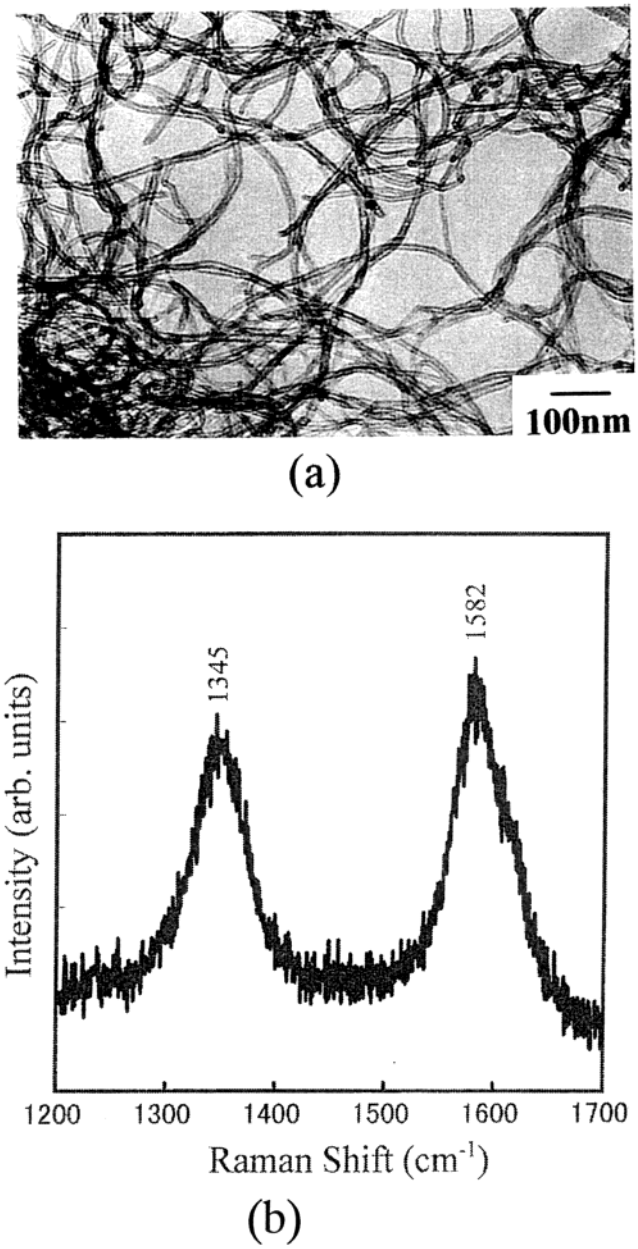

Figure 1. (a) TEM image and (b) Raman spectrum of MWNTs.

3. Results and Discussion

Figure 2 shows the electric conductivity as a function of the content of the conductive fillers, CB and MWNTs, used in the UHMWPE-based composites measured at room temperature. It is clearly seen that the percolation threshold of composites of MWNTs is much lower than that of the CB−UHMWPE composites. This should be

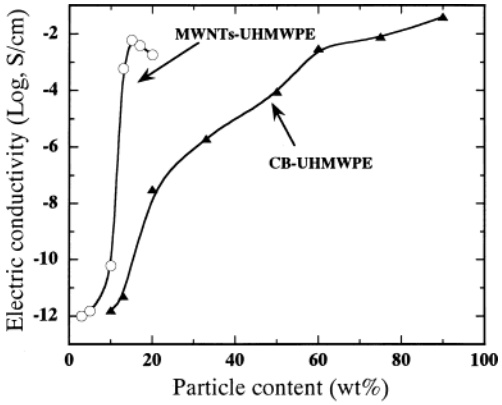

Figure 2. Electric conductivity of UHMWPE-based composites as a function of the content of MWNTs and CB at room temperature.

