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ORIGINAL CONTRIBUTION

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Morphology and electric conductivity of cross-linked polyethylene–carbon black blends prepared by gelation/crystallization from solutions

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Abstract Ultra-high-molecular-weight polyethylene (UHMWPE) – carbon black (CB) blends were prepared by gelation/crystallization from PE dilute solutions containing CB particles. The UHMWPE/CB composition chosen were 1/0.15, 1/0.25, 1/0.5, 1/0.75, 1/1, 1/3, 1/5, and 1/9, etc. The cross-linking of PE chains was performed by chemical reaction of dicumyl-peroxide at 160 °C. X-ray diffraction patterns indicate that the crystallinity of PE within the blends decreased drastically through the chemical reaction at high temperature. The sample preparation method by gelation/crystallization provided the UHMWPE–CB system with various CB contents up to 90% and the conductivities for the resultant specimens were in the range from 10^{-9} to 1 $\Omega^{-1}\,\mathrm{cm}^{-1}$ corresponding to the electric conductivity range of semiconductors. The blends assured thermal stability of electric conductivity by cross-linking of PE chains, although the mechanical property such as the storage and loss moduli were very sensitive to temperature. The conductivity of the blends with CB content $\geq 20\%$ were almost independent of temperature up to 220 °C and the values in the heating and cooling processes were almost the same. On the other hand, for the UHMWPE–CB blends with 13% CB content corresponding to the critical one, temperature dependence of electric resistivity showed positive temperature coefficient (PTC) effect. The PTC intensities for non-cross-linked and cross-linked materials were lower than that of the corresponding low-molecular-weight-polyethylene (LMWPE)–CB blend but the maximum peak appeared at 160 °C which is higher than the peak temperature of LMWPE–CB blend.

Key words UHMWPE–CB blends – gelation/crystallization – cross-linking – thermal stability – electric conductivity – PTC effect

Introduction

Polymers in their pure state are excellent electrical insulators. But polymers can be modified in processing to be relatively good electrical conductors by simple creating mixtures of a good conductor and a polymer [1–26]. Among conductor-filled polymers, carbon black (CB) filled polyethylene (PE) is one of typical good conductive materials. The most of investigations has been concentrated on positive temperature coefficient (PTC) effect associated with a drastic increase in electric resistivity at temperature range close to melting point of PE indicating that the enlargement of the distance between two particles causes

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the conducting network to be broken up [3–11, 18–20]. The resistivity has a maximum peak around melting point of PE and it decreases with further increase in temperature. The values, however, were in the range 90–120 °C, since low molecular weight polyethylene (LMWPE) with low viscosity has been used as test specimens.

Apart from the study on PTC effect, it is of interest to consider thermal stability of the electric conductivity of blend materials with very large amounts of CB particles. For this purpose, ultra-high molecular weight polyethylene (UHMWPE) was employed as a test polymer because of very high viscosity even at temperatures higher than melting point. In accordance with our preliminary experiments, very high viscosity invoked the difficulty in preparing UHMWPE–CB composite materials by kneading technique. Accordingly, the sample preparation was done by gelation/crystallization from decalin solution [27–32], and this method has the advantages to prepare blends with various CB contents. The maximum CB content within LMWPE–CB blend prepared by kneading method was 65%. To assure further thermal stability of electric conductivity, cross-linking of PE was performed by chemical reaction by using dicumyl peroxide (DCP) [33–35]. In addition to the above concept, PTC effect of UHMWPE–CB materials is investigated by using the blend system with critical content of CB particles, in terms of the relationship between PTC intensity magnitude and the temperature showing the maximum peak of PTC intensity.

Incidentally, the present study has two purposes in terms of industrial aspect. One main purpose is the production of the materials with thermal stability of electric conductivity. The other is the production of self-regulating heaters which can be operated at higher temperatures than the usual temperature (100–120 °C) reported for LMWPE–CB systems already.

Experimental section

The sample preparation was done by using UHMWPE (Hercules 1900/90189) with an intrinsic viscosity of 30 dl/g corresponding to an average molecular weight of 6×10^6 and CB particles with commercial name of BLACK PEARLS 880 which was furnished by Cabot Co. Ltd. The observation by electron microscopy and DBP measurements indicated that the particles size of the CB particle is about 16 nm and the number of connected particles indicating a beads-like structure is about 10. The solvent was decalin. The UHMWPE/CB compositions were 1/0.15, 1/0.25, 1/0.5, 1/0.75, 1/1, 1/3 and 1/9, etc. The solutions containing 0.5% (w/w) UHMWPE and CB particles were prepared by heating the well-blended polymer/solvent mixture at 150 °C for 30 min under nitrogen [30–32]. The volume of solution was controlled to obtain the film whose thickness is 700–800 μm. The hot homogenized solution was quenched by pouring it into an aluminium tray at room temperature, thus generating a gel. The decalin was allowed to evaporate from their gel under ambient conditions. When the volume of the gel approached a 70% decrease, a decalin solution of DCP containing 5 or 20% of UHMWPE was poured into the aluminium tray at 50 °C. The nearly dry gels like rigid sponge were vacuum-dried for 1 day to remove residual traces of decalin as much as possible. Cross-linking was performed at 110 °C for 31 h or at 160 °C for 40 min by sandwiching the specimen between hot plates. The cross-linked specimen showed smooth surfaces like melt films.

The densities of the composite materials as well as PE dry gel and melt films were measured by a pycnometer using a mixture of carbon tetrachloride and toluene or a mixture of methyl-iodide and ethanol as a medium. Before the measurement was made, the specimen was cut into fragments and vacuum-dried for 1 d. Only for polyethylene dry gel and melt films, the degree of crystallinity was calculated by assuming intrinsic densities of the crystalline and amorphous phases to be 1.000 and 0.852 g/cm^3, respectively [36]. The measurements of the densities for obtaining the thickness of the blends is needful to estimate the cross-section area on measuring the storage and loss moduli.

