

INVESTIGATION OF MICROSTRUCTURE AND CONDUCTIVE MECHANISM OF HIGH DENSITY POLYETHYLENE/CARBON BLACK PARTICLE COMPOSITE BY POSITRON ANNIHILATION LIFETIME SPECTROSCOPY*

Yang-mei Fan^{a**}, Xian-feng Zhang^a, Bang-jiao Ye^a, Xian-yi Zhou^a, Hui-min Weng^a,
Jiang-feng Du^a, Rong-dian Han^a, Shao-jin Jia^b and Zhi-cheng Zhang^b

^a Department of Modern Physics, University of Science and Technology of China, Hefei 230027, China

^b Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230027, China

Abstract The microstructure and conductive mechanism of high density polyethylene/carbon black (HDPE/CB) composite were investigated by positron annihilation lifetime spectroscopy (PALS). The PALS were measured in two series of samples, one with various CB contents in the composites and the other with various γ -irradiation doses in HDPE/CB composite containing 20 wt% CB. It was found that CB particles distribute in the amorphous regions, the CB critical content value in HDPE/CB composite is about 16.7 wt% and the suitable γ -irradiation dose for improving the conductive behavior of HDPE/CB composite is about 20 Mrad. The result observed for the second set of samples suggests that γ -irradiation causes not only cross-linking in amorphous regions but also destruction of the partial crystalline structure. Therefore, a suitable irradiation dose, about 20 Mrad, can induce sufficient cross-linking in the amorphous regions without enhancing the decomposition of crystalline structure, so that the positive temperature coefficient (PTC) effect remains while the negative temperature coefficient (NTC) effect is suppressed. A new interpretation of the conductive mechanism, which might provide a more detailed explanation of the PTC effect and the NTC effect has been proposed.

Keyword Conductive mechanism, PALS, Free volume, HDPE/CB

INTRODUCTION

The resistivity of conductive particle-filled semi-crystalline polymer composite increases as the composite is heated. Especially, the resistivity jumps abnormally near the melting temperature (T_m) of polymer crystals and this characteristic is called the positive temperature coefficient (PTC) effect of resistance. The intensity of PTC has been defined as $\lg(\rho_{T_m} / \rho_{T_r})$ where ρ_{T_r} and ρ_{T_m} is the resistivity at room temperature and at the melting point of polymer, respectively. When the content of conductive filler in the composite exceeds a certain value the resistivity at room-temperature drops dramatically and then gently with further addition of conductive filler; this phenomenon is called the percolation and the critical content is called the percolation threshold. Among various composites showing the PTC property, polyethylene/carbon black (PE/CB) composite is the most attractive one because of its PTC property and low cost. It has been widely used in self-regulating heaters, self-resetting current overload protection elements and sensors, *etc.* However, PE/CB composite exhibits two obvious drawbacks, which greatly restrict its use. One is that at temperatures above T_m of the matrix, the composite exhibits a sharp decrease in resistivity, which is called the negative temperature coefficient (NTC) effect of resistance; the other is its poor reproducibility when it is subjected to repeated thermal cycling. However, it has been found that cross-linking in the polymer caused by γ -irradiation or by some chemical routes can effectively overcome these two

* This work was supported by the National Natural Science Foundation of China (Grant No: 19875050, 10075041, 10075044).

** Corresponding author: Yang-mei Fan (范扬眉), E-mail: rdhan@ustc.edu.cn

Received July 4, 2001; Revised September 17, 2001; Accepted September 24, 2001

shortcomings^[1-3].

Due to the strange conductive behavior and the wide usage of PE/CB composite, its conductive mechanism has attracted much attention. Since Frydman first observed the PTC phenomenon^[4] in polymer materials, many investigators have studied the conductive phenomena from various perspectives^[1-3, 5-20]. Kohl^[5] suggested that the conductive filler forms a network of conductive chains at temperatures below melting point, the sudden expansion taking place at the melting point results in a break-up of the conducting chains and the consequent anomalous jump of resistivity. However, he was not able to explain the NTC effect above T_m , when the expanded volume of the polymer still remains. Ohe and Natio^[6] suggested that the variation of resistance in the material results from the variation of the intergrain gaps' width between CB particles. In his paper the dependence of resistivity on gap and on applied electric field was calculated based on the tunneling effect; however the NTC behavior still remained unexplained. The tunneling model was later modified by Meyer^[7, 8] taking the effect of change in crystallinity into consideration. Meyer proposed that the conductive particles exist only in amorphous regions separated by crystalline films, which have been assumed to be more conductive than amorphous ones. Thus he suggested that the anomalous rise in resistivity near the melting point can be attributed to the melting of the crystals. He also suggested that the NTC behavior after melting resulted from the migration of the CB particles previously compressed in the original amorphous area into newly developed amorphous areas that cause CB particles to distribute uniformly, decreasing the difficulty of tunneling. Although Meyer's model can explain PTC and NTC phenomena, the model relies on a debatable assumption: thin films of crystalline polymer have high conductivity. Then Sherman^[9], in addition, stated the correlation between percolation and filler critical content and contended that three distinct physical processes, which are percolation, quantum tunneling and thermal expansion, control electron transport resulting in conductive behavior of the composite. But he has not referred to the effect of change of crystalline region and the NTC effect.

