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Morphology and electrical conductivity of ultrahigh-molecular-weight polyethylene–low-molecular-weight polyethylene–carbon black composites prepared by gelation/crystallization from solutions

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Abstract Composite materials based on ultrahigh-molecular-weight polyethylene (UHMWPE)–low-molecular-weight polyethylene (LMWPE) and carbon black (CB) particles were prepared by a gelation/crystallization process from dilute solution. The method was developed to obtain composite materials with an improved and reproducible positive temperature coefficient (PTC) effect. Drastic improvement of the PTC effect was achieved when specimens with a LMWPE/UHMWPE composition of 9/1 containing 13 wt% CB were treated at 170 °C without restraint before measurement. The maximum PTC intensity, defined as the ratio of the maximum resistivity to the resistivity at room temperature, was about 5 orders of magnitude, which equals that of the LMWPE-CB system prepared by a kneading method. Interestingly, electrical resistivity during the heating-cooling process showed good reproducibility in the temperature range 30–190 °C, but has never been reported before even for cross-linked LMWPE-CB compostie. Scanning electron micrographs revealed that CB particles were dispersed in the LMWPE matrix, but not on the UHMWPE fibrils. It turns out that the network structure of UHMWPE, with a very low melt index, plays an important role in removing the negative temperature coefficient effect usually observed for the LMWPE-CB system and in ensuring the quality and the reproducibility of the PTC effect.

Key words UHMWPE-LMWPE-CB composite – electrical conductivity – PTC effect – gelation/crystallization – kneading – heat treatment

Introduction

Polymers in their pure state are excellent electrical insulators; however polymers can be modified to be good electrical conductors by simply mixing them with good conductors. A number of papers concerned with theoretical and experimental aspects have been published [1–14]. Among conductor-filled polymers, polyethylene (PE) filled with carbon black (CB) is one of the typically good conductive materials. Considerably experimental effort has been devoted over several decades to the study of the basic electrical phenomena by using low-molecular-weight polyethylene (LMWPE) [4–6, 8–9]. Most of the investigations have been concerned with the positive temperature coefficient (PTC) effect associated with a drastic decrease in electrical conductivity in the temperature range close to the melting point of PE. This indicates that the enlargement of the distance between CB particles causes the conducting network to be broken up. According to some reports [5, 6], the resistivity has a maximum peak around 100 °C, which is close to the melting point of LMWPE, and it decreases drastically with further increase in temperature. The decrease in resistivity with temperature is due to the negative temperature coefficient (NTC) effect. Furthermore, the PTC effect decreases with thermal cycling. These unfavorable phenomena are due to the high melt index of LMWPE. To improve these weak points, Tang et al. [9]

pointed out that radiation cross-linking enhances the PTC intensity and decreases the NTC effect: by cross-linking, the reproducibility improves. In previous investigations [15, 16], ultrahigh-molecular-weight polyethylene (UHMWPE) was used as a test specimen to try and achieve further improvement; however, the viscosity of UHMWPE was too high to prepare composite materials by kneading techniques. In spite of lots of trials to seek the best condition to mix CB particles by a kneading method, the uniform mixing of UHMWPE powder and CB particles has never been obtained. As a result the kneading method has been limited to LMWPE-CB blend systems. To avoid this difficulty, a special sample preparation method was proposed in which large numbers of CB particles were introduced into UHMWPE solution followed by subsequent gelation/crystallization from solution. The PTC effect of UHMWPE-CB materials was investigated using the blend system with a critical content of CB particles. The measurements were made for the first and second heating runs. For the first run, the PTC intensity at 160 °C was more than 2 orders of magnitude higher than at the melting point (135 °C) of UHMWPE. Unfortunately, the PTC intensity for the second run was only 1 order of magnitude, indicating poor reproducibility.

To remove the unfavorable points of LMWPE-CB and UHMWPE-CB composites as PTC materials, we further investigated the PTC effect of LMWPE-UHMWPE-CB blends prepared by the gelation/crystallization method. The PTC effect as a function of LMWPE content at the critical concentration of CB particles was mainly investigated in terms of morphology and thermal properties. The main focus was on the relationship between the PTC effect and the heat-treatment effect of test specimens before measurement.

Experimental

The samples were prepared by using UHMWPE (Hercules 19000/90189) with an average viscosity molecular weight of 6×10^6, LMWPE (Sumikathene G201) with an average viscosity molecular weight of 4×10^4, and CB particles (BLACK PEARLS 880) with DBP/RCC/10 g which were furnished by Cabot Co. Observations by electron microscopy and DBP measurement indicated that the particle size is about 16 nm and the number of connected particles indicating a bead-like structure is about 10. A decalin solution containing UHMWPE, LMWPE and CB particles was prepared by heating the well-blended polymer/solvent mixture at 150 °C for 30 min under nitrogen. The total concentration of UHMWPE and LMWPE against solvent was fixed at 0.5 g/100 ml. The volume of the solutions was controlled to obtain films with 700-μm thickness. The hot homogenized solution was quenched by pouring it into an aluminum tray at room temperature, thus generating a gel [17–22]. The decalin was allowed to evaporate from the gels under ambient conditions. The nearly dry gels were vacuum-dried for 1 day to remove residual traces of decalin. The resultant dry films were pressed at 70 °C and subsequently heat-treated without restraint at various temperature. The composition of the LMWPE and UHMWPE blend was designated at the LMWPE/UHMWPE ratio. The composition is 9/1 when the content of LMWPE within a blend is 90%.