Electric conductivity was measured by the two-terminal method for the direction parallel to the film surface direction at 23 ± 2 °C and at relative humidity of 50 ± 5%. To prepare test specimens, the composite material was cut into strips of length 25 mm and width 15 mm. The electric conductivity was measured by using the specimen which was clamped between copper metal jaws. The distance between the jaws was 10 mm. Before the measurements, the specimen was polished by sandpaper to level off the both sides smoothly, since the contact resistance depends on the sample surface quality. The conductivity $> 10^{-6}\ \Omega^{-1}\,\mathrm{cm}^{-1}$ was calculated by measuring voltage yielded when a constant current of 0.1–1 mA was applied. On the other hand, the conductivity $< 10^{-6}\ \Omega^{-1}\,\mathrm{cm}^{-1}$ was calculated by measuring current yielded when a voltage of 10 VDC was applied. Electrical conductivity ($> 10^{-3}\ \Omega^{-1}\,\mathrm{cm}^{-1}$) of low-resistivity material was calculated by measuring the voltage yielded when a constant current of 1 mA to 100 nA was applied. The measurement was performed by four-point probe method.

The temperature dependence of the complex tensile modulus functions was measured by a visco-elastic spectrometer (VES-F) of the Iwamoto Machine Co. Ltd. The specimens used in this experiment were cut to a length of 60 mm and width of 1.5 mm and were clamped over a length of 10 mm at the ends. The measurement was carried out over a temperature range of −150 to 300 °C at a fixed frequency of 10 Hz [37]. In actual measurement, the film was subjected to static strain due to the desired stress in order to apply a dynamic displacement of 0.02–0.06 mm smoothly.

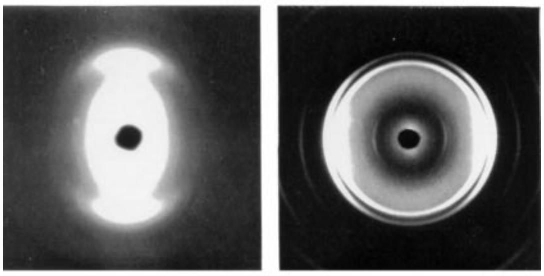
The thermal behavior was estimated from the melting endotherm in differential scanning calorimetry (DSC) and the morphology was investigated by wide angle X-ray diffraction (WAXD), small angle X-ray scattering (SAXS) and scanning electron microscopy. The procedure of these observations were same as described elsewhere [34].

Results and discussion

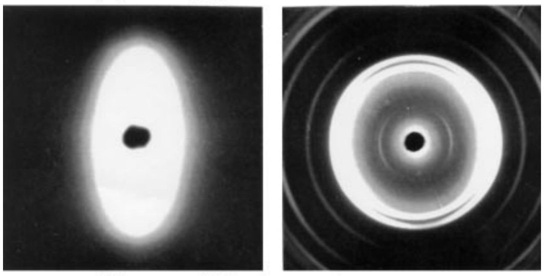
Morphology and thermal properties of UHMWPE–CB blends

Figure 1a shows SAXS and WAXD patterns (end view) from the dry gel PE film (original) containing no CB particle but 20% DCP. The WAXD pattern of the dry gel film with 20% DCP content indicates the preferential orientation of the *c*-axes perpendicular to the film surface and the corresponding SAXS pattern, the meridional scattering maxima corresponding to a long period of about 11 nm. The two patterns together indicate that within the lamellar crystals constituting the gel, the *c*-axes are oriented perpendicular to the large flat faces. This is due to the fact that when the as-cast PE gel films with 20% DCP are dried by slow evaporation of the solvent, the constituent lamellar crystals become oriented parallel to the film surface in a manner similar to mats of single crystals [29, 31, 38]. Such morphology is perfectly equal to that of an original dry gel film with no DCP reported already [38]. Namely, the morphology of dry PE gel is hardly affected by the introduction of DCP (20% content). When the specimen was heat-treated at 110 °C for 31 h, the scattering maxima in the SAXS pattern becomes indistinct indicating an increase in orientational fluctuation of the crystal lamellae and the preferential orientational degree of the *c*-axes observed by the WAXD pattern becomes slightly lower. When the annealing temperature is increased, the WAXD and SAXS patterns are strongly affected. The WAXD pattern from the specimen heat-treated at 160 °C for 40 min shows an amorphous ring and it is evident that the peroxide decomposition and concomitant cross-linking are enhanced with increasing chemical reaction temperature, since most of DCP contributes to the occurrence of vulcanization particles. Incidentally, the profile of SAXS pattern is similar to that for which the PE gel film without DCP was annealed.

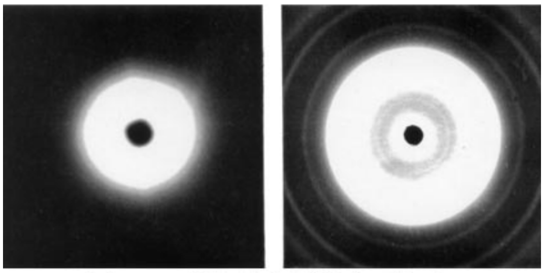
PE/CB= 1/0



(a) PE dry gel film with 20% DCP



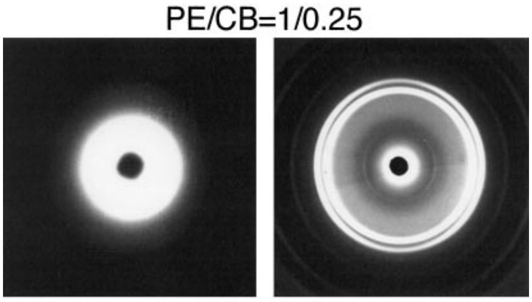
(b) cross-linked at 110℃ for 31h



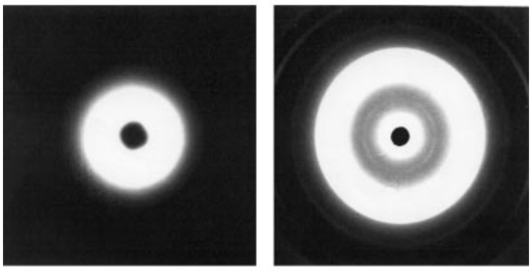
(c) cross-linked at 160℃ for 40 min

Fig. 1 WAXD and SAXS patterns (end view) from dry gel PE films in pairs. (a) PE dry gel film with 20% DCP, (b) cross-linked specimen at 110 °C for 31 h and (c) cross-linked specimen at 160 °C for 40 min