Nowadays it has been accepted by the scientific community that the PTC effect is due to the deaggregation of CB particles^[7-12, 17]; yet few investigators have provided detailed illustration of the PTC effect. However, it is not widely held that the NTC effect is due to reaggregation of CB particles though some investigators have proposed this point of view^[12-14]. Obviously, the dynamic factor resulting in reaggregation of CB particles has been considered their mutual attraction (such as van der Waals interaction or covalent bonds between them), which is too weak to overcome the separation resulting from the vigorous macromolecular movement at temperatures over T_m .

In recent years, some conductive polymer blends filled with carbon black have been studied more deeply; carbon black can further improve the electrical and mechanical properties of conductive polymers^[1, 15]. Therefore, the investigation of microstructure and the conductive mechanism of PE/CB composites is still of great significance in materials science and in industry. Various microstructure-exploring means have been used to study the conductive composite, such as scanning electron microscopy (SEM)^[15, 16], wide angle X-ray diffraction (WAXD)^[17], small angle X-ray scattering (SAXS)^[17, 18], small angle neutron scattering (SANS)^[18], transmission electron microscopy (TEM)^[19], nuclear magnetic resonance (NMR)^[20] and electron spin resonance (ESR)^[14]. Compared to these techniques, positron annihilation spectroscopy (PAS) has two prominent advantages, *i.e.*, the ability of detecting down to atomic scale and high sensitivity to the microstructure change of $\delta = 1$. Especially after the free volume theory was proposed, which indicates that most macro-characteristics of polymer materials are related to the free volume in polymer, PAS has been developed to directly determine the local free volume hole properties in polymeric materials^[21]. In this paper, we investigated the dependency of various CB contents and various γ -irradiation doses on the free volume of HDPE/CB composites, using positron annihilation lifetime spectroscopy (PALS). A new interpretation of NTC effect based on analyzing the free volume in HDPE/CB composites was proposed.

EXPERIMENTAL

Materials and Preparation of Samples

HDPE (melt flow rate = 2.0 g/min, density = 0.95 g/cm³) was commercially available from Lanzhou

Petrochemical Industries Ltd. Carbon black (surface area = 60–70 m²/g) was obtained from Chunan Chemical Factory.

The matrix and filler were first premixed in a high-speed mixer at 150°C for 15 min. The CB content varied between 0, 12, 14.5, 16.7, 20 and 23 wt%. Each mixture was molded at a pressure of 80 kg/cm² and a temperature of 150°C for 15 min to form a piece with a thickness of 2 mm, then cooled to room temperature. The pieces were cut into squares (20 × 20 mm²) as samples for PALS measurement. The samples (CB 23 wt%) were irradiated in a ⁶⁰Co-irradiation apparatus of USTC with various doses of 0, 2.5, 5, 10, 20 and 25 Mrad for studying the relationship between free volume and γ -irradiation dose. For resistivity measurements, the mixtures were formed into samples (125 × 12 × 2 mm³), and four copper wires were embedded in them as resistivity-measuring probes.

PALS and Resistivity Measurement

The positron lifetime measurements were performed using a conventional fast-fast coincident system produced by EG & G ORTEC Nuclear Instrument Company with a time resolution of 290 picosecond. A ²²NaCl positron source with an activity of 7 microcurie was sandwiched between two same HDPE/CB samples. 3 × 10⁶ counts were accumulated in each lifetime spectrum.

Measurements of specimen resistivity were performed using an ultra-high resistance tester produced by Analytic Instrument Company of Shanghai, under dc applied field and by a four-probe method. The dependence of resistivity on temperature was measured at a heating rate of 2 K/min.