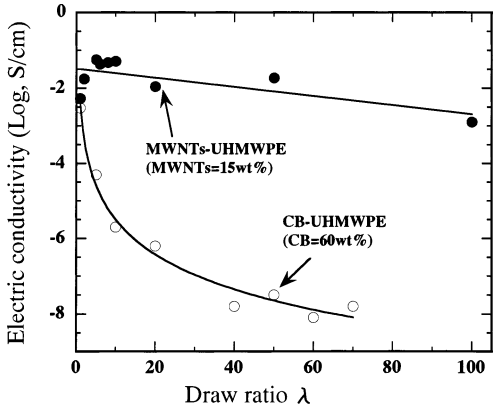

Figure 3. Electric conductivity of MWNTs−UHMWPE and CB−UHMWPE composites measured as a function of draw ratio at room temperature.

attributed to the high aspect ratio of MWNTs relating to the overlapping of the carbon fillers. MWNTs appear to be a typical example of a highly structured and extended material. These morphological features are responsible for the large effective volume and improved connecting of MWNTs. It is also well-known that the percolation point for polymeric composites is very sensitive to the experimental conditions (molding method, molding temperature, dispersion, etc.) and peculiarities of the components in the mixture (e.g., surface energy and size ratio). For instance, higher values of the percolation point are usually obtained if, during the preparation, the agitation of the polymer−carbon mixture is energetic enough to separate large carbon clusters. A composite of substantially increased resistivity is generated, since the resulting small carbon particles become isolated due to coating by a polymer layer.

Judging from the results in Figure 2, 15 wt % of MWNTs in MWNTs−UHMWPE composites is considered to be the optimum content ensuring the greatest drawability without drastic decrease in electric conductivity. The volume ratio of MWNTs is about 8%. It is seen that the electric conductivity of MWNTs−UHMWPE composites tends to decrease when MWNTs content is more than 15 wt %. The drop in electric conductivity at MWNTs contents higher than 15 wt % is thought to be due to the fact that uniform dispersion is correlated with content of MWNTs, and the shearing stress occurred under stirring process of the solution. Namely, at MWNTs content less than 15 wt %, UHMWPE solution with extremely high viscosity causes a strong shearing stress on MWNTs coils under the stirring process of the solution and the strong stress makes MWNTs disperse uniformly in the gel. At MWNTs content >15 wt %, however, the shear stress is thought to be too small to ensure the uniform dispersion of MWNTs in the solution, and then large amounts of MWNTs entanglements are still maintained under the stirring process.

Figure 3 shows electric conductivity against draw ratio measured for two kinds of composites, MWNTs−UHMWPE and CB−UHMWPE. The MWNTs content for MWNTs−UHMWPE was 15 wt %, corresponding to the highest value of electric conductivity as shown in Figure 2. The content of CB particles was chosen to be 60 wt %, which give almost the same conductivity as MWNTs−UHMWPE composite in their undrawn states. The maximum draw ratios were 100- and 70-fold for MWNTs−UHMWPE and CB−UHMWPE composites, respectively. When stretching, the electric conductivity of CB−UHMWPE composites decreases more than 10^{-3} S/cm while being drawn to 20-fold; the value decreases slowly to 10^{-8} S/cm and tends to level off during the further elongation. As contrasted with CB−UHMWPE composites, the conductivity of the MWNTs−UHMWPE composites decreases slightly with increasing draw ratio and maintains about 10^{-3} S/cm even at 100-fold. In the normal case, the stretching of carbon filler and polyethylene composites causes the separation of conductive particles from each other,[20] and then a number of conductive paths are cut off. Namely, the total contacting areas between conductive fillers decrease, so the electric conductivity decreases drastically.

To investigate the origin of the above strange phenomenon of MWNTs−UHMWPE composites, the morphology was observed by SEM. Figure 4 shows a photograph on the cross section of the MWNTs−UHMWPE film containing 15 wt % of MWNTs. As illustrated in photo (a), the texture of UHMWPE shows spongelike tissue characterizing the morphology of dry gel UHMWPE films prepared by gelation/crystallization from solution,[21] and the MWNTs were dispersed within the UHMWPE crystallites. In photo (b) as the magnification of (a), a number of dense networks of MWNTs can be observed assuming sufficient conductive paths.