Figure 2 shows SAXS and WAXD patterns (end view) in pairs, in which the patterns (a) and (b) were observed for original and cross-linked specimens with 1/0.25 composition, respectively. The original specimen means the blend prepared by gelation/crystallization from solution and dried without any heat-treatment and any cross-linking. For cross-linked specimen, the cross-linking was performed by chemical reaction at 160 °C for 40 min. In comparison with the SAXS and WAXD patterns in Fig. 1a for PE dry gel film with 20% DCP, it is seen that the introduction of 20% CB particles (1/0.25 composition) allows the drastic orientational fluctuation of crystal lamellae. To avoid misunderstanding, it should be noted that the apparent densities of PE and CB particles are 0.976 and 0.336 g/cm^3, respectively, since the CB particles contain a number of voids. Actually, 1/0.25 composition by weight fraction corresponds to 1/0.726 one by volume fraction. This means that the introduction of such amounts of CB particles hampers the orientation of the constituent lamellar crystal parallel to the material surface, when the

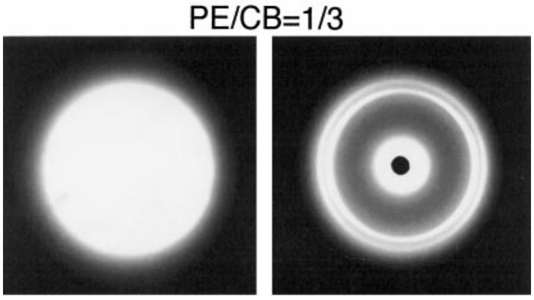


(a) original

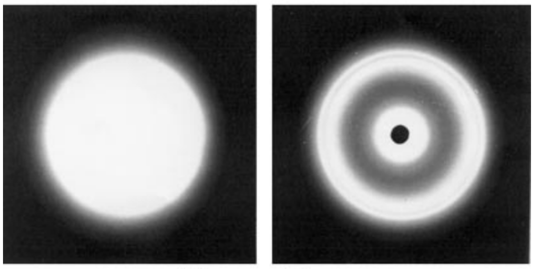


(b) cross-linked

Fig. 2 SAXS and WAXD patterns (end view) from two kinds of PE–CB blends with 20% content. (a) non-cross-linked blend and (b) cross-linked blend



(a) original



(b) cross-linked

Fig. 3 SAXS and WAXD patterns (end view) from two kinds of PE–CB blends with 1/3 composition (75% CB content). (a) non-cross-linked blend (original) and (b) cross-linked blend

as-cast PE gels are dried by slow evaporation of the solvent. Namely, the WAXD pattern shows diffraction rings from the (1 1 0) and (2 0 0) planes and SAXS pattern, circular-type diffuse scattering.

Figure 3 shows SAXS and WAXD patterns (end view) in pairs, in which the patterns (a) and (b) were observed for original and cross-linked specimens with 1/3 composition, respectively. The cross-linking was also performed by chemical reaction at 160 °C for 40 min. In comparison with the SAXS and WAXD patterns for the no-cross-linked (original) specimens in Figs. 1 and 2, the diffuse scattered intensity from CB particles in the SAXS pattern becomes more intense with increasing the content of CB particles. In contrast, it is seen that the WAXD rings from the (1 1 0) and (2 0 0) planes for cross-linked blend become more distinct than those for the PE film and the blend with 1/0.25 composition. This indicates that the introduction of a lot of the CB particles disturbs the cross-linking of PE chains. To check the phenomenon, WAXD intensity distribution was observed as a function of twice the Bragg angles.

Figure 4a shows diffraction intensity distribution for the cross-linked and non-cross-linked (original) PE dry gel films and Fig. 4b, for the cross-linked and non-cross-linked blends with 1/3 composition. The drastic decrease in the diffraction intensity from the (1 1 0) and (2 0 0) planes was observed by cross-linking at 160 °C and this tendency was more significant for the PE homopolymer. The decrease in the intensity from the (1 1 0) plane for PE homopolymer is more drastic than that for the 1/3 blend. This indicates that the cross-linking of PE chains becomes less pronounced by the introduction of large amount of CB particles. The small decrease in diffraction intensity of the (2 0 0) plane remains an unresolved problem. Incidentally, close observation reveals that a small shoulder associated with the scattering from the PE amorphous phase appeared at around 19.8° (twice the Bragg angle) for PE homopolymer and the PE/CB blend.

Figure 5 shows DSC curves for the four kinds of specimens with the indicated PE/CB compositions. In each part, the curves (a), (b) and (c) correspond to the cross-linked specimen, heat-treated specimen with no cross-linking, and the specimen without any heat-treatment (original), respectively. The heat-treatment was done for 40 min at 160 °C, higher than the equilibrium melting point (145.5 °C) [39] of PE and cooled down quickly to room temperature. The same heat-treatment condition was selected for the specimens with no DCP in order to make clear the cross-linking effect. To check the reproducibility of the profiles measured for cross-linked, heat-treated, and original specimens, DSC measurements about a given composition were carried out several times. For the curves of each original specimen, the endotherm peak intensity becomes smaller with increasing the CB content but the melting point of all the specimens appeared at 142 °C, which is independent of the CB content. For the