Correlation between Lifetime Spectrum and Free Volume

The measured lifetime spectra were deconvoluted into three lifetime components using the computer program PATFIT, and the variances χ^2 of fits were smaller than 1.2. The shortest-lived components τ_1 (0.15–0.17 nanoseconds) are attributed to the annihilation of para-positronium (*p*-Ps) and free positron. The attribution of the intermediate-lived τ_2 (0.40–0.42 ns) is complicated and related to more factors in the HDPE/CB composite. The longest-lived components τ_3 (1.8–2.5 ns), which are very sensitive to the structural changes of polymers, are attributed to the pick-off annihilation of ortho-positronium (*o*-Ps) in free volume holes. I_1 , I_2 and I_3 (in %) are the intensities of the three lifetime components, respectively.

A correlation between the free volume in macromolecular systems and the observed *o*-Ps pick-up annihilation lifetime has been formulated^[22, 23]. This correlation is expressed in a semi-empirical equation Eq. (1)^[24], which connects the *o*-Ps pick-up lifetime τ_3 (in nanosecond) with the radius R (in nanometer) of the free volume hole as

$$\tau_3 = \frac{1}{2} \left[1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin \frac{2\pi R}{R_0} \right]^{-1} \quad (1)$$

where $R_0 = R + \Delta R$, $\Delta R = 0.1656$ nanometer, which is the best fitting parameter for polymers.

Thus τ_3 and I_3 are related to the size and number of the free volume hole. A semi-empirical equation $V_f = AV_R I_3$ has been developed^[24] to determine the fraction of free volume in polymer where V_R is the volume of a free volume hole with radius R and the value of constant A ranges from 0.001 to 0.002. To simplify the equation, a relative fraction F_v of the free volume has been defined as:

$$F_v = \frac{4}{3} \pi R^3 I_3 \quad (2)$$

i.e. constant A is assigned as one^[25, 26].

It has been realized that the conductive behavior in polymer/CB composite is predominantly due to the distribution of carbon black particles, which should exist in the amorphous region instead of in the crystalline area because of their size. So by PALS, the most significant parameters for evaluating microstructure change in the material are the third parameters: τ_3 , I_3 and F_v . Therefore, we pay special attention to the variation of these parameters. We call them the three parameters of the free volume.

RESULTS AND DISCUSSION

Dependence of Free Volume on CB Content

The dependence of τ_3 , I_3 and F_v at room temperature on CB content are shown in Figs. 1–3, respectively. The *o*-Ps lifetime τ_3 does not vary greatly with respect to increased CB content when the CB content is less than 16.7 wt%, and then decreases linearly when the CB content continues to increase; *i.e.* τ_3 deflects at a CB content of about 16.7 wt%. The *o*-Ps intensity I_3 decreases along with increased CB content in an linear relationship. Except a sudden rise near a CB content of 16.7 wt%, the relative fraction F_v of the free volume has the same tendency as the *o*-Ps intensity I_3 . Analyzing the dependence of free-volume on CB content, the following two known conclusions are again abstracted from the data of PALS.

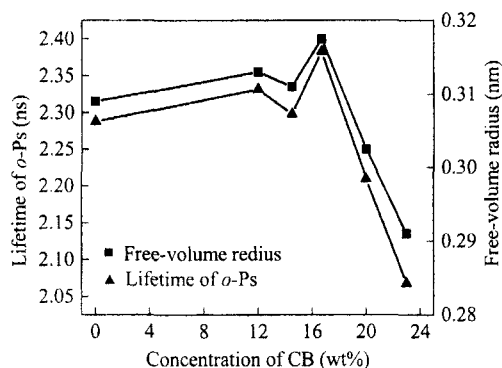


Fig. 1 Variation of *o*-Ps lifetime (▲) and free-volume radius (■) with CB content in HDPE/CB composites

