PTC Behavior of Polymer Composites Containing Ionomers upon Electron Beam Irradiation

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Abstract: We have prepared polymer composites of low-density polyethylene (LDPE) and ionomers (Surlyn 8940) containing polar segments and metal ions by melt blending with carbon black (CB) as a conductive filler. The resistivity and positive temperature coefficient (PTC) of the ionomer/LDPE/CB composites were investigated with respect to the CB content. The ionomer content has an effect on the resistivity and percolation threshold of the polymer composites; the percolation curve exhibits a plateau at low CB content. The PTC intensity of the crosslinked ionomer/LDPE/CB composite decreased slightly at low ionomer content, and increased significantly above a critical concentration of the ionomer. Irradiation-induced crosslinking could increase the PTC intensity and decrease the NTC effect of the polymer composites. The minimum switching current (I_{trip}) of the polymer composites decreased with temperature; the ratio of I_{trip} for the ionomer/LDPE/CB composite decreased to a greater extent than that of the LDPE/CB composite. The average temperature coefficient of resistance (α_T) for the polymer composites increased in the low-temperature region.

Keywords: carbon black, electron beam irradiation, ionomer, polymer composite, positive temperature coefficient (PTC).

Introduction

In recent years, the conducting polymers and their polymer composites with the conductive fillers have been attractive due to their potential applications for the electrochromic devices, chemical sensors, electrochemical devices, solid polymer electrolytes, and rechargeable batteries.[1-5] When conductive fillers such as carbon black (CB) and metal powder are added to the polymer matrix which is electrically insulating materials, the conductivity of the polymer composites is changed from insulator to conductor.[6,7] It is caused by electron tunneling through the conductive pathway formed by loaded fillers, when the concentration of conductive fillers is over a critical value. As temperature approaches to the melting temperature of the polymer matrix, the resistivity of

the conductive filler added polymer composites increases rapidly.[8,9] The effect is known as the positive temperature coefficient (PTC). Voet[10] suggested that PTC effect of the CB filled semicrystalline polymer composite was caused by the increase in the average interparticle or aggregate distance of the CB in a semicrystalline polymer. Therefore, the increase in the PTC effect of the semicrystalline polymer composites was attributed to a larger thermal expansion upon the melting of the crystalline phase compared with the amorphous phase.[6] On the contrary, the sudden decrease in the resistivity with increasing temperature can be described as the negative temperature coefficient (NTC) effect. PTC effect has been especially pronounced in the semicrystalline polymers like polyethylene (PE) near the melting temperature.[11,12] Usually, materials with a PTC effect have been made of doped $BaTiO_3$ ceramics, in which the transition from the ferroelectrics to the para-electrics state at the Curie temperature is utilized. Thermistors made of these materials which

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exhibit a fairly large PTC effect at the Curie temperature have been widely used for a long time, in spite of their disadvantages of the relatively high resistivity at room temperature and high manufacturing cost. The polymer-based materials like CB particles dispersed in an insulating matrix of PE,[13] have been developed to reduce the resistivity at room temperature and manufacturing cost. Application of polymer PTC materials has been widely extended due to their good processability, and the most successful examples of its application are a resettable over-current protection device and a self-regulating heater.[14] The resistivity at room temperature of the CB filled conductive polymer composite can be influenced by various factors, including the structure and amount of CB,[6,15] polymer characteristics such as chemical structure and crystallinity, polymer-CB interaction,[16] and processing methods and conditions.[17,18] PTC effect of the CB filled conductive polymer composite is mainly caused by two factors such as the percolation threshold that is defined as the critical fraction of fillers at which conductive paths begin to form throughout the polymer composites and the volume expansion coefficient of the polymer matrix that is changed enormously at the melting temperature of the polymer matrix.[19-23] Although the highly CB filled composite has low resistivity at room temperature, high filler content causes high melt viscosity and brittleness of the final products, and crucially decreases PTC effect. When thermoplastic materials like PE was used as a polymer matrix, a strong NTC effect was observed above PTC transition due to thermally induced movement of the conducting particles to form a new network across the medium. Unstable electrical reproducibility and NTC effect are main drawbacks for the application of PTC materials, because NTC effect is caused by the decrease in the elastic modulus of polymer matrix above the melting temperature.[20] The chemical crosslinking is limited to applications because it occurs above the melting temperature of the composites, while the radiation cross-linking is carried out at room temperature, and is one of the most effective ways to improve PTC effect and eliminate NTC effect. Thus, the crosslinking of polymer matrix has been performed to eliminate NTC effect and increase reproducibility by forming network structures and reducing the freedom of movement of the CB particles.[21] Generally, the polymer PTC device can be produced by adding the PTC materials that prepared by dispersing the conductive fillers into the polymer matrix between the electrodes. However, the adhesion between the components in the PTC device is poor. Since the ionomer possesses high polar ingredients, it may enhance the adhesion properties with metal foil used as an electrode of the PTC devices. The contact resistance between the conductive polymer composite and the metal foil is commonly affected by this adhesion properties.[16] It is expected that the PTC materials containing the ionomer can minimize the contact resistance by improving the adhesion with metal foil used as an electrodes without any decrease

in the PTC performance and retain higher maximum hold current by lowering the resistivity at room temperature.