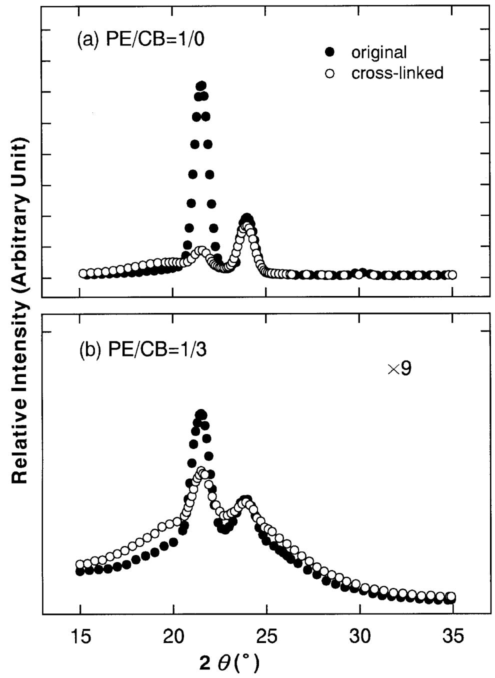


Fig. 4 X-ray diffraction intensity distribution (a) non-cross-linked (original) and cross-linked PE films; (b) non-cross-linked and cross-linked PE–CB blends with 1/3 composition

heat-treated specimens, the drastic decrease in peak intensity was observed and the peak shifts to 136 °C. This is due to the decrease in crystallinity and the decrease in crystal size. In accordance with preliminary experiments, the crystallinity for the specimen with 1/0 composition (PE homopolymer) decreased from 84.0% to 57.3% and the peak shape by X-ray diffraction measurements became broader. The peak becomes smaller in proportional to the CB content but the peak appeared at 136 °C for all the specimens. This indicates that the changes in crystallinity and crystal size by heat-treatment are independent of the introduction of CB particles. For each cross-linked specimen, the peak shifts to lower temperature and the melting point is affected by the amount of the CB particles. The peak of the cross-linked specimen with 1/9 composition could not be observed, since the PE content within the original specimen is very small. Interestingly, the melting point of the specimen with 1/3 composition is higher than those of the specimens with 1/1 composition indicating that change in crystallinity and crystal size become less pronounced, as the CB particles increase. Namely, this indicates that the existence of CB particles hampers the cross-linking of PE by chemical reaction. This result supports the profile of peak intensity which was obtained by X-ray diffraction (see Fig. 4).

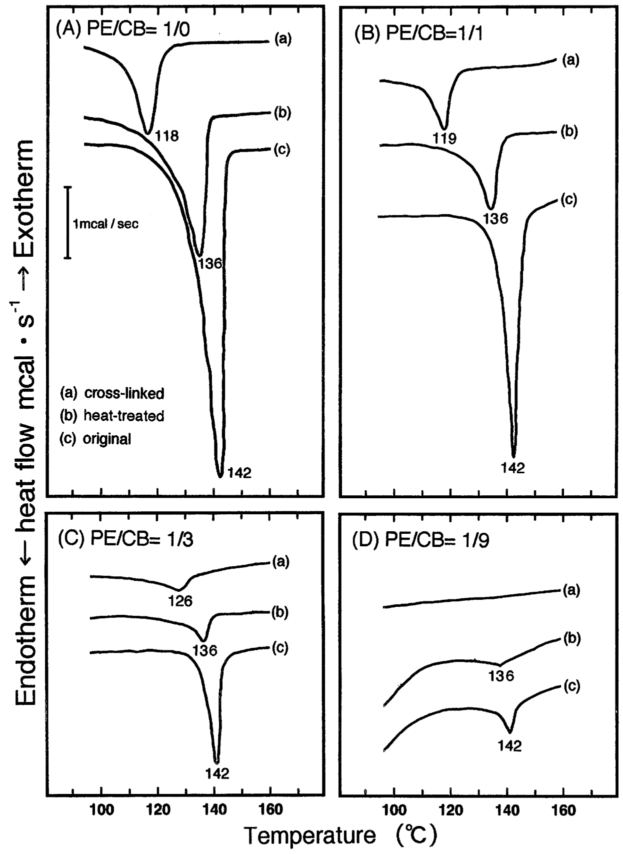


Fig. 5 DSC curves measured for four kinds of specimens with the indicated UHMWPE/CB compositions, (A) 1/0, (B) 1/1, (C) 1/3 and (D) 1/9, in which curve (a) cross-linked blends, (b) heat-treated blends with no-crosslinking, and (c) blends without any heat-treatment (original)

Figure 6 displays scanning electron micrographs for the 1/0.25, 1/1, and 1/9 blends. Because of very high surface energy of the CB, CB particles could not be observed for the 1/0.25 and 1/1 blends. Thus, a series of the micrographs was taken from the edge view of each specimen which was immersed into liquid nitrogen and splited by hands. In micrographs of the non-cross-linked (original) specimens, the fine filaments twine the CB particles but the number of fine filaments decreased drastically with increasing the CB content. Even so, CB particles within 1/9 blend were not fallen away by weak frictional force on the surface. The block with 40 mm x 20 mm x 20 mm, which was prepared only to estimate the impact resistance, was not broken when the block at 3 m height was fallen plumb down to a concrete floor indicating enough impact resistance to use as the industrial materials. For the cross-linked specimens, the edge becomes smooth surface. This is due to the melting of UHMWPE in the process of the cross-linking by chemical reaction for 40 min at 160 °C. The fine filaments within the original 1/1 blend were melted and the melted substance formed large rod-like structure (see

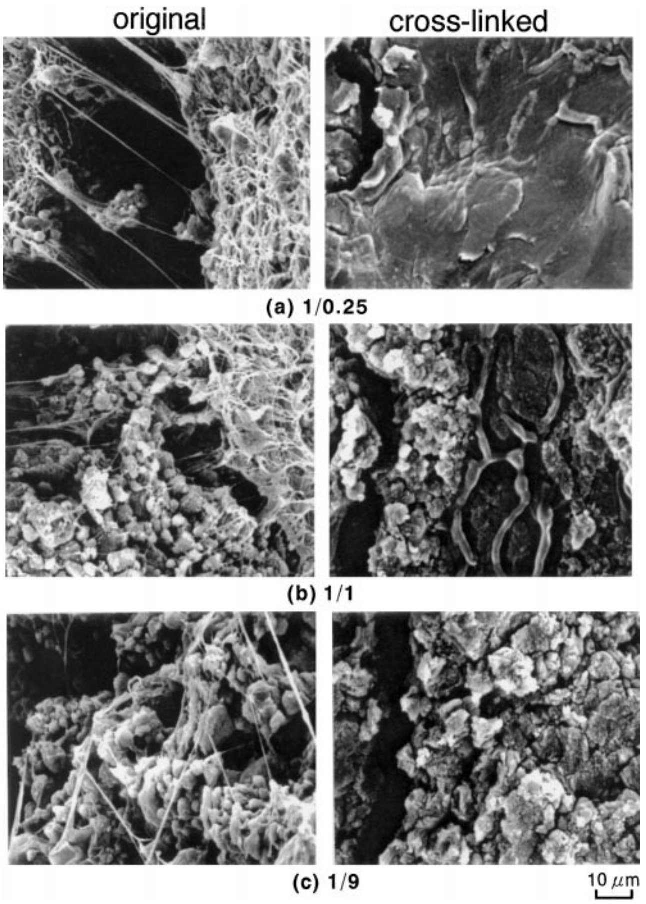


Fig. 6 Scanning electron micrographs for the non-cross-linked (original) and cross-linked UHMWPE–CB blends with 1/0.25, 1/1 and 1/9 compositions. All the micrographs were taken by the same magnification