Samples were also prepared by a kneading method at 160 °C for LMWPE-CB composites and for LMWPE-UHMWPE-CB composites whose LMWPE/UHMWPE composition was 9/1. With further introduction of UHMWPE it was difficult to ensure uniform mixing using the kneading technique. Subsequently the specimen was maintained in the molten state at 150 °C for 20 min to prepare a sheet and was then cooled down to room temperature.

Electrical conductivity was measured by the two-terminal method for the direction parallel to the film surface direction. To prepare the test specimens, the composite material was cut into strips of length 25 mm width 15 mm. Before the measurement, the specimen was polished with sandpaper to smooth both sides. The conductivity greater than 10^{-6} $s \cdot cm^{-1}$ was estimated by measuring the voltage at a constant current of 0.1–1 mA, while the conductivity less than 10^{-6} $s \cdot cm^{-1}$ was estimated by measuring the current yield at a voltage of 10 V d.c. The measurement was carried out using the specimen clamped between copper metal jaws. As a preliminary experiment, silver paste was used to ensure complete contact between the specimen surface and the copper jaws. The values, however, were almost equal to those measured without using silver paste. Moreover, precise measurements by a four-terminal method were carried out for specimens with electrical conductivities greater than 10^{-3} $s \cdot cm^{-1}$, but the values were almost equal to those measured by the two-terminal method. Hence, the following measurements were made by the two-terminal method without silver paste.

The thermal behavior was estimated from the melting endotherm in differential scanning calorimetry (DSC). On measuring, specimens with circular shape, weighing 10 mg, were placed in standard aluminum sample pans and heated at a constant rate of 5 °C min^{-1}. The morphology was investigated by wide-angle X-ray diffraction (WAXD) and scanning electron microscopy. The procedures of the measurements were the same as described elsewhere [23].

Results and discussion

Characteristics of LMWPE – UHMWPE blends without CB

The melting point, heat of fusion and crystallinity associated with UHMWPE and LMWPE crystallites which were measured for original gel films (without CB) of 0/1 (UHMWPE homopolymer), 1/1, 2/1, 4/1 and 9/1 compositions estimated from DSC measurement are given in Table 1. Surprisingly, the 9/1 blend gels can form a film. According to previous investigations [24], it was confirmed that LMWPE cannot form a film because of very few entanglement meshes. The formation of a film is thought to be due to an increase in entanglement meshes by the introduction of UHMWPE [25]. The melting points of UHMWPE and LMWPE crystallites at higher- and lower-temperature sides appeared separately, indicating that UHMWPE and LMWPE crystallize independently by gelation from solution. The peak position of UHMWPE crystallites shifts to lower temperature with increasing LMWPE content, while the peak position of LMWPE crystallites appears at 101 °C, independent of UHMWPE content. Each heat of fusion was calculated by the relationship: heat of

Table 1 Melting point, heat of fusion H_u (kJ/kg) and crystallinity X_c (%) of low-molecular-weight polyethylene (*LMWPE*)ultrahigh-molecular-weight polyethylene (*UHMWPE*) composites

LMWPE/ UHMWPE (w/w)	LMWPE			UHMWPE		
	m.p. (°C)	H_u (kJ/kg)	X_c (%)	m.p. (°C)	H_u (kJ/kg)	X_c (%)
0/1	–	–	–	141	211.63	73.79
1/1	101	74.08	25.83	136	202.98	70.78
2/1	101	76.61	26.71	132	190.00	66.25
4/1	101	78.78	27.47	131	189.51	66.08
9/1	101	82.29	28.69	131	184.59	64.36

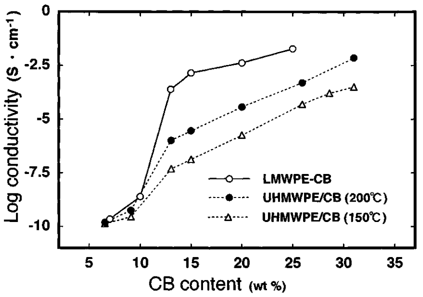

Fig. 1 Electrical conductivity measured for low-molecular-weight polyethylene (*LMWPE*)-carbon black (*CB*) by the kneading method and two kinds of ultrahigh-molecular-weight polyethylene (*UHMWPE*)-CB specimens heat-treated at 200 and 150 °C, respectively

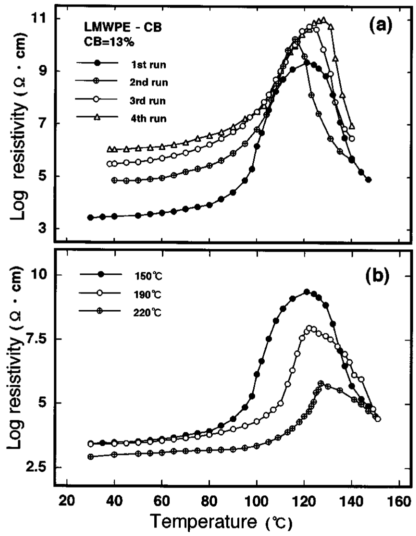

Fig. 2a, b Electrical resistivity against temperature of LMWPE-CB composites with 13 wt% CB which were prepared by the kneading method. **a** Results for four heating runs; **b** results measured for specimens with three press temperatures for the first run

fusion = observed value/content of UHMWPE (or LMWPE). The crystallinity was calculated by assuming the heat of fusion of fully crystalline polymer to be 286.8 kJ/kg [26]. The crystallinity of LMWPE within the blend increases slightly and that of UHMWPE decreases as LMWPE content increases.