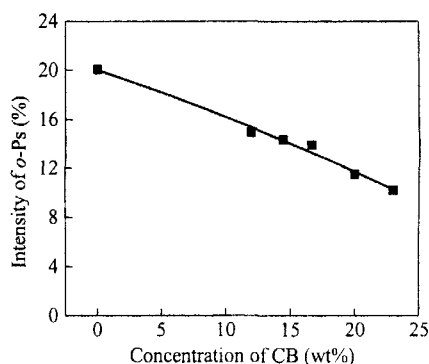


Fig. 2 Variation of *o*-Ps intensity with CB content in HDPE/CB composites

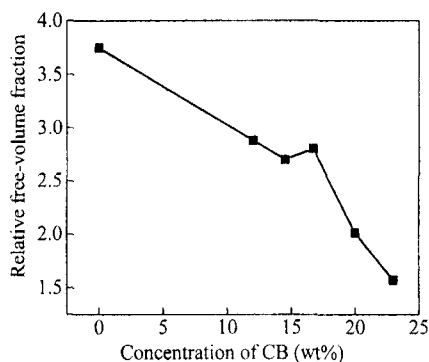


Fig. 3 Variation of relative free-volume fraction with CB content in HDPE/CB composites

Carbon black particles exist in the amorphous regions and they occupy and jostle into the free volume of the amorphous regions^[7, 8, 13, 17] and cause the number of the free volume hole and the fraction of the free volume to decline in a linear fashion as the CB content increases.

The critical CB content in HDPE/CB composite is about 16.7 wt%. This percolation threshold value is in agreement with Ref. [12, 13, 27]. According to the free volume theory of polymers^[28], a deflection of the parameters of the free volume implies the existence of a phase transition point. Analogously, the deflection point of F_v , τ_3 at a CB content of 16.7 wt% implies a microstructure change, a transformation of CB particles' distribution from dispersion to flocculation, *i.e.* aggregation, which constructs the paths of electric current for percolation. Wassailing^[16] has held the same view and presented a series of SEM photographs to prove it.

Dependence of Free Volumes on Irradiation Dose

Dependence of free volume on irradiation dose in HDPE/CB composite with CB content of 20 wt%

The dependence of τ_3 , I_3 and F_v in HDPE/CB composite containing 20 wt% CB on irradiation dose of 0, 2.5, 5, 10, 20 and 25 Mrad are shown in Figs. 4–6, respectively. The three parameters of the free volume have the same tendency.

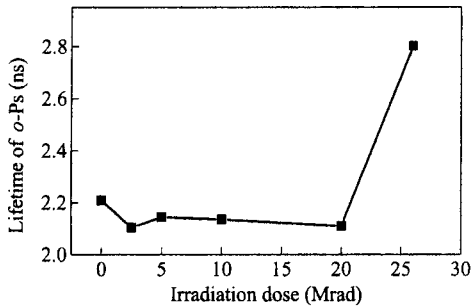


Fig. 4 Dependence of o-Ps lifetime on irradiation dose in HDPE/CB composites

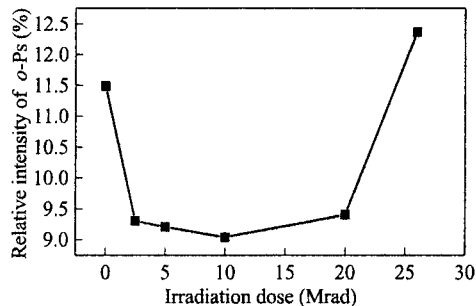


Fig. 5 Dependence of intensity of o-Ps on irradiation dose in HDPE/CB composites

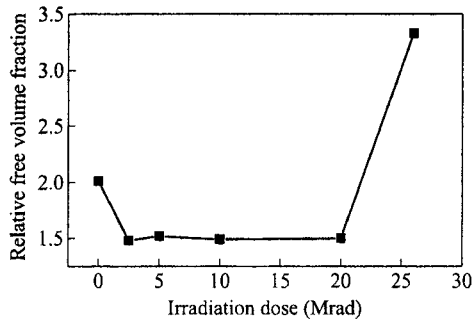


Fig. 6 Dependence of relative free-volume fraction on irradiation dose in HDPE/CB composite

Below 2.5 Mrad, the three parameters of the free volume all decrease quickly with the increase of dosage. This indicates that at this low irradiation dose, cross-linking in amorphous regions occurs and increases continuously which decreases the three parameters of the free volume, and decomposition of crystals still does not occur which increases the three parameters of the free volume. Therefore, the three free volume parameters decrease. Between 2.5 Mrad and 20 Mrad, all the three free volume parameters hardly vary with increased irradiation dose. This suggests that in this irradiation dose interval, cross-linking in the amorphous region continuously increases and, at the same time, a small fraction of crystals decomposes. These two effects offset each other, so the three parameters almost keep constant. Over 20 Mrad the three parameters of the free volume all increase sharply. This indicates that cross-linking in the amorphous region tends to reach the limitation but crystals still decompose acutely.