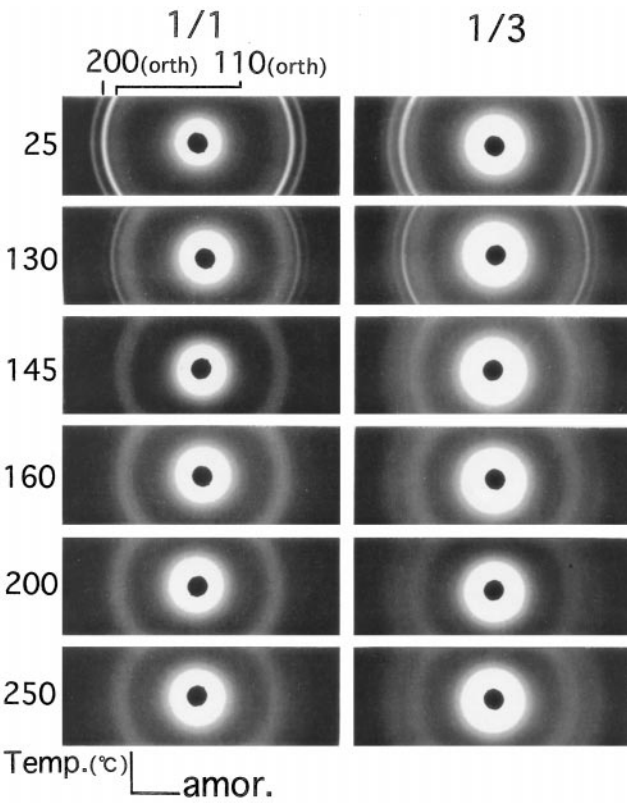


Fig. 7 Change of WAXD patterns at elevated temperatures measured for cross-linked PE–CB blends with 1/1 and 1/3 compositions

the center part of micrograph (b)). For the 1/9 blend, the residual substance by melting of fine filaments could not be observed because of large amount of CB particles. Actually, the cross-linked 1/9 blend was very brittle.

Here it is of interest to consider the morphology beyond the equilibrium melting point (145.5 °C) of PE. To check this problem, WAXD patterns were observed with increasing temperature, in which the specimen was fixed at a constant stress of about 0.1 MPa to avoid shrinkage of the specimen. Figure 7 shows the results for cross-linked specimens with 1/1 and 1/3 compositions. The specimens were annealed for 20 min at the indicated temperature prior to taking a picture. The exposuring time to take an X-ray photograph was 2 h. In comparison with the patterns at 25 and 130 °C for 1/1 and 1/3 blends, it is evident that the reflections from the (1 1 0) and (2 0 0) planes shift to the scattering center and their intensities become weaker up to 130 °C. Beyond 145 °C, the reflections disappear and the broad scattering from the amorphous phase appears. No change of the amorphous scattering occurs up to 250 °C. The scattering from CB particles is very weak in spite of the large amounts of CB particles. The weak scattering and the diffraction of the (2 0 0) plane are overlapped for the 1/3 blend. The scattering from the CB particles can be recognized at the outer part of the amorphous scattering beyond 145 °C. The scattering became more indistinct with increasing temperature. Incidentally, no scattering from the CB particles can be observed for the 1/1 blend.

Mechanical properties of UHMWPE–CB blends

Figures 8–10 show the temperature dependence of the storage and loss moduli for the non-cross-linked (original) and cross-linked blends with 1/0, 1/1, and 1/9 compositions, respectively. As can be seen in Fig. 8, the storage modulus of PE homopolymer (1/0) corresponding to the dry gel film is higher than that of the cross-linked PE over the given temperature range. This is due to the large difference of crystallinity between the dry gel film and the

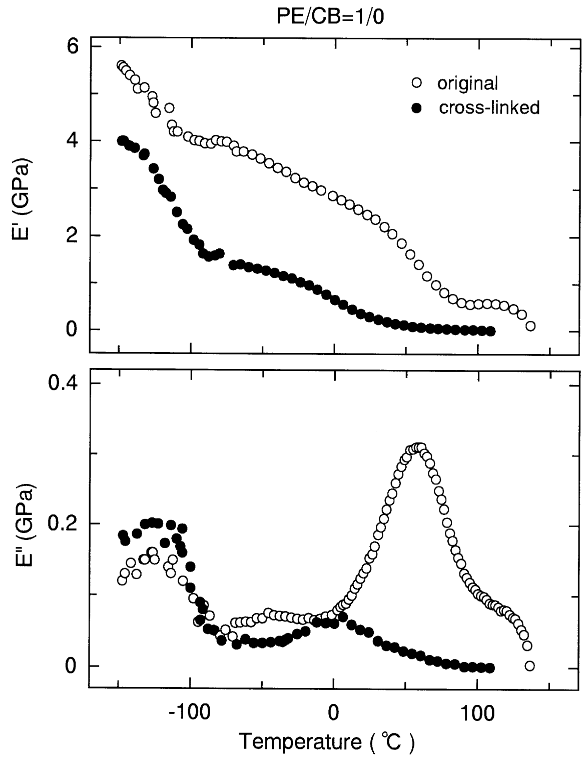


Fig. 8 Temperature dependence of the storage and loss moduli for original and cross-linked PE films