Electrical conductivity of LMWPE-CB and UHMWPE-CB blend systems

The electrical conductivity as a function of CB content within LMWPE melt pressed films and UHMWPE dry gel films at 23 ± 2 °C and at a relative humidity of 65 ± 5% is shown in Fig. 1. For UHMWPE-CB dry gel composites, heat treatment was done without restraint at various temperatures for 20 min. Results for specimens heat-treated at 150 and 200 °C are shown as an example. According to our preliminary experiments for UHMWPE-CB composites, the conductivity of blends with CB increased with increasing heat-treatment temperature of the specimens and took a constant value beyond 200 °C. This is due to the easy alignment of CB particles to form conductive channels because of the disappearance of voids within the blend gel film by heat treatment. In Fig. 1, electric conductivity is shown to increase with increasing CB content, this tendency being most significant for the LMWPE-CB composites. A drastic increase in electrical conductivity occurs in the range 10–13 wt% CB which is the so-called "critical concentration". Among the three curves, the conductivity of LMWPE-CB system increases most drastically around the critical concentration. Such an increase provides good PTC effects which will be discussed later in terms of PTC intensity as a function of LMWPE content within the LMWPE-UHMWPE-CB system.

The temperature-dependence of resistivity for the LMWPE-CB composite with 13 wt% CB is shown in Fig. 2. The reproducibility of the resistivity for the four cycles of the heating-cooling run, in which the specimens were pressed at 150 °C for 20 min, is shown in Fig. 2a, while Fig. 2b shows the temperature-dependence of LMWPE-CB composites measured for the first run by using the specimens heat-treated at 150, 190 and 220 °C for 20 min. The solid circles in Fig. 2a are the same as those in Fig. 2b. In Fig. 2a, the resistivity is seen to increase gradually with increasing temperature and it suddenly increases by several orders of magnitude around 100 °C, which is close to the melting point

Table 2 Positive temperature coefficient intensity measured for various LMWPE/UHMWPE/Carbon black (*CB*) composites as a function of heating cycling

Composites		Heating cycling			
		1st	2nd	3rd	4th
LMWPE-CB (kneading)		1.10×10^6	1.25×10^6	2.84×10^5	1.00×10^5
LMWPE-UHMWPE-CB (kneading, heat-treated at 150 °C)		2.96×10^5	1.07×10^2	1.00×10^2	
LMWPE-UHMWPE-CB	(9/1)	8.13×10^5	1.29×10^2		
(gelation/crystallization,	(3/1)	1.05×10^4			
heat-treated at 150 °C)	(1/1)	6.92×10^2			
LMWPE-UHMWPE-CB (gelation/crystallization, heat-treated at 170 °C)	(9/1)	1.07×10^5	4.68×10^5	1.03×10^5	1.01×10^5

(106 °C) of LMWPE. According to Narkis et al. [5], the PTC intensity was defined as the ratio (R_P/R_{RT}) of peak resistivity R_P to room temperature resistivity R_{RT}. For the present specimen, the values R_P and R_{RT} increase as the heating run cycle continues. The PTC intensities for each run are listed in Table 2. The resistivity increases by 5 or 6 orders of magnitude, but a weak point at PTC materials for self-regulating heaters, current limiters and over-current protectors is the increase in resistivity at room temperature with thermal cycling. PTC materials must satisfy the condition that the resistivity at room temperature is independent of thermal cycling. In addition, their PTC intensity must increase by 5 or 6 orders of magnitude. From Fig. 2b, the resistivity versus temperature measurement shows that 150 °C ensures the maximum value of the ratio (R_P/R_{RT}) and is therefore the best heat-treatment temperature.

In addition to the poor reproducibility of resistivity at room temperature (Fig. 2a), another weak point of LMWPE-CB composites as PTC materials is poor dimensional stability. To improve this a lot of effort has been made to develop UHMWPE-CB composites, since the shape of UHMWPE films can be maintained without any flow for several hours even at 180 °C higher than the equilibrium melting point (145.5 °C) [27]. To eliminate the two weak points, the temperature dependence of resistivity was investigated for two kinds of LMWPE-UHMWPE-CB blends prepared by the kneading method and the gelation method.

Electrical conductivity of LMWPE-UHMWPE-CB blend systems

The temperature dependence of resistivity for the LMWPE-UHMWPE-CB composite with LMWPE/UHMWPE composition of 9/1 for three heating runs is shown in Fig. 3a. The specimen was prepared by the kneading method. The PTC intensity, R_P/R_{RT}, for the first run is about 5 orders of magnitude. The ratio (R_P/R_{RT}), however, decreases drastically in the second run, but the value is not affected by the third run. The drastic decrease in R_P/R_{RT} with the number of thermal cycles is a serious drawback for a PTC material. Even so, the introduction of small amounts of UHMWPE ensures better reproducibility of the resistivity at room temperature in comparison with LMWPE-CB composites (Fig. 2).