In this research, the polymer composite based on low-density polyethylene (LDPE) and ionomer (Surlyn 8940) having polar segments and metal ions were prepared by melt blending process with the CB as conductive filler. Change of the conductivity for the polymer composites with the CB content and temperature dependence of the resistivity for those was investigated. The variations of resistivity at room temperature, PTC effect, and switching characteristics induced by the ionomer and effects of the irradiation crosslinking on PTC effect of the polymer composite were also investigated.

Experimental

Materials and Preparation. Carbon black (CB) used as conductive filler in this research was N660 provided by Columbian Chem. Co. in U.S.A. Its average particle size is 49-60 nm; surface area by N_2, 34 m^2/g, and dibutyl phthalate (DBP) absorption value is 89.1 mL/100 g. Low-density polyethylene (LDPE 5321, Hanwha Petroleum Chem. Co. in Korea) with the melt flow index (MFI) of 3.0 g/10 min, density of 0.92 g/cm^3, tensile strength of 75 kg/cm^2, and melting temperature of 107 °C was used as the polymer matrix. The ionomer used in this research was Surlyn 8940 provided by DuPont Co. in U.S.A. Surlyn 8940 thermopalstic resin is an ionomeric ethylene/methacrylic acid (E/MAA) copolymer, in which MAA acid groups have been partially neutralized with sodium ions. Its MI is 2.8 g/10 min; density 0.95 g/cm^3, tensile strength 150 kg/cm^2, and melting temperature is 94 °C. The CB filled composites were prepared using a Brabender Plasticorder model PLE 330 at 160 °C and 20 rpm for 15 min. The CB was added when the polymers were melted in order to improve the dispersion of the CB particles, and the polymer composites were made into a sheet form by compression molding machine at 150 °C. The sheets were slowly cooled down to the room temperature in air and stored in an ambient condition to remove residual thermal stress during the melt processing. The specimens were 12.7 mm in diameter and 0.3 mm in thickness. Silver paste was coated on both side of the specimen to serve as an electrode. In addition, the specimens were irradiated with the irradiation dose of 250 kGy for the electron beam (EB) accelerator in air at room temperature to investigate the effects of cross-linking on PTC effect of the polymer composites.

Characterization. The resistivity at room temperature of the polymer composites was measured by using the four-probe method. Keithley model 2420 (Keithley Instruments Inc., U.S.A.) was used to measure the resistivity below 10^8 ohm and mega-ohmmeter MMG 550 (Keithley Instruments Inc., U.S.A.) was used over 10^8 ohm resistivity. Temperature dependence of the resistivity was measured by using the

FP82HT heating stage (Mettler-Toledo International Inc., Switzerland) with a heating rate of 3 °C/min. The electrical switching characteristics of the polymer composites and the temperature (I_{trip} vs. temperature) were determined by using the measurement system composed of the electrical power source (Sourcemeter model 2420, Keithley Instruments Inc., U.S.A.), the ambient temperature controller (Hot chuck system, Instek/Good Will instrument Co. Ltd., U.S.A.), IR thermometer, and data station. The constant voltage (10 V) was imposed on the specimen from the electrical power source, and the switching time of the samples was measured under the ambient temperature. The current of the device switched in 10 sec was defined as minimum switching current (I_{trip}). Differential scanning calorimeter (DSC) analysis was performed with a Perkin-Elmer DSC7. The samples were heated to 160 °C at a heating rate of 10 °C/min, kept for 5 min, and then cooled to 30 °C at a cooling rate of 10 °C/min. The morphology of the ionomer/LDPE/CB composites was observed with the field emission scanning electron microscope (FE-SEM).

Results and Discussion

DSC thermograms of Surlyn/LDPE/CB composites are shown in Figure 1. The thermal behavior of the prepared composites was investigated since the percolation phenomenon could be influenced by the compatibility of the polymer blends. There were one or two peaks in the endothermic and exothermic curves with different composition ratios. However, the positions of the characteristic peaks for LDPE were unchanged apparently with Surlyn content, and all the heights of the melting and crystallization peaks of LDPE phase that are related to the crystalline content followed the linear relation of the rule of mixture.[24] It may be considered that LDPE and Surlyn are incompatible in the crystalline region. The melting and crystallization peaks of LDPE in the composites would be lower than those of neat LDPE due to the dilution effect of Surlyn component if LDPE and Surlyn phases were compatible in the amorphous region.[25] The Surlyn and LDPE phase in the composites might be incompatible or partially compatible in the amorphous region.[26]