Further observation on the ultradrawn MWNTs−UHMWPE film by SEM shows that the morphology of MWNTs in the drawn matrix plays an important role in the unvarying of its conductivity in the stretching direction. Figure 5 shows SEM photographs on the surface of composites with a draw ratio of 100-fold. The high orientation of PE fibrils and the alignment of MWNTs in the stretching direction can be observed from photo (a). Photo (b) is the magnification of the part framed in photo (a), and further magnification is shown in photo (c) where the continuous three-dimensional networks of MWNTs could be clearly seen. The networks of MWNTs are aligned highly together with oriented polyethylene fibrils along the elongation direction. It is obvious that the continuous networks of MWNTs formed most effective conductive paths in the composite materials. The photographs reveal a good compatibility between UHMWPE and MWNTs prepared by the gel method. They assembled together and entangled with each other in their composites. This is the origin why the ultradrawing to more than 100-fold did not make a

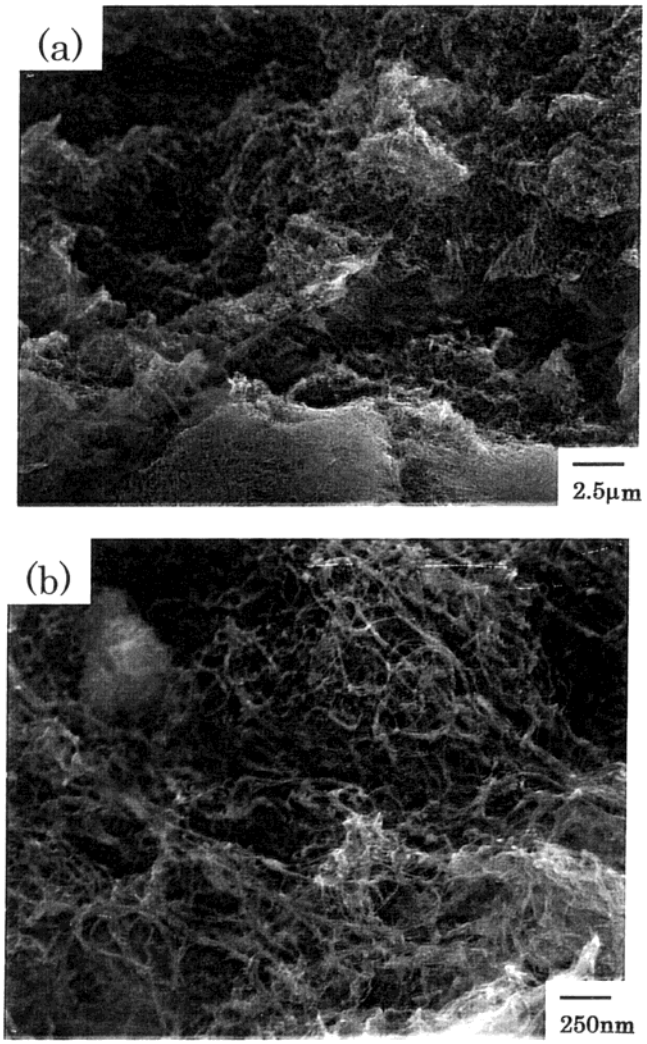

Figure 4. SEM photographs observed on the cross section of MWNTs−UHMWPE composite (MWNTs = 15 wt %) in the undeformed state.

large decrease in electrical conductivity in the elongation direction.

Figure 6 presents the WAXD patterns observed from the MWNTs−UHMWPE composite with different draw ratios, while the X-ray beam was directed perpendicular to the film surface (through view). The patterns indicate the preferential orientation of the *c*-axes with respect to the stretching direction, and this tendency becomes more pronounced with increasing draw ratio (λ). At $\lambda = 100$, the diffraction arcs from crystal planes (110) and (200) of PE become spots, suggesting that the *c*-axes are oriented highly with respect to the stretching direction. In contrast, the diffraction of MWNTs cannot be observed clearly because the diffraction is weak comparing the diffraction intensity from (110) and (200) planes of highly oriented UHMWPE.

Figure 7 compares the temperature dependence of E' and E'' for the MWNTs−UHMWPE composites with 10 and 15 wt % of MWNTs as well as the pure UHMWPE gel film (MWNTs = 0 wt %) at $\lambda = 100$. Even though the storage modulus for the composites were lower than pure UHMWPE films, it is of interest to find that E' of composites with 15 wt % is much higher than that with 10 wt %. This means that the higher content of MWNTs reinforces the strength and modulus of the composite. The exceptional feature in the mechanical property of