According to the above analysis, one conclusion and one suggestion are abstracted as follows.

The suitable γ -irradiation dose for improving the conductive property of the HDPE/CB composite should be about 20 Mrad at which sufficient cross-linking is created in the amorphous regions and little crystalline structure is disrupted. In order to validate this conclusion, the resistivity-temperature correlation curves of the two samples (one irradiated with 20 Mrad and the other unirradiated) were measured, and are shown in Fig. 7. The two curves' outlines from room temperature to the melting point, *i.e.* the two PTC parts, are almost the same. Each PTC part can be divided into three temperature segments by two deflection points at temperature T_{d1} and T_{d2} with the same rising speeds: in sequence, slight rise, linear rise, and steep rise in a semi-logarithm plot. However, in

the temperature range above T_m the difference is obvious: the NTC in the irradiated composite is reduced by about three orders of magnitude.

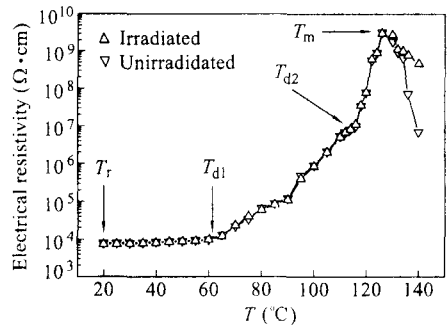


Fig. 7 Plot of resistivity against temperature in unirradiated (▽) and Irradiated (Δ) HDPE/CB composite

One suggestion is that the cross-linking section in amorphous regions and the decomposition section in crystalline regions are both very small (the nuclear magnetic resonance (NMR) measurement^[20] has given the cross-linking section as less than 10^{-4}). So we suppose that the cross-linking network in the amorphous region induced by 20 Mrad irradiation dose would not affect the movement of carbon black particles in the amorphous domain, but would impede carbon black particles moving into new amorphous regions, which are crystals at first and then melted when the temperature is over T_m . This is one of the basic points in our new interpretation of the conductivity mechanism of PE/CB composite.

Dependence of free volumes on irradiation dose in composite without CB

With an interest in knowing more about how the filler affects the matrix in the irradiation procedure, the correlations of τ_3 , I_3 and F_v with irradiation dose in the composite without carbon black particles were measured and shown in Figs. 8–10. Comparing τ_3 , I_3 and F_v in Figs. 4–6 with their corresponding values in Figs. 8–10, the following features are obvious. The values of τ_3 , I_3 and F_v in the composite with CB are all smaller than that in the composite without CB, but both have approximately similar tendency in their deflecting points and changing intervals of the change. This indicates that the influence of CB particles on the basic structure of the HDPE matrix is not obvious. From these data, it is again proved that the CB particles are located only in the amorphous regions and jostle into the free volume. Thus, the size of the free volume holes is shrunk, their number decreases and the fraction of free volume is reduced, as well as the resistivity of the material.

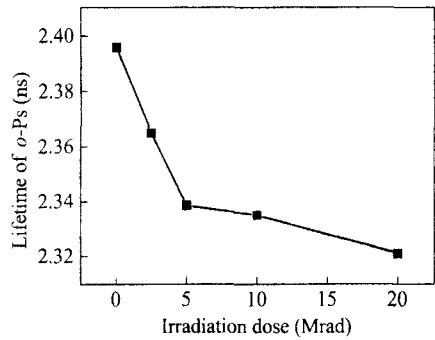


Fig. 8 Dependence of o-Ps lifetime on irradiation dose in pure HDPE

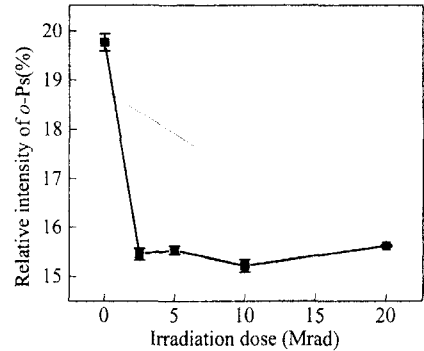


Fig. 9 Dependence of intensity of o-Ps on irradiation dose in pure HDPE

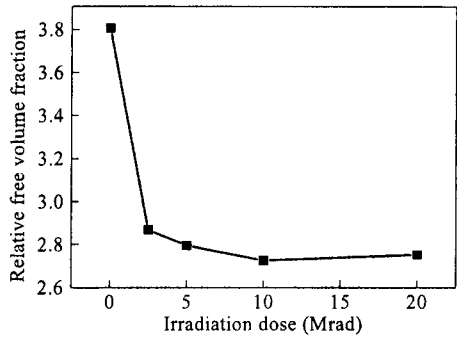


Fig. 10 Dependence of relative free-volume fraction on irradiation dose in pure HDPE