The dependence of the resistivity at room temperature for Surlyn/LDPE/CB composites on CB content is shown in Figure 2. The resistivity of LDPE/CB composite was linearly decreased with increasing CB content up to 30 wt%. However, the resistivity of Surlyn/LDPE/CB composite was decreased slowly at low CB content and then was decreased steeply above 15 wt% of CB content due to the inclusion of Surlyn component, as expected in accordance with double percolation concept.[27] The percolation threshold of the CB filled Surlyn/LDPE (30/70) composite shifted to lower resistivity with CB content less than 25 wt% compared with that of LDPE/CB composite. However, the resistivity of
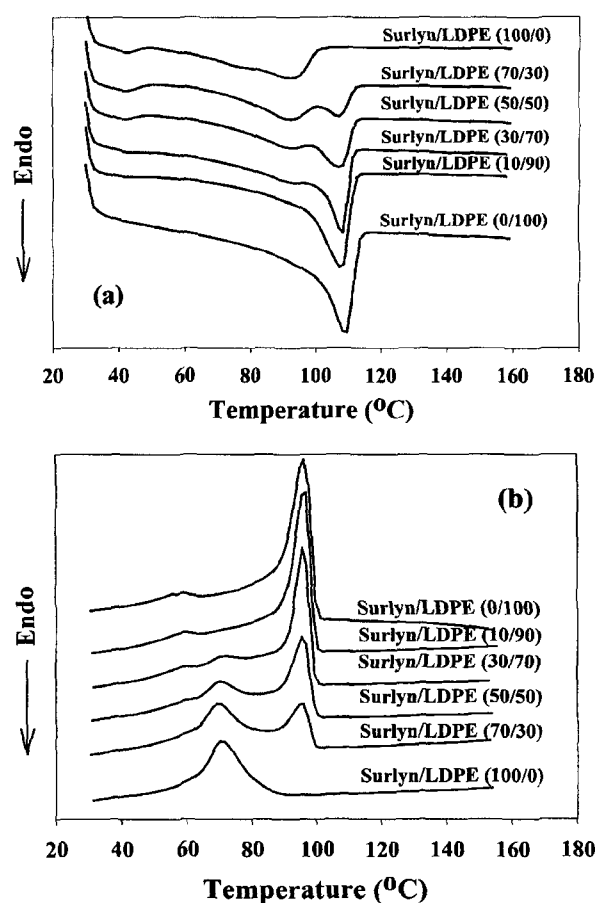

Figure 1. DSC thermograms of (a) heating and (b) cooling scans of Surlyn/LDPE/CB composites (CB content = 25 wt%).
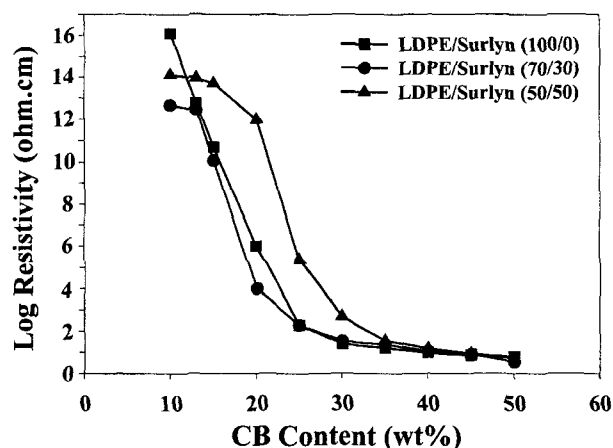

Figure 2. Logarithmic resistivity of Surlyn/LDPE/CB composites with CB content at room temperature.

Surlyn/LDPE (50/50) composite with increasing CB content was increased relatively in the entire region investigated, which suggested that this double percolation phenomenon is

mostly independent of CB content in Surlyn/LDPE/CB composite and the uneven dispersion of CB may cause the different mechanism. Surlyn has a unique structure by a positive charged metal ion and forms three dimensional network structures by the metal ion like elastomeric material at room temperature and physical properties of Surlyn is similar to that of elastomeric materials. However, at the melt state, heat energy breaks the physical crosslinking formed at room temperature, and then, Surlyn shows a plastic behavior like thermoplastics.[28,29] The conductive filler, CB has various functional groups on the surface,[30,31] which is thought as a factor that it is predominately dispersed in the Surlyn phase. As CB content approaches to the certain saturation limit in Surlyn component, CB may be located in Surlyn/LDPE interfacial region or amorphous region of LDPE.[32] Thus, the resistivity is nearly constant with increasing CB content beyond saturation concentration.

The morphology of the CB filled composites was analyzed by FE-SEM to investigate the dispersion state of CB particles with different composition ratios. As shown in Figure 3, CB particles in the pure LDPE were widely dispersed, while CB particles in Surlyn/LDPE (30/70) composites tended to concentrate in Surlyn phase to form the cluster.

For Surlyn/LDPE (50/50) composites, it can be assumed that Surlyn phase has been changed from discontinuous phase to continuous phase, and CB particles in those were also dispersed within Surlyn domains similar to the case of Surlyn/LDPE (30/70) composites. However, CB particles in Surlyn/LDPE (50/50) composites were relatively dispersed in the wider region due to higher Surlyn content compared with Surlyn/LDPE (30/70) composites, and the interparticle distance of CB was relatively increased.