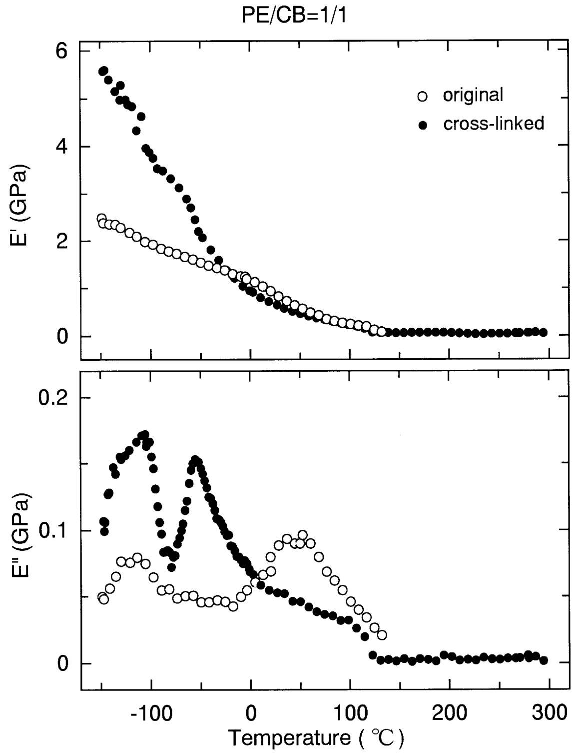


Fig. 9 Temperature dependence of the storage and loss moduli for the non-cross-linked (original) and the cross-linked PE–CB blends with the 1/1 composition

cross-linked film. Namely, the crystallinity of the dry gel film is about 84%, while the crystallinity of the cross-linked film decreases, which is confirmed by the disappearance of crystal phase owing to the chemical reaction at 160 °C higher than the equilibrium melting point of PE (see Figs. 1 and 4a). The loss modulus E'' of non-cross-linked (original) film shows maxima around 60 and -50 °C corresponding to the α mechanism associated with crystal dispersion [40, 41] and the β mechanism associated with amorphous dispersion, respectively [41]. The very broad β dispersion means high crystallinity of the specimen. The γ dispersion shows a peak around -130 °C but this peak is indistinct because of scattered values. For the cross-linked film, the β mechanism could be observed clearly around 0 °C indicating the drastic decrease in crystallinity by the chemical reaction at 160 °C, in addition to the indistinct γ dispersion. Because of softness of the cross-linked film at temperatures beyond 120 °C, the complex dynamic moduli could not be measured. However, the sample could be maintained without melting. Incidentally, it is reported that the γ dispersion is attributed to the relaxation mechanism of the local motions of side groups associated with the amorphous friction and defects in crystalline phase [42].

Figure 9 shows the complex dynamic moduli of the non-cross-linked (original) and cross-linked blends with 1/1 composition. Here it should be noted that cross-linking causes a significant thermal effect on the PE–CB blend. The cross-linked blend was maintained beyond 300 °C. The maximum measurable temperature was 300 °C for the present instrument used in this experiment. Hence, it is evident that the specimen could be maintained beyond 300 °C. In comparison with the results in Fig. 8, the storage modulus of non-cross-linked specimen was lower than that of PE dry gel film. This is due to the fact that the CB particles did not contribute to enhance the mechanical properties but the cross-section area increases with increasing CB content. The corresponding loss modulus E'' of the non-cross-linked (original) blend shows two clear maxima around at 50 and -110 °C corresponding to the α dispersion and the γ dispersion, respectively. The β dispersion could not be observed clearly because of high crystallinity of the specimen and this result is in good agreement with the sharp profile of DSC curve for the original specimen (see part (B) in Fig. 5). For the cross-linked specimen, it may be noted that the storage modulus increased drastically as temperature decreased and the value at temperature lower than -50 °C became much

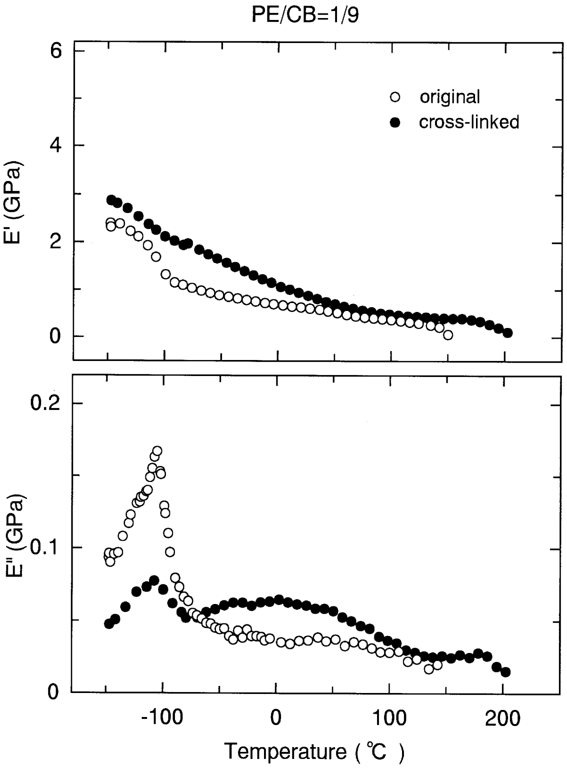


Fig. 10 Temperature dependence of the storage and loss moduli for the non-cross-linked (original) and the cross-linked PE–CB blends with the 1/9 composition

higher than the corresponding value of the original blend. Such a drastic increase is thought to be due to the transition from plastic to glassy region.

For the temperature dependence of the E'', the α dispersion peak disappeared and the two peaks appeared around at -55 and $-110\,^{\circ}\mathrm{C}$, which are associated with the β and γ dispersions, respectively. The disappearance of α the peak and the appearance of such a sharp β peak mean the large increase in the amorphous phase by the cross-linking due to chemical reaction at 160 °C. Namely, the higher the amorphous fraction, the more intense is the β relaxation. Actually, the WAXD showed the decrease in the intense of the (1 1 0) and (2 0 0) peaks and the DSC curve showed a very small endotherm peak, as discussed before. Judging from the drastic decrease in the storage modulus E' with increasing temperature, the β dispersion is thought to be due to the glass transition. The origin of the sharp γ peak shall be discussed later.