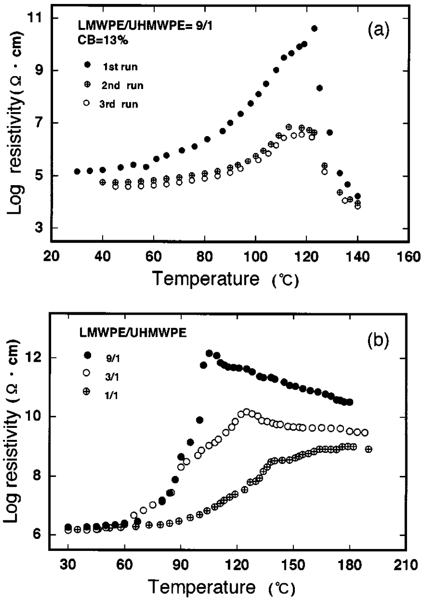

Fig. 3 a Electrical resistivity against temperature of LMWPE-UHMWPE-CB kneading specimens with LMWPE/UHMWPE of 9/1 and 13 wt% CB. **b** Electrical resistivity against temperature of LMWPE-UHMWPE-CB gel films with LMWPE/UHMWPE of 9/1, 3/1, 1/1 and 13 wt% CB, in which the specimens were heat-treated at 150 °C after being pressed at 70 °C

The temperature dependence of resistivity for LMWPE-UHMWPE-CB systems for three kinds of LMWPE/UHMWPE compositions, 9/1, 3/1 and 1/1 is shown in Fig. 3b. The CB content was 13 wt%, corresponding to the critical concentration. The composites were prepared by gelation/crystallization from solution and the resultant dry films were pressed at 70 °C and subsequently heat-treated at 150 °C for 35 min. The PTC intensity increases with increasing

LMWPE content and the value reaches 6 orders of magnitude for the 9/1 composition indicating that LMWPE plays an important role in improving the PTC effect. Furthermore, the resistivity at room temperature achieves almost the same value, independent of LMWPE content. In Fig. 3, it is evident that the value of R_P/R_{RT} of the composite obtained by the gelation method is almost the same as that obtained by the kneading method, but the NTC effect of the gel film beyond 120 °C is less intense.

Figure 4 shows the temperature dependence of resistivity for LMWPE-UHMWPE-CB composites with LMWPE/UHMWPE of 9/1 and 13 wt% CB which were prepared by the gelation method and pressed at 70 °C and which were subsequently heat-treated at the indicated temperatures for 35 min. For the specimen pressed at 70 °C, the resistivity is almost independent of temperature and the values are in the range 10^9–10^{10} Ω cm. Interestingly, the PTC effect suddenly becomes significant for the specimen after heat treatment at 150 °C. This effect, however, becomes less intense with further increase in the heat-treatment temperature. Especially, the significant increase in resistivity could not be observed for the specimens heat-treated above 190 °C. The drastic change in resistivity with increasing temperature is very sensitive to the heat-treatment temperature of the test specimens, and is due to the change in morphology of the specimens. Preliminary WAXD experiments revealed that the specimen pressed at 70 °C perfectly maintains the original morphology of the specimen which was prepared by gelation/crystallization and which was dried under ambient conditions; namely, the specimen is composed of crystal lamellae which are highly oriented with their large flat faces parallel to the film surface but are randomly oriented with respect to the film surface, and within the crystal lamella, the *c*-axes are oriented perpendicular to the large flat faces. Such morphology is similar to that of single crystal mats. Such specimens contain a number of voids which hamper the formation of conductive channels of CB particles and provide large resistivity at room temperature. Because of the disappearance of a number of voids with increasing heat-treatment temperature, alignment of CB particles makes it easier to form conductive channels and the resistivity becomes lower. However, the question which arises is why the specimen heat-treated above 190 °C shows a poor PTC effect. This is probably due to the fact that a number of conductive channels within the specimen are broken by thermal expansion of the specimen. The preferential orientation of the *c*-axes with respect to the film surface becomes poorer and no fibrous structure within the specimen heat-treated above 190 °C could be observed under scanning electron microscopy. Accordingly, we emphasize that the heat-treatment temperature of test specimens is one of the most important factors to ensure a good PTC effect.

Returning to Fig. 3, it is seen that the maximum PTC intensity for the specimen of 9/1 composition prepared by the gelation method is almost the same as that for the specimen prepared by the kneading method for the first run, but the NTC effect for the specimen prepared by the gelation method is less pronounced indicating better thermal properties for PTC materials. To check such thermal behavior, DSC measurement was made. The results obtained for the specimens treated above 150 °C are shown in Fig. 5. Two endotherm peaks become drastically smaller compared with those of the original specimen indicating the decrease in crystallinity of LMWPE and UHMWPE. Detailed observation reveals that the endotherm peaks become slightly smaller with increasing heat-treatment temperature beyond 150 °C but the change can be negligible. This means that regardless of the proposal by Meyer [2–3] the PTC effect is not sensitive to the crystallinity, but is affected by the disappearance of a number of voids within the test specimens, as discussed before.

To check the reproducibility of the resistivity with temperature, measurements were carried out during heating and cooling cycles for the 9/1 composition

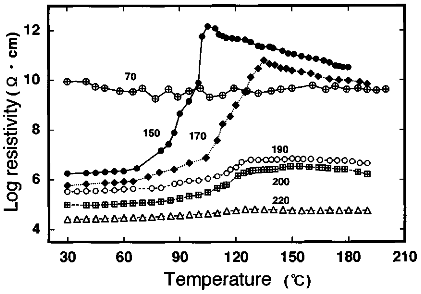

Fig. 4 Electrical resistivity against temperature of LMWPE-UHMWPE-CB gel films with LMWPE/UHMWPE of 9/1 and 13 wt% CB content, in which the specimens were heat-treated at various temperature after being pressed at 70 °C

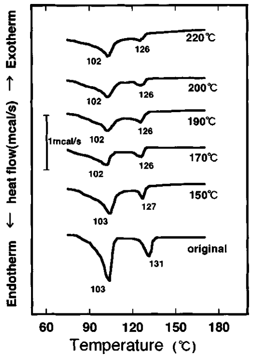

Fig. 5 Differential scanning calorimetry curves for specimens corresponding to those in Fig. 4

(13 wt% CB) heat-treated at 150 °C (Fig. 6). In the first run, the difference in resistivity between the heating and cooling processes is not so large; however the resistivity during the second heating run is much lower than that during the first heating run as the temperature is higher than 90 °C. Unfortunately, this behavior indicates that the specimen heat-treated at 150 °C is not superior to the LMWPE-CB systems shown in Fig. 2 as PTC materials.