The variations of the resistivity at room temperature with composition ratio of Surlyn/LDPE composites are shown in Figure 4. The resistivity of the composites was not changed up to Surlyn content of 30 wt%, while it was increased dramatically when Surlyn content was over 30 wt%. It was attributed to the uneven dispersion of CB in Surlyn/LDPE composites in which dispersed predominantly in Surlyn phase. The increase in Surlyn content at the same CB content for the composites may result in the decrement of the effective CB content. For LDPE/CB composite, CB particles have a tendency to concentrate at the amorphous region of LDPE phase, and the resistivity of LDPE/CB composite was decreased by forming the conductive path. Compared with LDPE/CB composites, CB particles in Surlyn/CB
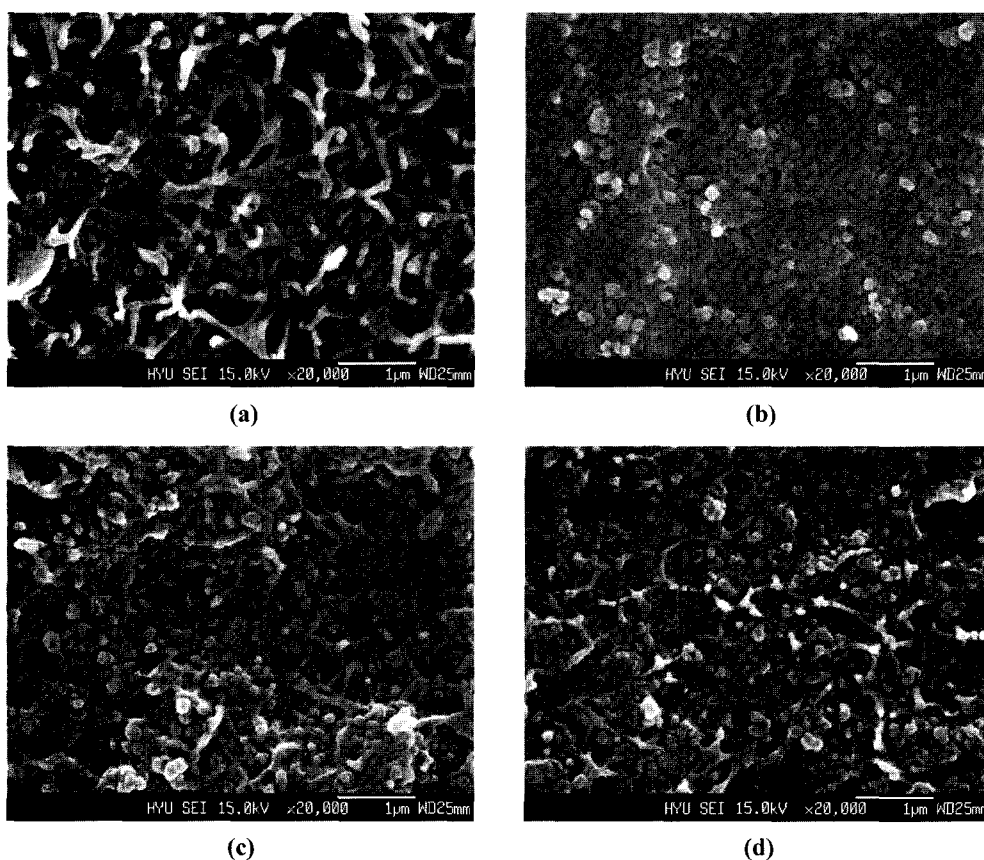

(a)

(b)

(c)

(d)

Figure 3. FE-SEM micrographs of the 25 wt% CB filled composites; (a) Surlyn/LDPE (0/100), (b) Surlyn/LDPE (30/70), (c) Surlyn/LDPE (50/50), and (d) Surlyn/LDPE (100/0).
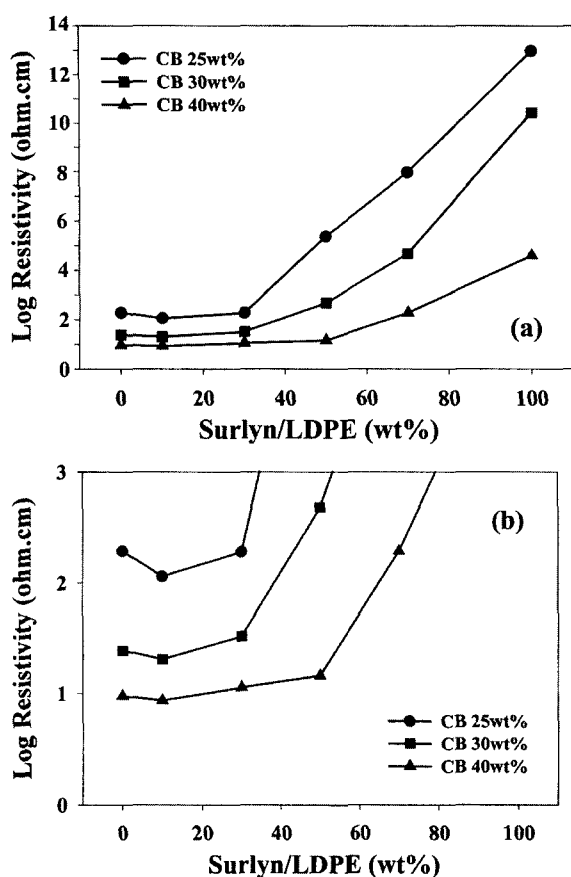
Figure 4. Logarithmic resistivity of Surlyn/LDPE composites with (a) various CB contents and (b) enlarged diagram at room temperature.