Figure 10 shows the temperature dependence of the storage and loss moduli for the non-cross-linked (original) and the cross-linked blends with 1/9 composition. The behavior is quite different from the result in Fig. 9, indicating that the thermal property of the cross-linked material becomes worse. Namely, the specimen could not be maintained at temperature higher than 200 °C and the drastic increase in E' with decreasing temperature could not be observed. Furthermore, the sharp peak associated with the β dispersion does not appear and a very broad peak in the temperature range -80–$100\,^{\circ}\mathrm{C}$ is observed. These different phenomena are attributed to the very small amount of cross-linked PE within the 1/9 blend. However, it is seen that the γ dispersion shows a very sharp peak in spite of the small amount of PE. Accordingly, the appearance of the sharp γ peak shown in Figs. 9 and 10 is thought to be due to the friction at boundary regions between CB particles and PE dry gels or the local motion of side group within amorphous phase.

Electric conductivity of UHMWPE–CB blends

Figure 11a shows electric conductivity against the content of CB particles for three kinds of specimens; blends without any heat-treatment (original), cross-linked blends, and blends prepared by melting the original specimens at 180 °C for 22 min and recrystallized them at room temperature (heat-treated). The electric conductivity increases with increasing the CB content and the value reached $1\,\Omega^{-1}\,\mathrm{cm}^{-1}$ at 90% CB content (1/9 composition). The value, $1\,\Omega^{-1}\,\mathrm{cm}^{-1}$, corresponds to the intrinsic value of CB [43]. In the given CB content, the values are in the range 10^{-9}–$1\,\Omega^{-1}\,\mathrm{cm}^{-1}$, which correspond to electric conductivity range of semiconductor. At each CB content, the conductivity of the cross-linked specimen is almost equal to that of non-cross-linked (original) specimen. Namely, the conductivity is hardly affected by the cross-linking. But, the conductivities of the heat-treated blend (non-cross-linked) are slightly higher than those of the other specimens. This indicates that the melting at 180 °C causes significant effect on the easy alignment of CB particles to form conductive channels owing to the disappearance of a number of voids, while the melting at 160 °C slightly remains the original morphology of the dry gel PE. This phenomenon was confirmed by preliminary SAXS and WAXD experiments, which were not shown in this paper. The relationship between electric conductivity and crystallinity could not be discussed directly for the blend specimens because of the difficulty in estimating the crystallinity. But, from the comparison with X-ray data for the 1/3 (75%) blend (see Fig. 4b), it may be expected that the decrease in crystallinity plays a part in increasing conductivity. Anyway, the conductivity, $1\,\Omega^{-1}\,\mathrm{cm}^{-1}$, has never been reported for the PE-CB blends. Here we must emphasize that although the preparation of LMWPE–CB blends by kneading method have been employed generally, this common method is unsuitable to

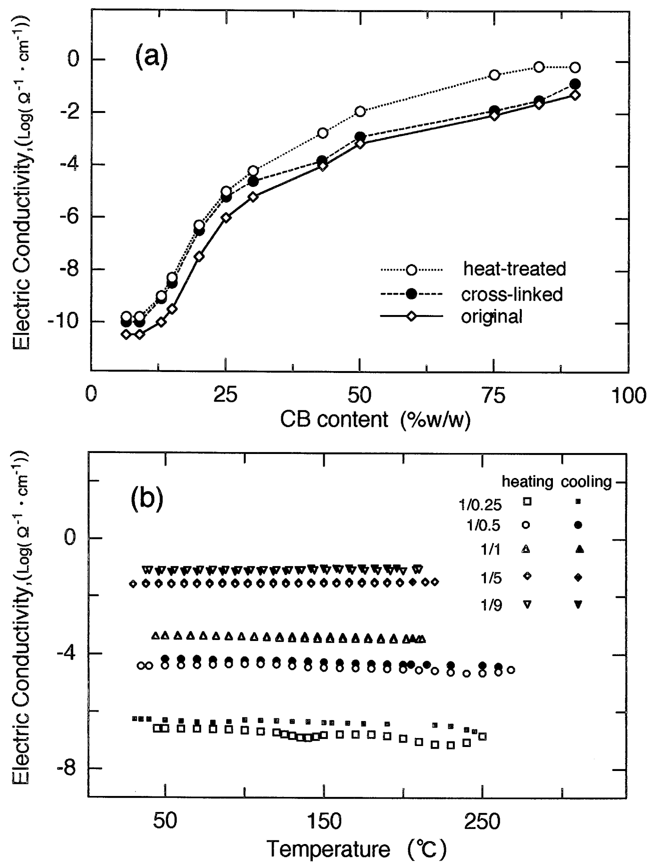


Fig. 11 (a) Electric conductivity against the content of CB particles measured for three kinds of blends, blends (original) without any heat-treatment and cross-linking, cross-linked blends, blends prepared by melting at 180 for 22 min and recrystallized them at room temperature. (b) Temperature dependence of electric conductivity for cross-linked blends with various PE/CB compositions. The measurements were carried out under heating and cooling processes

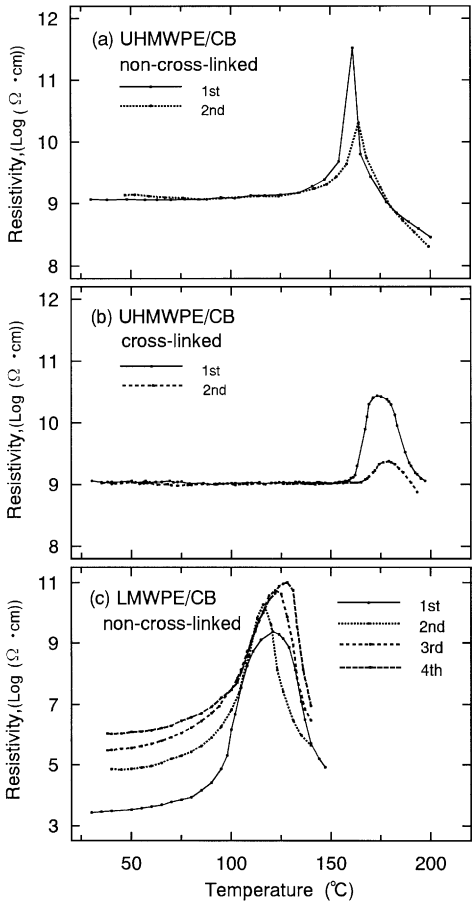


Fig. 12 Electric conductivity against temperature of PE–CB blends with 13% CB content, measured as heating cyclings. (a) Non-cross-linked UHMWPE/CB blend, (b) cross-linked UHMWPE/CB blend, (c) non-cross-linked LMWPE–CB blends prepared by a kneading method

prepare LMWPE– CB blends with CB content ≥65% and UHMWPE–CB blends with content ≥10%.