To look for more improved reproducibility, the temperature dependence of resistivity was measured for the specimen heat-treated at 170 °C. Figure 7a shows the results during heating and cooling processes for the first and second runs, while Fig. 7b shows the results during the heating process for four cycles. The test specimen shows good reproducibility. The same experiment was done for 15 samples and good reproducibility could be confirmed for all specimens. The resistivity during the cooling process takes almost the same values as those of the heating process. Such good reproducibility has never been reported for LMWPE-CB composites prepared by the kneading method. Incidentally, the same reproducibility was maintained for increases in the number of thermal cycles of up to 10 times. In spite of heating up to 190 °C, the NTC effect is not considerable and the resistivity at room temperature is almost constant within experimental error as increasing in the number of thermal cycles. This indicates a much better PTC effect than that observed for cross-linked LMWPE-CB composites. Preliminary experiments confirmed that the NTC effect of the cross-linked LMWPE composites becomes considerable at 170–190 °C due to flow of PE chains. Consequently, the reproducibility becomes worse with thermal cycling. Of course, the reproducibility became better with increasing cross-linking points by increasing the anti-oxidant such as dicumyl peroxide, but the PTC effect was less intense.

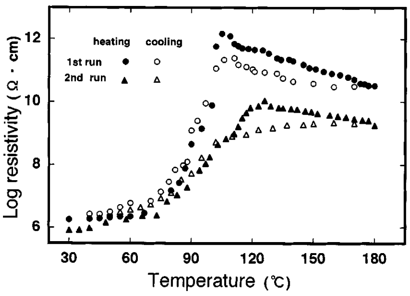

Fig. 6 Reproducibility of electrical resistivity against temperature of LMWPE-UHMWPE-CB gel films with LMWPE/UHMWPE of 9/1 and 13 wt% CB during repeated temperature cycles, in which the specimen was heat-treated at 150 °C after being pressed at 70 °C

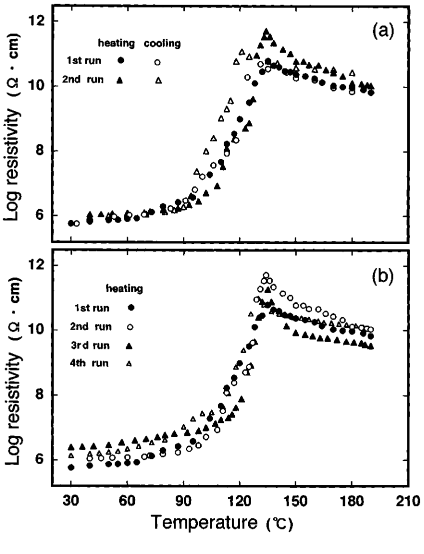

Fig. 7a, b Electrical resistivity against temperature of LMWPE-UHMWPE-CB gel films with LMWPE/UHMWPE of 9/1 and 13 wt% CB under repeated temperature cycles, in which the specimen was heat-treated at 170 °C after being pressed at 70 °C. **a** First and second heating and cooling runs, **b** four thermal cycles

X-ray diffraction intensity distributions at high temperature measured for the gel films heat-treated at 70, 170 and 220 °C are shown in Fig. 8. After measuring X-ray intensity distributions at 180–220 °C, the specimens were slowly cooled down to room temperature. In spite of the big difference in the PTC effects at the different heat-treatment temperatures shown in Fig. 4, the specimens corresponding to each heat-treatment temperature show similar diffraction profiles at elevated temperature. This means that the X-ray diffraction technique is meaningless for the analysis of the heat-treatment effect of the PTC effect. Even so, the X-ray profiles give important information about the PTC intensity. The increase in resistivity occurs during the melting process of the crystallites. Moreover, the maximum of the PTC effect appeared at 135 °C and was associated with complete melting of the crystallites.

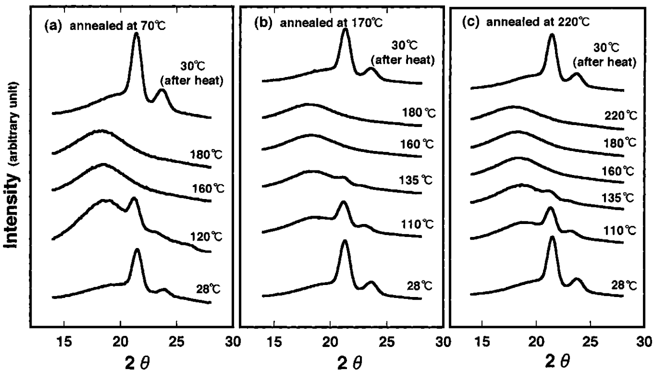

Fig. 8 X-ray diffraction intensity distribution curves at elevated temperatures measured for gel films which were heat-treated at **a** 70 °C, **b** 170 °C and **c** 220 °C

Different heat-treatment temperatures show similar X-ray intensity profiles for the three specimens in the temperature range 160–220 °C.