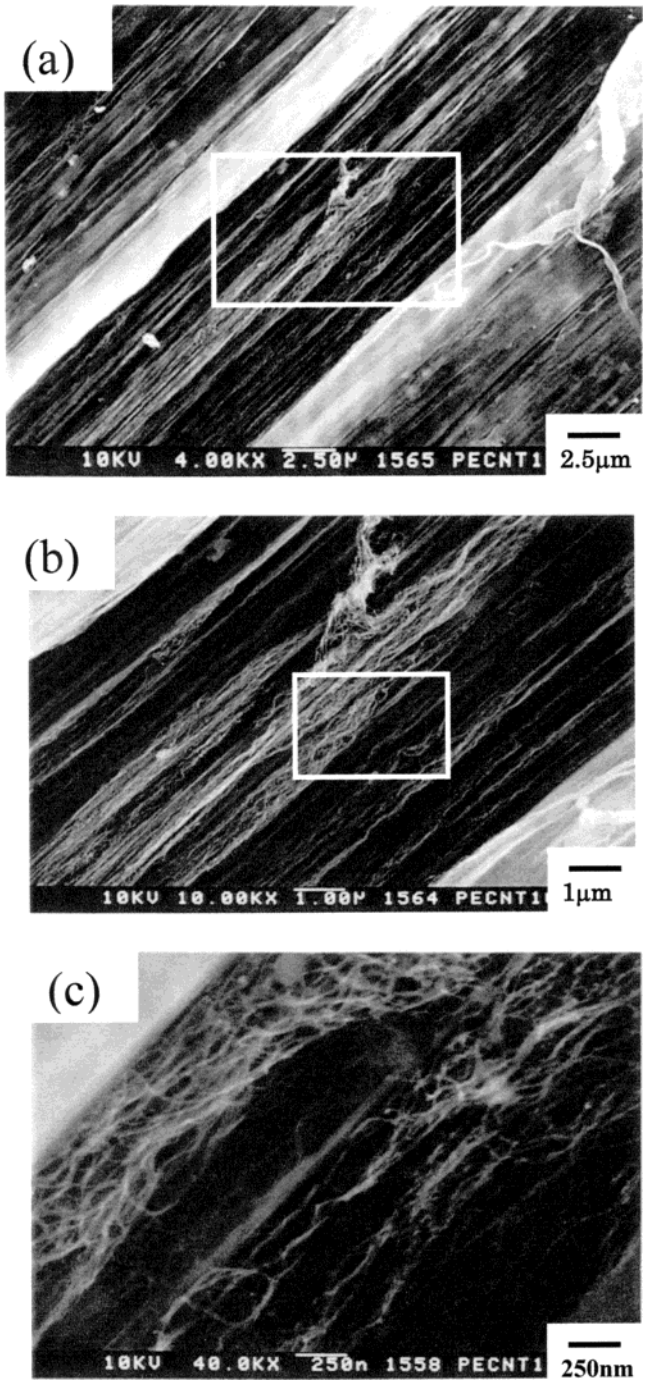

Figure 5. SEM photographs observed on the surface of MWNTs−UHMWPE composite (MWNTs = 15 wt %) drawn up to 100-fold.

MWNTs−UHMWPE composites attributed to the morphology with continuous three-dimensional networks of oriented MWNTs, as shown in Figure 5. A series of experiments indicate that the content of 15 wt % MWNTs was the optimum concentration, ensuring the greatest drawability without drastic decrease in electric conductivity as shown in Figure 3.

The temperature dependence of storage modulus (E') and loss modulus (E'') were measured for the MWNTs−UHMWPE composites containing 15 wt % of MWNTs in their undrawn state and ultradrawn state. The results are shown in Figure 8. E' increases with increasing draw ratios. In comparison with Young's modulus of the undrawn film, 1.5 GPa at 20 °C, the