A New Interpretation about Conductive Mechanism of PE/CB Composite

Based on the above discussion, we propose a new interpretation of the conductive mechanism of PE/CB composite, which could better explain the PTC effect and NTC effect. Figure 11 is a group of schematic pictures showing the variation of distribution of carbon black particles in a PE/CB composite containing CB content beyond its threshold value in three temperature segments. In the pictures, strip-shaded frame represents the crystalline domain, the area outside the frames representing the amorphous regions, and each black spot represents a carbon black particle. Figures 11 (a) and (b) represent the distribution of CB particles in the temperature range below/at T_r and in the temperature interval from T_r to T_m , respectively. Figures 11(c) and (d) represent the distribution of CB particles in the temperature range over T_m in an unirradiated and an irradiated composite, respectively. In the two pictures a frame surrounded by dotted line represent a newly developed amorphous region with expanding volume owing to the melting of crystals.

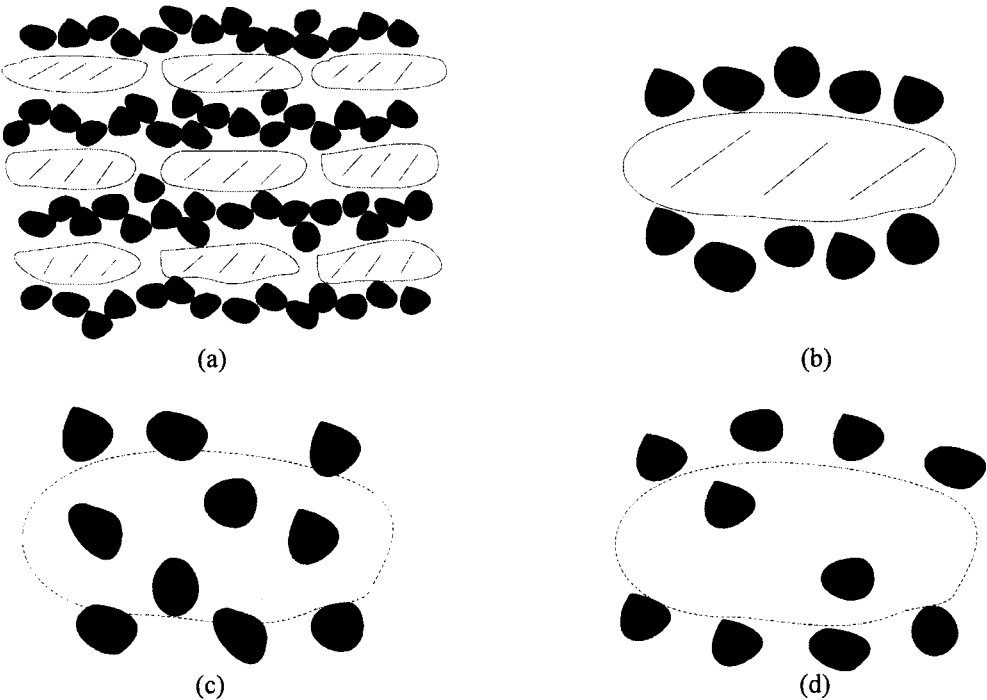


Fig. 11 Schematic distributions of CB particles in three different temperature ranges (a) Below and/or at room temperature; (b) Temperature interval from room temperature to melting point; (c) Temperature range over melting point (unirradiated HDPE/CB composites); (d) Temperature range over melting point (irradiated HDPE/CB composites)

The distribution of CB particles depends on the competition between the aggregation caused by the attraction between CB particles and the disaggregation, which is the result of the movement of molecular chain segments of the polymer and/or the Brownian movement of CB particles. The former depends largely on distance, *i.e.* the width of the intergrain gap between CB particles, but little on temperature; the latter relies greatly on temperature.