Figure 9 shows $\Delta L/L_0$ measurement against temperature under no stress for gel films, where L_0 is the original length before heating, and ΔL is given as $L - L_0$, where L is the length at the measuring temperature. At $\Delta L > 0$, the specimen exhibits thermal expansion, while at $\Delta L < 0$ the specimen undergoes thermal shrinkage. Figure 9a shows the behavior of specimens (13 wt% CB) with 3/1 and 9/1 compositions heat-treated at 150 °C, in which $\Delta L/L_0$ takes positive values in the given temperature range. Beyond 120 °C, $\Delta L/L_0$ increases drastically for the specimen with 3/1 composition; in contrast, $\Delta L/L_0$ for the 9/1 composition tends to level off and increases drastically at 180 °C. Returning to Fig. 3b, the PTC intensity for the 9/1 composition appears at 105 °C and is more intense than that for 3/1 composition at 122 °C. This result is contradictory to the common sense view of the PTC effect. According to the previous concept [28], the PTC effect is due to the fact that the enlargement of the distance between two particles causes the conducting network to be broken up owing to a drastic increase in thermal expansion of the specimen at temperatures close to melting point of PE. If this was the case, the increase in $\Delta L/L_0$ for the 9/1 composition should be more pronounced in comparison with that for the 3/1 one. This still remains an unsolved problem.

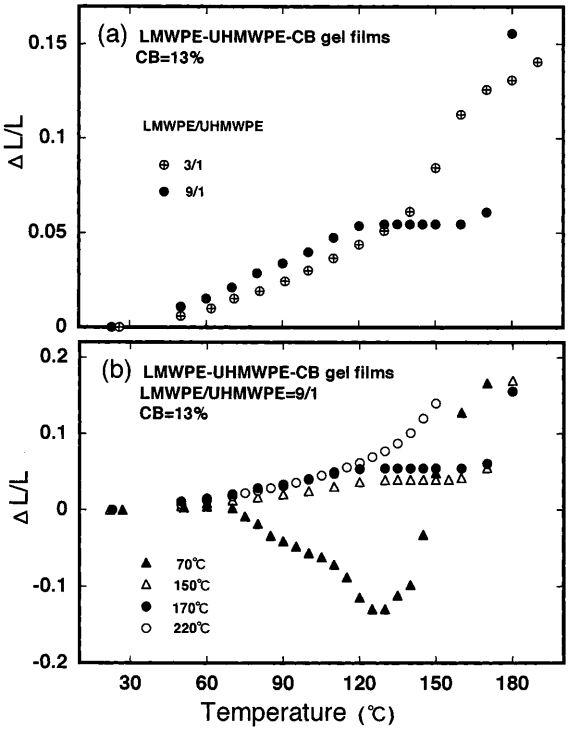

Fig. 9a, b $\Delta L/L_0$ against temperature for LMWPE-UHMWPE-CB gel films. **a** LMWPE/UHMWPE = 3/1 and 9/1 with 13 wt% CB, in which specimens were heat-treated at 150 °C after being pressed at 70 °C. **b** LMWPE/UHMWPE = 9/1 and 13 wt% CB, in which specimens were heat-treated at various temperatures after being pressed at 70 °C

Figure 9b is concerned with the thermal behavior of composites with 9/1 composition and 13 wt% CB heat-treated at different temperatures. When the specimen is pressed at 70 °C, $\Delta L/L_0$ takes negative values in the given temperature range indicating rubber elasticity and this tendency becomes more pronounced up to 125 °C: the reverse relationship occurred above 125 °C and $\Delta L/L_0$ takes positive values beyond 150 °C. When the specimen is heat-treated at 220 °C, $\Delta L/L_0$ takes positive values and the value increases drastically beyond 120 °C. The thermal behavior of the heat treatment at 170 °C is almost similar to that of the heat treatment at 150 °C.

Let us consider the relationship between the thermal behavior in Fig. 9b and the PTC effect in Fig. 4. When specimens are heat-treated as 150 °C and 170 °C, $\Delta L/L_0$ takes constant values in the range 120–170 °C, indicating dimensional stability of the specimen which is the reason for the low NTC effect. However, in Fig. 4, the resistivity of the specimen pressed at 70 °C decreases slightly up to 120 °C and tends to level off at further elevated temperature. The slight decrease in resistivity reflects the negative value of $\Delta L/L_0$, but the resistivity takes constant values in spite of the drastic increase in $\Delta L/L_0$. This contradiction is also observed for specimens heat-treated at other temperatures. In spite of large thermal expansion, PTC the effect of the specimen heat-treated at 220 °C is not intense. Thus, the result of Fig. 4 and 9b are contradictory to the common sense view that the PTC effect is due to the thermal expansion of the specimen causing the enlargement of the distance between two particles and disturbing the conducting network.