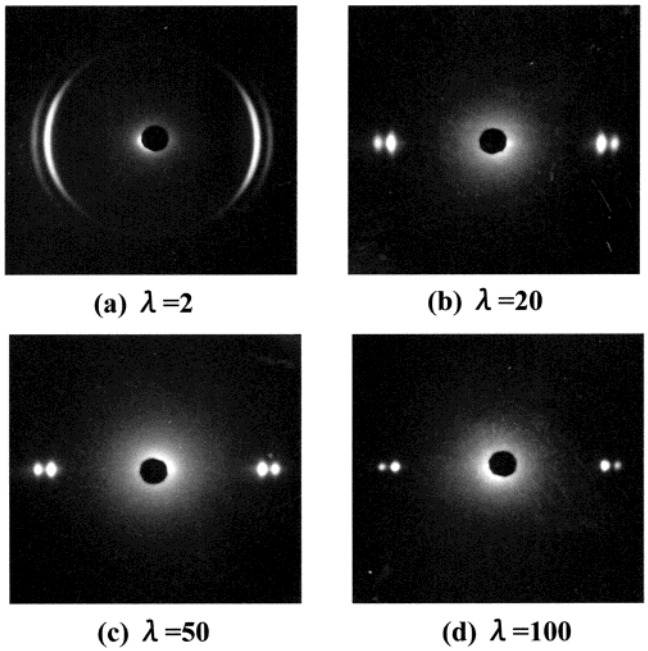

Figure 6. WAXD patterns observed from MWNTs−UHMWPE composites (MWNTs = 15 wt %) with the indicated draw ratios.

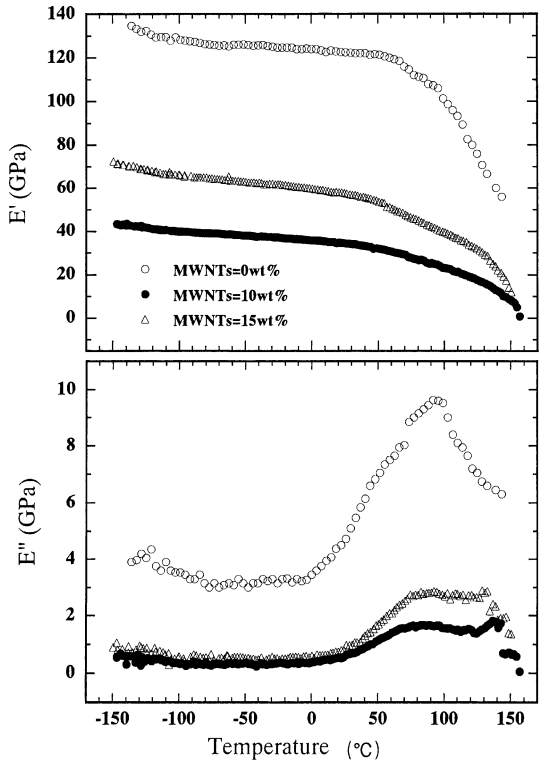

Figure 7. Temperature dependence of E' and E'' for MWNTs−UHMWPE composites with 0, 10, and 15 wt % contents of MWNTs at $\lambda = 100$.

values reached 49 and 58 GPa for the drawn film with 50- and 100-fold, respectively. This means the Young's modulus was improved more than 30 times through ultradrawing. The value of E' of the composite with $\lambda = 100$ at 20 °C is close to the Young's modulus of aluminum. This is due to an increase in orientation degree of UHMWPE crystallites, as shown in Figure 6. Because of an increase in crystallinity of UHMWPE with draw ratio, the temperature dependence of E'' reveals that the magnitude of the β relaxation peak

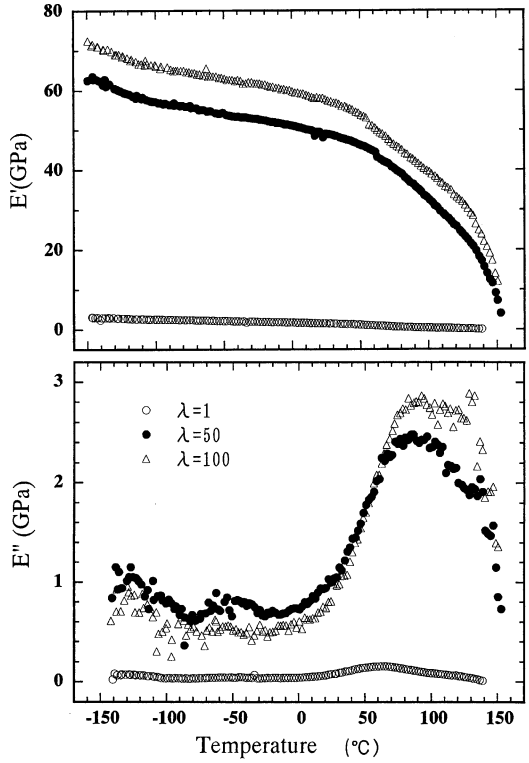

Figure 8. Temperature dependence of the storage modulus (E') and loss modulus (E'') for MWNTs−UHMWPE composites (MWNTs = 15 wt %) at $\lambda = 1$, 50, and 100.

around −50 °C associated with the amorphous dispersion[22] is very small. The peak position of the α relaxation associated with crystal dispersion,[22] which appears around 50−100 °C, slightly shifts to higher temperature with increasing λ, indicating the growth of crystallites by oriented crystallization.