In the temperature range below and at T_r , the distribution of carbon black particles in the composite having a CB content beyond its threshold value is shown in Fig. 11(a). The width of the intergrain gaps equals or nearly equals zero, which results in ohmic connection of CB particles. Thus, the flow of electric current in the composite comes from, in essence, the infiltration-flow of electrons between carbon particles, which is called the percolation current. Or the course of cooling down from melting point to low T_r temperature range, the CB particles are at first swept by crystalline fronts pushing them into amorphous regions. And then CB particles become closer to each other under the retarded movement of the molecular chain segment of the polymer and the attraction between CB particles increases due to their sufficiently high density in the amorphous regions. The attraction exceeds the repulsion between CB particles; thus the distribution in Fig. 11(a) has been developed. Otherwise, in a composite having a CB content below its threshold value, the CB particles in amorphous solid separate from one another because of the weak density of carbon black particles; the flow of electric current in this composite comes completely from tunneling current.

In the temperature range from room temperature to melting point, the CB particles start and then continue to disaggregate as shown in Fig. 11(b) because the movement of the molecular chain segment of the polymer increases and the viscosity decreases with rising temperature. The conductive mechanism changes from percolation current to tunneling current. In more detail, we try to explain the correlation of resistivity-temperature variation with the three temperature segments of the PTC part in Fig. 7. Based on tunneling effect, Ohe has deduced some equations about the relationship between the resistivity ρ and the mean gap width λ of CB grains, that can be presented as an equation^[6]:

$$\rho = \rho_0 + A\lambda \exp(B\lambda) \quad (3)$$

where ρ_0 is the resistivity of the filler, A and B both include some constants and parameters related to the applied field and materials, or in other words, A and B do not depend on temperature. Equation (3) means that the resistivity is determined by the product of a polynomial function and a positive exponential function of the width of the gap. In the temperature range of $T_r - T_{d1}$ the gap width is still almost near zero because of the attraction between CB particles and the mild molecular thermal movement. If we do not take the slight rise into consideration, which is caused by the mild increased thermal movement of macromolecule and conductive particles, according to Eq. (3) the resistivity almost equals ρ_0 . The resistivity of this temperature segment corresponds to the percolation current. In the temperature segment of $T_{d1} - T_{d2}$, because gap width starts to extend owing to the gradually intensifying molecular thermal movement the attraction begins to disappear; hence, the gap width extends mainly under molecular thermal movement and probably in a linear width-temperature relationship. In addition, when the gap width becomes bigger, the positive exponential function is more significant than the polynomial function in Eq. (3). Thus, the resistivity rises basically as an exponential function of temperature, *i.e.* in a linear function in semi-logarithm plot like that in the segment of $T_{d1} - T_{d2}$ shown in Fig. 7. In the temperature segment of $T_{d2} - T_m$, a small temperature range of a few degrees below the melting point, CB particles gain more space for movement and hence the gap width becomes much larger because the boundary of crystals starts to melt. Thus, the steeply rising resistivity occurs. However, it is necessary to note that the gap width is not the size of the free volume hole, though a positive function relationship might exist between both of them.

At temperatures higher than the melting point, crystalline regions completely melt and their volume suddenly expands at the melting point. In an unirradiated composite, the distribution of CB particles is like that shown in Fig. 11 (c): carbon black particles enter into the new amorphous regions and remain there. Despite the continuing extension of the gap width, a new network of tunneling current has been formed throughout the entire

composite; the total effect decreases the difficulty of tunneling and results in an obvious NTC effect. In an irradiated composite as shown in Fig. 11(d), the formation of the tunneling current network is difficult, because the cross-linking network in the initial amorphous regions impedes the entry of carbon black particles into the newly developed amorphous regions; therefore the NTC effect is well-suppressed. Furthermore, the resistivity-temperature reproducibility in an irradiated composite subjected to repeated thermal cycling is also improved because in a thermal cycle CB particles return back nearly to their initial location much easier than in an unirradiated one.

Compared to previous models and ideas, our new interpretation has the following two distinct features.

(1) Two distinct conductive mechanisms, percolation and tunneling, control the electron transport in PE/CB composites. In a PE/CB composite having a conductive particle content beyond its threshold value these two mechanisms all give contributions to conductive behavior; at temperatures below and near room temperature, a percolation mechanism prevails; at temperatures above T_{d1} , tunneling is prevailing and the conductive mechanism tends to transform percolation into tunneling. Otherwise, in a composite having a conductive particles content below its threshold value, tunneling is prevailing throughout.