Figure 11b shows temperature-dependence of the electric conductivity for cross-linked blends with various CB contents beyond 20%. This experiment was carried out to check the thermal stability of the electric conductivity. As can be seen in this figure, the conductivities of all the specimens are almost independent of temperature up to 220 °C and the values in the heating and cooling process are almost the same. This indicates good thermal stability due to cross-linking of PE chains. The good thermal stability for the 1/9 blend (90% CB content) is desirable as the thermal semiconductive materials, since the range application of PE is limited by its low melting point.

Apart from the main purpose to develop the PE–CB blends with high electric conductivity, positive temperature coefficient (PTC) effect must be studied as an another important problem. PTC effect is associated with a drastic decrease in electric conductivity at temperature range close to melting point of PE and main focus has been concentrated on LMWPE–CB blends prepared by kneading methods. Part (a) in Fig. 12 shows electric resistivity against temperature for the UHMWPE–CB blend with 13% CB content. The specimen was prepared by melting of the dry gel film at 180 °C for 22 min. Incidentally, 13% CB content is the critical one where the resistivity drops precipitously by many orders of magnitude. The measurements were done for the first and second heating cyclings. For the first cycling, the curve reveals that the resistivity increases gradually with increasing temperature but it increases more than two orders of magnitude suddenly. The maximum peak appeared at 160 °C, higher than melting point (135 °C) estimated by DSC. At the second heating,

Table 1 Change in values of R_P/R_{RT} with increasing heating run cycle

	1st	2nd	3rd	4th
UHMWPE/CB	2.89×10^2	1.50×10		
LMWPE/CB	1.10×10^6	1.25×10^6	2.84×10^5	1.00×10^5

the resistivity increases only one order of magnitude at the peak top but the maximum peak shifts to slightly higher temperature. According to Narkis et al., a maximum PTC intensity was defined as the ratio(R_P/R_{RT}) of peak resistivity R_P to the room temperature resistivity R_{RT} [7]. The drastic decrease in the maximum peak by the second heating cycle means poor thermal stability. The values are listed in Table 1.

Recently, interesting results for PTC effect were reported by Chan et al. using composites prepared by sintering a mixture of UHMWPE powder and CB particles [26]. The resistivity for the composite with 2% CB concentration increased about four order of magnitude at the peak top around 180 °C, although the composite did not form a film and it seems to be brittle.

Part (b) shows electric resistivity against temperature for the cross-linked PE–CB blend with 13% CB content. The thermal reproducibility by cross-linking was studied to check the temperature dependence of electric resistivity due to heating cycle effect. Unfortunately, the cross-linking effect do not enhance the PTC intensity and do not improve the thermal reproducibility of electric resistivity. The result obtained for cross-linked LMWPE–CB blend showed that the PTC intensity maintains almost a constant value with further increase in temperature beyond the maximum value [18]. This effect plays an important role as the self-regulating heaters, since electron transport stops beyond a certain temperature. The decrease in resistivity with temperature is termed as NTC effect. According to Tang et al. [18] the better reproducibility and the decrease in NTC effect are due to the fact that cross-linking enhances the shear modulus of polymer and CB particles are strongly attached to cross-linked PE networks. They pointed out that the strong attachment to cross-linked networks is, thus, expected to reduce the freedom of movement of CB particles at high temperature, including at the melting region, which is of concern of the PTC/NTC phenomena, especially at amorphous region in which CB particles are dispersed. Accordingly, further investigation must be taken into consideration for cross-linked UHMWPE/CB blends to improve the magnitude of PTC intensity and the decrease in NTC effect.

Part (c) shows temperature-dependence of LMWPE–CB blend (non-cross-linked) with 13% CB content. The blend material was prepared by kneading method, since the dry gel of LMWPE was confirmed not to form film [44]. The resistivity increases gradually with increasing temperature and it increases several orders of magnitude suddenly around melting point of PE. The values R_P and R_{RT} increase as heating run cycle increases. Each maximum PTC intensity defined as R_P/R_{RT} are listed in Table 1. The scattered value indicates slightly poor thermal stability of the specimen. Unfortunately, we have no instrument to pursue cross-linking by electron irradiation and we cannot present any data. Comparing part (c) with part (a), it is evident that the maximum PTC peak for UHMWPE–CB blend appeared at higher temperature than that for LMWPE–CB blend. This causes significant effects on the manufacture of PTC materials and further expectation can be derived to produce the self-regulating heaters at various temperatures. At present, however, the maximum PTC intensity defined as R_P/R_{RT} for UHMWPE–CB blend is much lower than that for LMWPE–CB blend.

Conclusion

The gelation/crystallization method was successful to prepare the UHMWPE–CB system with various CB contents up to 90% and the conductivity for all the blends was in the range from 10^{-9} to $1\,\Omega^{-1}\text{cm}^{-1}$. The blends also provided thermal stability of electric conductivity by cross-linking of PE chains, although the storage and loss moduli were very sensitive to temperature. The conductivity of the blends with CB content $\geq 20\%$ were almost independent of temperature up to 220 °C and the values in the heating and cooling process were almost the same. Furthermore, the UHMWPE–CB blends with 13% CB content showed PTC effect. The measurements were done for the first and second heating cyclings. For the first heating cycling, a maximum PTC intensity defined as the ratio (R_P/R_{RT}) took more than two orders of magnitude but the value at the second heating cycling, one order, indicating poor thermal stability. The PTC intensities for UHMWPE–CB blends were lower than that of the corresponding LMWPE–CB blend but the maximum peak appeared at 160 °C higher than the peak temperature of LMWPE–CB blend. At a critical concentration of CB particles (13%), the cross-linking of UHMWPE chains did not enhance the PTC intensity and did not improve the thermal reproducibility of electric resistivity.

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