Here we must explain briefly the reason why the tensile modulus of the composite tape containing MWNTs is lower than that of pure UHMWPE at the same draw ratio. This is thought to be due to the fact that the networks of MWNTs are obstacles to the orientation of UHMWPE. Accordingly, the mechanical properties of the composites with $\lambda = 100$ only reached the value of UHMWPE homopolymer film with $\lambda = 25$ because both UHMWPE and MWNTs did not orient perfectly yet. However, the value, 58 GPa, is sufficient enough for electrical conductive tapes as usual applications. It is just the continuous networks which aligned along the stretching direction to ensure the high electrical conductivity for the ultradrawn composite tape. Of course, it must be taken into consideration to prepare composites of UHMWPE and MWNTs oriented perfectly in the stretching direction.

Incidentally, we have to explain that the tensile strength could not be measured for our specimens because they were too strong to be broken during elongation in our experiment. It always slides from the chucks instead of being broken in all kinds of test conditions.

As is well-known, the electric conductivity of carbon−polymer the composites is very sensitive to temperature.[23−25] Figure 9 shows the electric conductivity measured against temperature for MWNTs−UHMWPE gel films with 5 and 10 wt % of MWNTs in their undrawn states. The measurements were done for two cycles. For the first cycle, the conductivity first increases

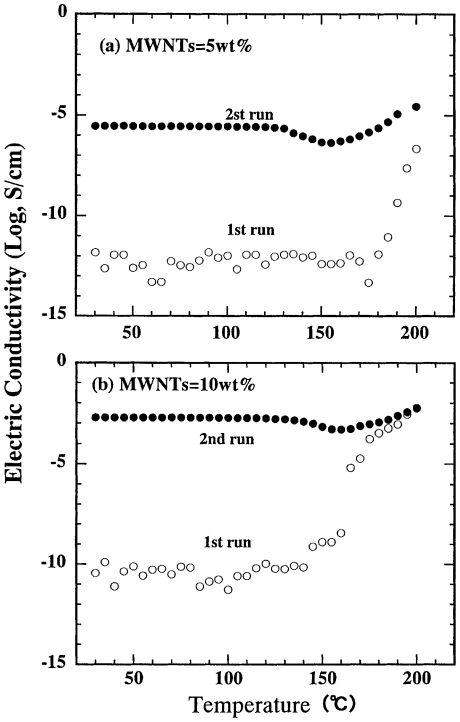

Figure 9. Temperature dependence of electric conductivity measured for the undrawn MWNTs−UHMWPE composites during two thermal cycles. The content of MWCNT was (a) 5 wt % and (b) 10 wt %.

gradually with increasing temperature, but it increases more than 5 orders of magnitude suddenly when the melting point of PE reached. The sudden change point is 170 and 160 °C for the composites with 5 and 10 wt % content of MWNTs, respectively. After the first heating, the specimen was cooled to room temperature. At the second cycle, the conductivity is maintained constantly during the heating process up to 130 °C and tends to decrease slightly. But the values increase again beyond 160 °C. Such thermal behavior of the MWNTs−UHMWPE composite is considered to be due to the fact that the considerable mobility of UHMWPE chains beyond the melting point causes the active movement and the rearrangement of MWNTs and then provides an increase in contacting points between MWNTs. But the thermal expansion of UHMWPE is not significant enough to cause the separation of the contacted MWNTs, so conductive paths for charge transportation are maintained. On the other hand, the thermal expansion of CNTs is very small, and the mobility of polymer was controlled by CNTs. The conductivity for the MWNTs−UHMWPE composite in the second cycle shows almost constant values at temperatures < 130 °C, indicating that the adhesion between MWNTs becomes tighter than the thermal expansion of UHMWPE after the first cycle heat treatment.