(2) One of the most basic dynamic factors is the thermal movement of macromolecule chain segment. The influence of this factor on the conductive behavior of PE/CB composites is effective throughout the whole temperature range, in other words, the influence of the factor is on PTC and NTC effects. And it closely correlates with the free volume and thermal expansion of the material. Otherwise the influence of crystalline melting on conductive behavior is only small in a temperature range starting at a few degrees below T_m .

CONCLUSION

The dependency of PALS on various CB contents in HDPE/CB composites and on various irradiation doses in the composite with a CB content of 20 wt% have been measured. In PE/CB composite, CB particles exist in the amorphous region. The critical CB content in HDPE/CB composite is about 16.7 wt%. The suitable irradiation for improving conductive behavior of the composite is about 20 Mrd. These results prove that the PAS probe and the correlative free volume in the polymer are very important methods for exploring the microstructure of polymeric materials and the relationship between microstructure and macro-characteristics of polymers.

A new interpretation of the conductive mechanism of HDPE/CB composite is established, in which the PTC effect does result from the disaggregation of CB particles. Nevertheless, the NTC effect might result from a more uniform distribution of CB particles instead of from reaggregation or inhomogeneous distribution of CB particles.

Acknowledgments The authors would like to thank Y. Bai, J.D. Shi and W. Kong for their assistance in this work.

REFERENCES

- 1 Yu, G. and Zhang, M.Q., *Polym. Eng. Sci.*, 1999, 39: 1678
- 2 Tang, H., Piao, J., Chen, X., Luo, Y., and Li, S., *J. Appl. Polym. Sci.*, 1993, 48: 1795
- 3 Narkis, M. and Vaxman, A., *J. Appl. Polym. Sci.*, 1984, 29: 1639
- 4 Frydman, E., 1948, U.K. Patent Spec., 604, 695
- 5 Kohl, F., 1966, U.S. Patent, 3, 243,753
- 6 Ohe, K. and Natio, Y., *Japanese J. Appl. Phys.*, 1971, 10: 99
- 7 Meyer, J., *Polym. Eng. Sci.*, 1973, 13: 462
- 8 Meyer, J., *Polym. Eng. Sci.*, 1974, 14: 706
- 9 Sherman, R.D., *Polym. Eng. Sci.*, 1983, 23: 36
- 10 Klason, C. and Kubat, J., *J. Appl. Polym. Sci.*, 1978, 19: 831

- 11 Voet, A., Rubber Chem. Technol., 1981, 54: 42
- 12 Lee, G.J. and Suh, K.D., Polym. Eng. & Sci., 1998, 38: 471
- 13 Al-Allak, H.M., Brinkman, A.W. and Woods, J., J. Materl. Sci., 1993, 28: 117
- 14 Tang, H., Liu, Z.Y., Piao, J.H., Chen, X.F., Lou, Y.X. and Li, S.H., J. Appl. Polym. Sci., 1994, 51: 1159
- 15 Feng, J. and Chan, C. M., Polym. Eng. Sci., 1999, 39: 1207
- 16 Wessling, B., Polym. Eng. Sci., 1991, 31: 1200
- 17 Luo, Y. L., Wang, G.C., Zhang, B.G. and Zhang, Z.P., Eur. Polym. J., 1998, 34: 1221
- 18 Wignall, G.D., J. Materl. Sci., 1990, 25: 69
- 19 Chan, C.M. and Cheng, C.L., Polym. Eng. Sci., 1997, 37: 1127
- 20 O'Dommell, J.H. and Whittaker, A.K., Brit. Polym. J., 1985, 17: 51
- 21 Jean, Y.C., Microchem. J., 1990, 42: 72
- 22 Tao, S.J., J. Phys. Chem., 1972, 56: 5499
- 23 Eldrup, M., Lightbody, D. and Sherwood, J.N., J. Chem. Phys., 1981, 63: 51
- 24 Wang, Y.Y., Nakanishi, H. and Jean, Y.C., J. Polymer. Sci. B, 1990, 28: 1431
- 25 Kanaya, T., Tsukushi, T., Kaji, K., Bartos, J. and Kristiak, J., Physical Review E, 1999, 60: 1906
- 26 Wang, C.L. and Wang, S.J., Physcal Review B, 1995, 51: 8810
- 27 Miyasaka, K., Watanabe, K., Jojina, E., Aida, H., Sumita, M. and Ishikawa, K., J. Materl. Sci., 1982, 17: 1610
- 28 Ferry, J.D., "Viscoelastic Properties of Polymers", 3rd ed. NewYork, Wiley, 1980, p.364–367