Scanning electron microscopy for LMWPE-UHMWPE-CB blend systems

Scanning electron micrographs for gel films with 9/1 composition and 13 wt% CB are shown in Fig. 10. In these specimens, CB particles could not be observed on the surface, indicating that the surface energy of CB is much higher than that of PE. Hence, a series of micrographs was taken from the edge of each specimen, which was immersed into liquid nitrogen and split by hand. In Fig. 10a, fine UHMWPE filaments can be observed within the original dry gel film. The fine filaments were buried in the LMWPE matrix by pressing at 70 °C (Fig. 10b). On heat treatment at 170 °C, the fine filaments of UHMWPE became a mesh-like continuous structure covering the LMWPE

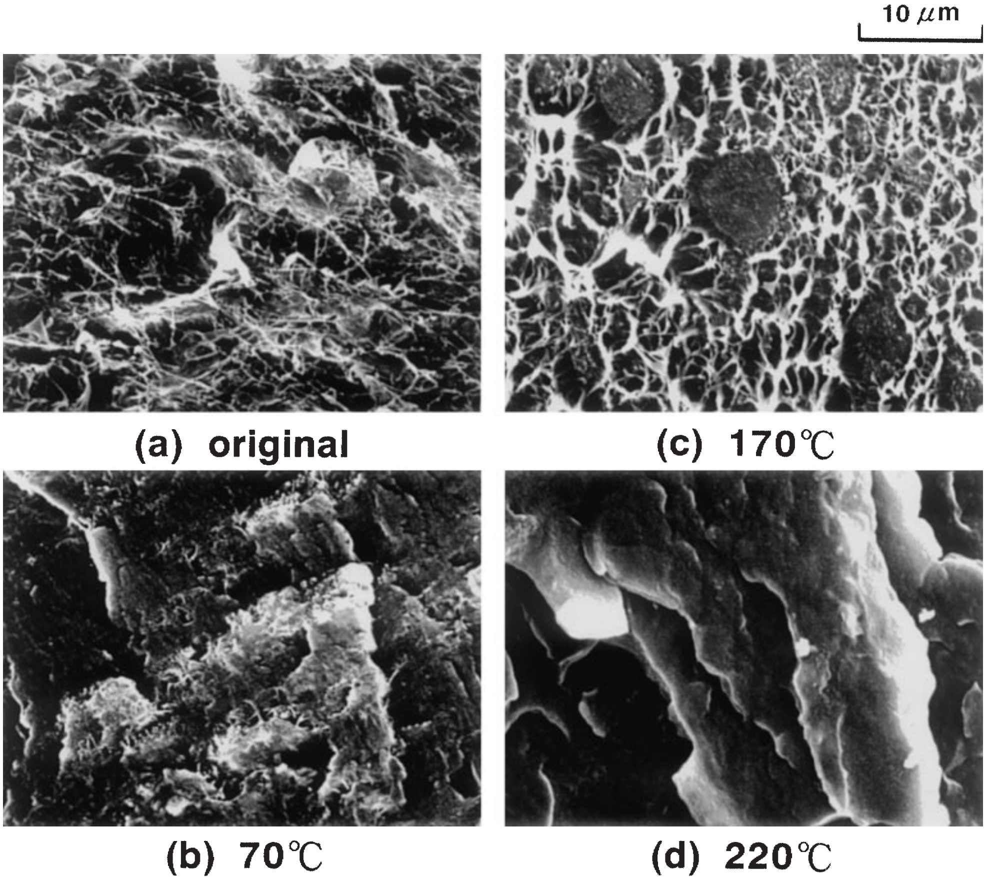

Fig. 10a–d Scanning electron micrographs of specimens prepared by gelation/crystallization. The specimens were heat-treated at various condition. **a** Original dry gel (no heat treatment), **b** pressed at 70 °C, **c** heat-treated at 170 °C after being pressed at 70 °C, **d** heat-treated at 220 °C after being pressed at 70 °C

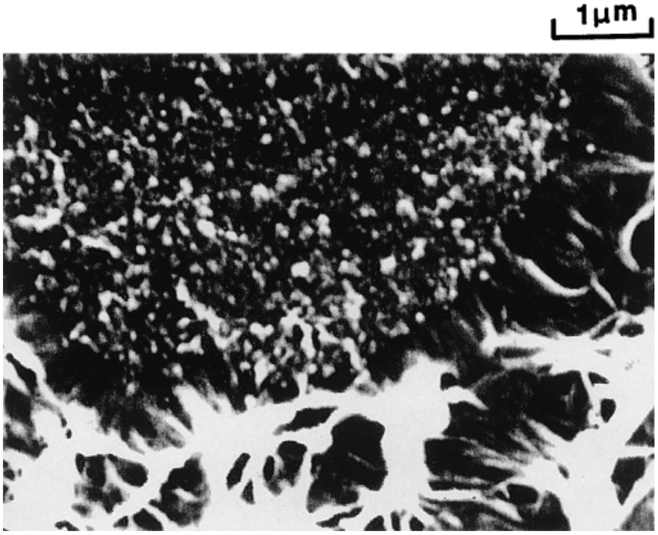

Fig. 11 Enlargement of photograph **c** in Fig. 10

domains (Fig. 10c). This mesh-like structure disappeared on melting at 220 °C (Fig. 10d), indicating that mixing of UHMWPE and LMWPE occurred at a macroscopic level. The same specimen treated at 220 °C did not show a significant PTC effect. Judging from the results shown in Figs. 4 and 7, it is evident that the PTC effect is strongly affected by the UHMWPE mesh-like structure.

CB particles did mix with UHMWPE and mixed only with LMWPE as shown in Fig. 11, which corresponds to the enlargement of Fig. 10c. It is seen that a number of CB particles (observed as an agglomerate of white particles) are dispersed in the LMWPE matrix and no CB particles could be observed in the UHMWPE fibrils.

Scanning electron micrographs for LMWPE-CB and LMWPE-UHMWPE-CB (9/1 composition) prepared by the kneading method are shown in Fig. 12. The micrographs on the right side are enlargements of those on the left side. Heat treatment of LMWPE-CB and LMWPE-UHMWPE-CB was carried out at 150 and 170 °C, respectively. No fibrous structure of UHMWPE within the 9/1 composite is observed in Fig. 12b. The PTC effect for both specimens are shown in Figs. 2 and 3a. Both specimens have a PTC intensity of 5–6 orders of magnitude, but the reproducibility was poor.