Figure 10 shows the electric conductivity measured against temperature for the MWNTs−UHMWPE composite where MWNTs' content is 15 wt %. The undrawn film and the drawn films with $\lambda = 50$ and 100 are used. The results for three heat cycles are shown in the figure as first, second, and third runs. For the first run, the conductivity of the undrawn composite increases gradually with increasing temperature, but it increases more than 1 order of magnitude beyond 140 °C. The conductivity of the films with $\lambda = 50$ and 100 shows the similar tendency, but the sudden increase is less pronounced

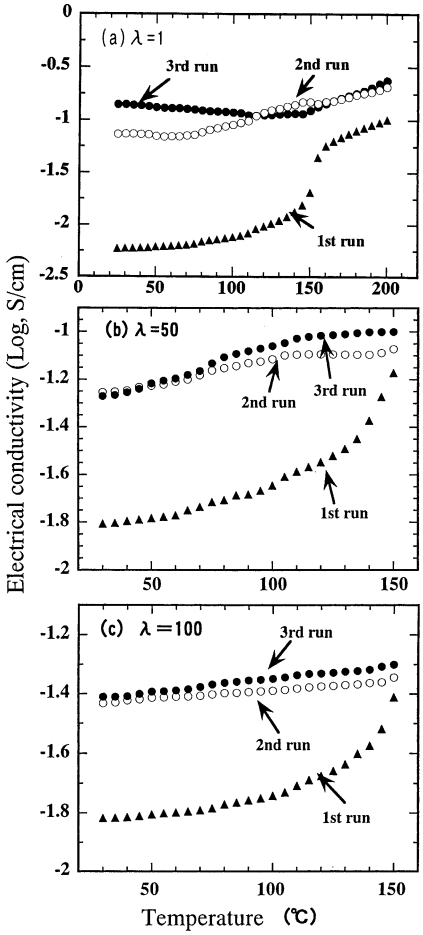

Figure 10. Temperature dependence of electric conductivity measured for MWNTs−UHMWPE composites with 15 wt % MWNTs: (a) undrawn ($\lambda = 1$), (b) $\lambda = 50$, and (c) $\lambda = 100$. The heat treatments were done for three thermal cycles.

than that of the undrawn film. Of course, the conductivity did not change under the cooling process for the two specimens. However, the amplitude of varying in conductivity during heating cycle is extremely lower than the case for the specimens containing 5 and 10 wt % MWNTs shown in Figure 9. It indicates that the optimum content of MWNTs ensures the most stable form. At the second and third runs, the conductivity increases slightly with temperature, but the tendency is much smaller in comparison with that of the first run. Beyond the fourth run, the route of the temperature dependence similar to the third run was confirmed, which indicates more stable electrical properties by heat treatment. The conductivity of the undrawn composite was in the range from $10^{-1.8}$ to $10^{-0.7}$ S/cm, while that of the drawn composite is from $10^{-1.3}$ to $10^{-1.1}$ S/cm. The extraordinary stability in electric conductivity is completely different from the normal carbon−polymer composites.[24,25] This means that the MWNTs−UHMWPE composites with 15 wt % of MWNTs drawn up to $\lambda = 100$ are absolutely thermal stable conductive materials with high mechanical properties. The similar results were confirmed for CNTs−UHMWPE composites by using other CNTs as filler. A number of applications to the industrial fields shall be prospected in the near future for the composites containing CNTs prepared by gelation techniques.

4. Conclusions

MWNTs and UHMWPE composites were prepared by gelation/crystallization from solutions. The optimum condition, the content of MWNTs being 15 wt % against UHMWPE and the concentration of UHMWPE against the decalin solvent being 1 g/100 mL, was determined through a number of preliminary experiments. The dried composite film could be elongated up to over 100-fold; the electric conductivity was about 10^{-3} S/cm, and the Young's modulus reached 58 GPa at 20 °C. These values give the proposal of producing the conductive materials with high mechanical properties. The unique features of MWNTs to develop electrical conductive materials with high mechanical properties were confirmed under SEM observation. As a result, it was found that the continuous three-dimensional networks of MWNTs aligned highly along the oriented PE fibrils, ensuring the effective electric conductive paths.

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