composite were uniformly dispersed in the polymer matrix due to CB-polymer interactions such as ionic bonding and polar interaction. However, CB particles in Surlyn/LDPE blend system were predominantly dispersed in Surlyn phase because the dispersion mechanism of CB in the polymer matrix could be influenced by the interaction between Surlyn and CB. In general, the dispersion of the conductive particles in the polymer matrix can be determined by competing between the particle-particle and particle-polymer interactions.[33,34] The CB has a greater surface area to contact with the polymer matrix because of the physical or chemical interaction between the CB particles and polymer matrix.[35] The polymer PTC materials containing the ionomer have a unique physical crosslinking structure due to the ionomer in the polymer matrix, which was attributed to the ionic bond formed between metallic ions and acid groups of the polymer. The conductive particles have a different dispersion mechanism in the polymer matrix with the polarity of the polymer used. As the polarity is high, the mutual force between the particles and polymer matrix is increased, resulting in the stronger bonding between the CB particles and polymer matrix. For this reason, the form of the disper-

sion for the CB particles in the polymer matrix has different characteristics, and the distribution of the CB particles is influenced by the distribution structure of the ionomer having the polar group. The electronic path can be easily formed relatively in the PTC materials. The interaction between the CB particles and polymer matrix is constant irrespective of the temperature, so that the change of the position or aggregation of the CB particles within the polymer matrix can be restrained. Thus, change of the effective CB content with Surlyn content in LDPE matrix would affect the formation of the conductive path, and the shift of percolation threshold and change of the resistivity for Surlyn/LDPE (50/50) composites could be explained by the concept of the effective CB content.

It is well known that the PTC performance of polymer composites are characterized by the PTC intensity.[16,36,37] The PTC intensity can be expressed as the logarithm value of the ratio of the maximum resistivity (R_{max}) to the resistivity at room temperature (R_{RT}) as the following equation[38,39]:

$$\text{PTC Intensity} = \text{Log} (R_{max}/ R_{RT}) \qquad (1)$$

As the temperature was increased to the vicinity of the melting temperature of semicrystalline polymer, a large thermal expansion occurred due to the increased molecular movement by the melting of crystallites in the composites.[6,10] PTC effect of the conductive composites resulted from the different thermal expansion coefficients between the polymer matrix and conductive filler, and might be caused by two factors such as the interparticle distance and the number of conductive paths. It was reported that the large thermal expansion coefficient of polymers could increase the interparticle distance, and reduce the number of conductive paths.[40] According to the tunneling theory,[41] tunneling probability of the electron was related to the interparticle distance, resulting in the increased resistivity with increasing the interparticle distance. The interparticle distance in the polymer composite with low CB content may be longer than the distance that electrons are able to jump with increasing temperature. The larger interparticle distances and smaller number of conductive paths could increase significantly the resistivity of the composites. However, CB particles in the composite with high CB content would form the continuous conductive networks, and the interparticle distances might be very small. Therefore, the increase in the interparticle distance may be the main factor to cause the increase in the resistivity, which was explained by the decrease in the PTC intensity with CB content.[6,23,42-44]

The variations of PTC intensity at different composition ratios of Surlyn/LDPE with CB content are shown in Figure 5, which corresponded well with the previously described tendency that PTC intensity was decreased with CB content. However, PTC intensity of Surlyn/LDPE/CB composite was almost constant irrespective of CB content. The temperature

dependence of the resistivity and PTC intensity were determined by the competitive results of PTC effect that increased the resistivity by activating molecular chain movement with temperature and NTC effect occurred by migration of molecular chains after the melting of crystallites in high temperature region. At the lower temperature than the melting temperatures of Surlyn and LDPE, only the thermal expansion would affect the polymer matrix with temperature. However, at the higher temperature than the melting temperature of LDPE, Surlyn molecules can migrate and form aggregates. Surlyn aggregates may accelerate the reformation of the conductive paths, and the resistivity does not increase any more, and thus, PTC intensity of Surlyn/LDPE composites with low CB content was relatively low.

As shown in Figure 5, PTC intensity of the crosslinked composite with CB contents was higher than that of the uncrosslinked composite. As the accelerated electron is irradiated on the polymer, C-H bond in main chains and single or double bonds of side chain are broken down, and radicals are generated. The irradiation crosslinking of polymer chains are progressed by these radicals.[45] For Surlyn/LDPE composites, the irradiation crosslinking can greatly increase PTC intensity especially at low CB content com-

pared with the uncrosslinked composite. The variation of PTC intensity for this blend system changed to the general tendency of which PTC intensity decreases with CB content similar to the case of LDPE/CB composite. For the cross-linked composite, the decrease in the elastic modulus at higher temperature was reduced, and the molecular bonding might be formed between LDPE and Surlyn phase, which disturbed the molecular chain migration. Because the cross-linking prevented the agglomeration by migration of Surlyn into LDPE phase with increasing temperature, the CB agglomeration was reduced or disappeared, and PTC intensity was influenced by only interparticle distance.