Returning to Fig. 7, it may be noted that the best PTC effect and reproducibility are obtained for the specimens heat-treated at 170 °C. Judging from the micrographs in Fig. 10 and 11, the PTC effect of the gel

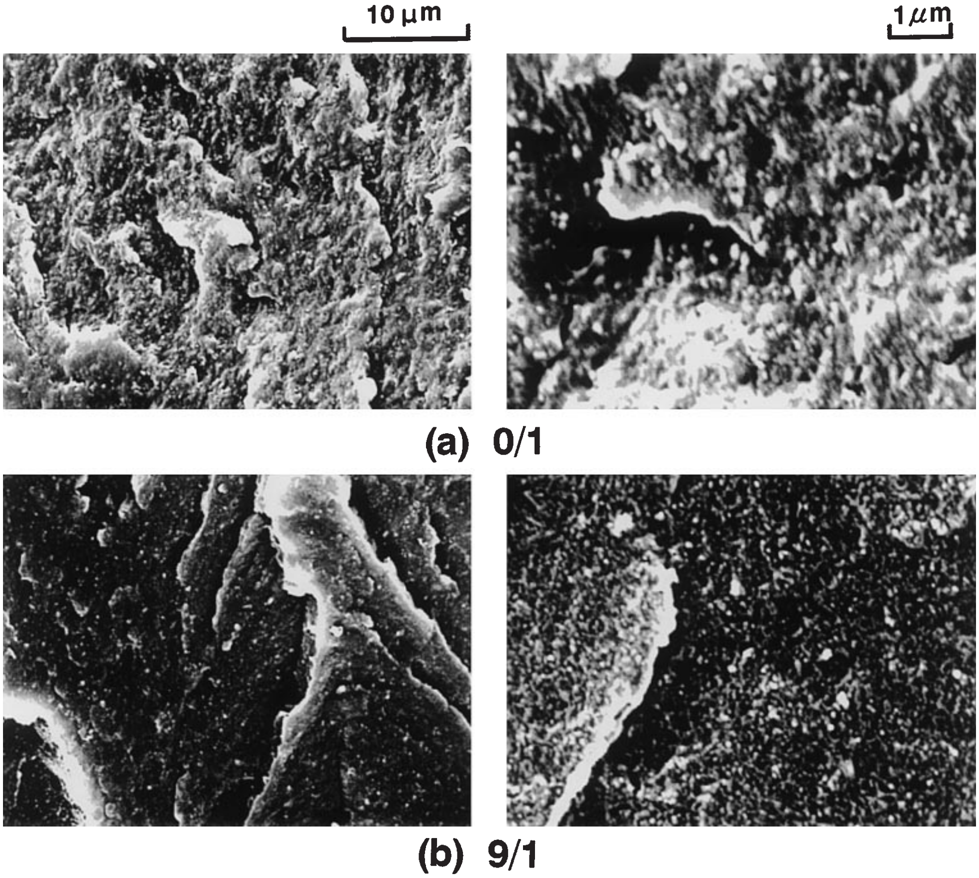

Fig. 12a, b Scanning electron micrographs of the specimens prepared by the kneading method, in which the micrographs on the right side are enlargements of those on the left **a** LMWPE-CB composite (13 wt% CB), **b** 9/1 composition (13 wt% CB)

film is similar to that of LMWPE-CB prepared by the kneading method, since most of the CB particles are dispersed in LMWPE. Accordingly, it may be concluded that the mesh-like continuous structure of UHMWPE, which has very low melt index, plays important roles. First, to avoid the drastic NTC effect which has been observed for the LMWPE-CB system, second, to ensure a PTC intensity of 5 orders of magnitude, and third, to provide good reproducibility of the PTC effect. In other words, it is indispensable to avoid flowing of the LMWPE chains to ensure drastic improvement of reproducibility.

Conclusion

Drastic improvement of the PTC effect was achieved using LMWPE-UHMWPE-CB blends prepared by gelation/crystallization from dilute solution. The PTC effect was most significant for specimens with a LMWPE/UHMWPE composition of 9/1 containing 13 wt% CB heat-treated at 170 °C. The maximum PTC intensity was about 5 orders of magnitude, which was almost equal to that observed for LMWPE-CB composites prepared by the kneading method. The resistivity versus temperature during cooling was almost the same as that during heating. The resistivity at room temperature was almost independent of the number of thermal cycles. Such good reproducibility has never been reported for LMWPE-CB composites. X-ray diffraction experiments and the thermal expansion of specimens revealed that the melting of crystallites and the enlargement of the distance between two CB particles are not sensitive to the achievement of a better PTC effect. Under scanning electron microscopy, phase separation of LMWPE and UHMWPE could be observed in specimens heat-treated at 170 °C. UHMWPE formed a continuous network fibrous structure covering the LMWPE domains. CB particles were dispersed only in the LMWPE matrix and no CB particles were found on the UHMWPE fibrils. Such morphology implies that the PTC effect of the LMWPE-UHMWPE-CB system is similar to that obtained in LMWPE-CB composites prepared by a kneading method. The essential difference between the PTC effects of LMWPE-UHMWPE-CB composites prepared by gelation and those of LMWPE-CB composites prepared by kneading is thought to be due to the existence of a network structure of UHMWPE with a very low melt index.

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