The variations of the resistivities of the uncrosslinked and crosslinked composites with temperature are shown in Figure 6. On the crosslinking by electron beam irradiation, temperature dependence of the resistivity of polymer composites exhibited different behavior. For the crosslinked composites, PTC effect was increased and NTC effect was decreased or disappeared at higher temperature than the melting temperature of the polymer matrix. As temperature was increased up to approximately 100 °C, the resistivity of the crosslinked composites was increased continuously. For the crosslinked composites, it was reasonable to suggest that the NTC effect
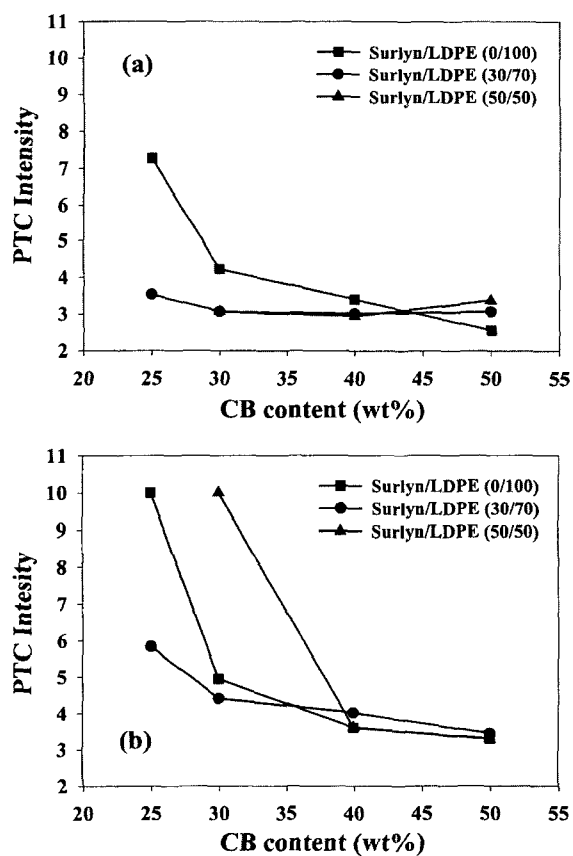

Figure 5. PTC Intensity of Surlyn/LDPE/CB composites with CB contents; (a) uncrosslinked and (b) crosslinked by EB irradiation.
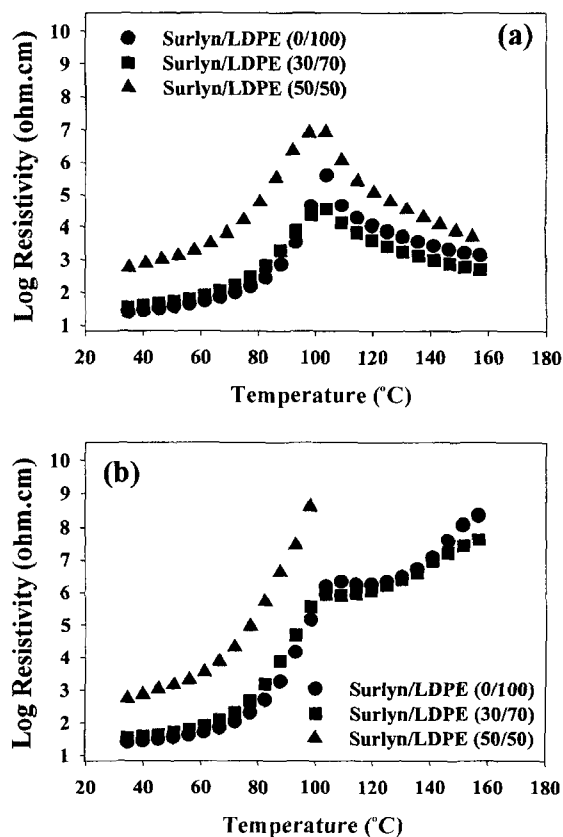

Figure 6. Logarithmic resistivity of Surlyn/LDPE/CB composites with temperature; (a) uncrosslinked and (b) crosslinked by EB irradiation.

resulted from the reaggregation of CB particles by the decrease in the elastic modulus at high temperature.[20] The crosslinked composites have three-dimensional network structures, which could enhance the elastic modulus of the polymer in high temperature region as well as CB-polymer interaction.[44] It was expected that the freedom of movement of CB particles at higher temperature was reduced, and NTC effect caused by the CB reagglomeration in the composites might be decreased.

The changes of PTC intensity for Surlyn/LDPE composites with CB content and Surlyn/LDPE composition ratio are shown in Figure 7. PTC intensity of the crosslinked composite was higher than that of the uncrosslinked composite. PTC intensity of the uncrosslinked composite was decreased rapidly with increasing Surlyn content from 0 to 10 wt%, and thereafter, was nearly unchanged or slightly increased as Surlyn content was increased. PTC intensity of the crosslinked composite also exhibited similar trends. However, PTC intensity was abruptly increased when Surlyn content was over 30 wt%, which may be caused by the complex reasons such as change of morphology, uneven dispersion of CB, and interparticle distance in the polymer composites.
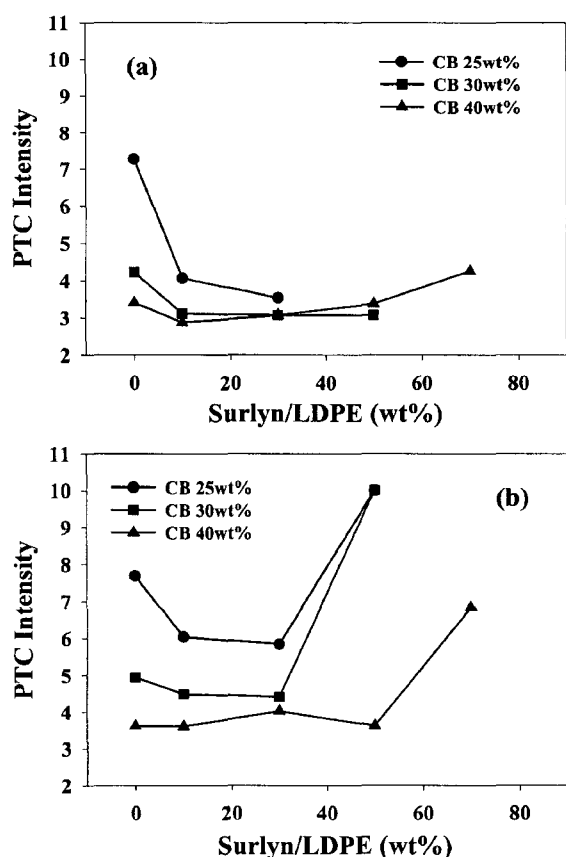

Figure 7. PTC intensity of Surlyn/LDPE/CB composites with CB content; (a) uncrosslinked and (b) crosslinked by EB irradiation.

At CB content higher than 40 wt%, CB particles can form a continuous conductive network, and the interparticle distances can be very small. As the resistivity was increased by the thermal expansion of the polymer matrix with increasing temperature, the interparticle distance was the major factor for the increment of the resistivity in the homogeneous polymer matrix. However, for Surlyn/LDPE composites with low Surlyn content, CB particles were dispersed in the discontinuous Surlyn phase, resulting in the increased resistivity of the composites. It could be caused by the decrease in the number of conductive paths and the increase in the interparticle distance. Thus, PTC intensity of Surlyn/LDPE (30/70) composite was higher than that of Surlyn/LDPE (50/50) composite. However, further increase in Surlyn content caused the decrease in the effective CB content in Surlyn phase, resulting in the great increment of PTC intensity, especially for Surlyn/LDPE (70/30) composites.

When current flows through the device made up of conductive polymer composite, temperature of the device is increased by joule heating (I^2R heating), and the device shows PTC behavior. The operation of the device is based on an overall energy balance described by the following equation[46]:

$$mC_p(\Delta T/\Delta t) = I^2R - U(T - T_a)$$ (2)

where I is the current flowing through the device; R is the resistance of the device; Δt is the change in time; m is the mass of the device; C_p is the heat capacity of the device; ΔT is the change in device temperature; T is the temperature of the device; T_a is the ambient temperature, and U is the overall heat-transfer coefficient. From the Eq. (2), the current flowing through the device generates heat at a rate equal to I^2R. All or some of the heat is lost to the environment at a rate described by the term $U(T - T_a)$. Any heat does not lost to the environment contributes raising temperature of the device at a rate described by the term, $mC_p(\Delta T/\Delta t)$. Sufficiently high current causes the device to generate heat at a rate greater than the rate at which heat can be lost to the environment, thus causing the device to heat up rapidly. At this stage, a very large increase in the resistance occurs for a very small change in temperature, and then, the device switched from conductor to high resistor. Changes of the switching time for the current applied through the device made up of LDPE/CB composite are shown in Figure 8. When the current through the device is 0.7 A, current flows constantly and the device was not switched. Under this condition, the heat generated by the device and the heat lost by the device to the environment are in balance at room temperature. However, the device was switched when the applied current was over 1.0 A. Switching time by increasing heating rate was shorter as the current through the device was increased. In here, the current of 1.2 A, switched the device at about 10 sec, is defined as minimum switching
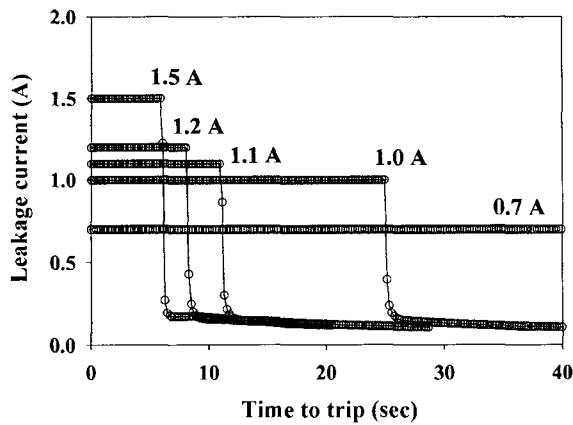
Figure 8. Switching time of LDPE/CB composite with different applied current at room temperature (CB content = 40 wt%).

current (I_{trip}). Accumulated heat inside of the device is determined by the generated heat rate as well as lost heat rate to environment by the change of temperature as shown in the Eq. (2). Changes of the I_{trip} with temperature for the device composed of LDPE/CB composite and Surlyn/LDPE/CB composite are shown in Figure 9. The I_{trip} linearly decreased with increasing temperature, which was attributed to the reduction of the lost rate of heat to environment by increasing temperature. As summarized in Table I, the decreasing ratio of I_{trip} for the device composed of Surlyn/LDPE/CB composite with temperature was greater than that of LDPE/CB composite. Since the condition of ambient temperature and design of the device were same condition, the term of heat lost rate, $U(T - T_a)$ in the Eq. (2), is not responsible for this difference. The difference of the decreasing ratio of I_{trip} with temperature was related to the heat-generating rate (I^2R). In this experiment, the difference of heating rate at each ambient temperature is just determined by the change of resistance (R) under the ambient temperature condition because the current (I) depends on the resistance (R) of the device. The more increase a resistance with temperature, the more increase a heating rate of the device, and thus, the decreasing ratio of I_{trip} increases. As summarized in Table II,
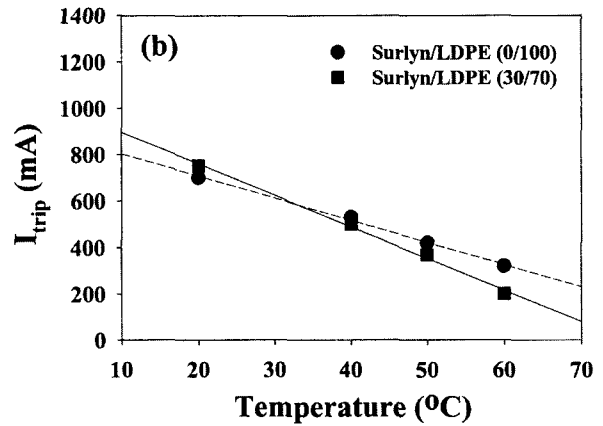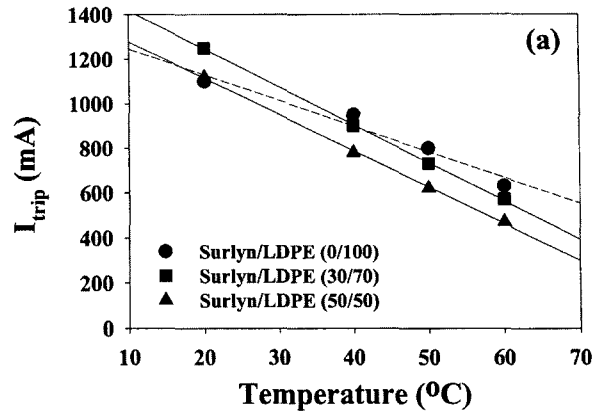

Figure 9. The decrement of the minimum switching current with temperature for Surlyn/LDPE/CB composites; (a) CB content = 40 wt% and (b) CB content = 30 wt%.

the resistance of the device composed of Surlyn/LDPE/CB composite with temperature is higher than that of LDPE/CB composite. The average thermal coefficient of resistance $(\alpha_T)^{47}$ can be calculated by the following equation.

$$\alpha_T = \frac{100}{(T_p - T_b)} \times \ln\frac{R_p}{R_b} \qquad (3)$$

Table I. The Average Minimum Switching Current (I_{trip}) Decreasing Ratio of Various Surlyn/LDPE/CB Composites

Temperature	I_{trip} (mA)				Average I_{trip} Decreasing Ratio (%/10°C)
	20°C	40°C	50°C	60°C	
CB = 40 wt%					
Surlyn/LDPE (0/100)	1100	950	800	630	-10.45
Surlyn/LDPE (30/70)	1250	900	730	570	-13.64
Surlyn/LDPE (50/50)	1120	780	620	470	-14.56
CB = 30 wt%					
Surlyn/LDPE (0/100)	700	530	420	320	-13.59
Surlyn/LDPE (30/70)	750	500	367	200	-18.09

Table II. The Resistance of Devices at the Different Temperature and α_T in the Temperature Range of 20~60 °C

Temperature	Resistance of Devices (mohm)				Average Thermal Coefficient of Resistance $(\alpha_{T\,[20-60°C]})$
	20 °C	40 °C	50 °C	60 °C	
CB = 40 wt%					
Surlyn/LDPE (0/100)	220	366	476	639	2.67 .
Surlyn/LDPE (30/70)	250	400	483	842	3.04
Surlyn/LDPE (50/50)	320	490	653	1169	3.24
CB = 30 wt%					
Surlyn/LDPE (0/100)	510	740	1079	2258	3.72
Surlyn/LDPE (30/70)	700	1140	1620	3698	4.16

where α_T is the average thermal coefficient of resistance; T_p is the higher temperature; T_b is the lower temperature; R_p is the resistivity at higher temperature, and R_b is the resistivity at lower tmperature. The $\alpha_{T[20-60°C]}$ of the device composed of Surlyn/LDPE/CB composite was higher than that of LDPE/CB composite, which was attributed to the addition of Surlyn having relatively lower melting temperature than that of LDPE, which was confirmed by the DSC results as shown in Figure 1. The molecular movement is more activated at the low temperature region of 20~60°C, and thus, the resistivity increases with increasing ratio at this temperature range. It can be confirmed by PTC curve as shown in Figure 6, representing the highly increased resistivity of Surlyn included composites and the rapid increase in the resistivity at low temperature.

Conclusions

The resistivity and PTC behavior of Surlyn/LDPE/CB composites were different from those of LDPE/CB composites, which was attributed to the uneven dispersion of CB accounted for the inclusion of Surlyn having metal ion and polar group. The resistivity of LDPE/CB composite was decreased linearly with CB content. However, the resistivity of Surlyn/LDPE/CB composites was decreased slowly at low CB content, and was decreased rapidly at CB content higher than 15 wt% due to the incorporation of Surlyn. PTC intensity of the crosslinked composites by EB irradiation was higher than that of the uncrosslinked composites, and that of the uncrosslinked Surlyn/LDPE/CB composite was nearly constant irrespective of CB content. The NTC effect caused by the decrease in the elastic modulus of the polymer was reduced by EB irradiation crosslinking.

PTC intensity of the crosslinked Surlyn/LDPE/CB composites was decreased slightly up to the critical content of Surlyn, and thereafter, was significantly increased with further increasing Surlyn content. The minimum switching current (I_{trip}) was decreased with temperature, and the decreasing ratio of I_{trip} for Surlyn/LDPE/CB composite was

higher than that of LDPE/CB composite. It was attributed to Surlyn component, resulting in the increment of the average temperature coefficient of resistance (α_T).

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