

Conductive-Filler-Filled Poly(ϵ -caprolactone)/Poly(vinyl butyral) Blends. II. Electric Properties (Positive Temperature Coefficient Phenomenon)

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ABSTRACT: The electric properties of poly(ϵ -caprolactone) (PCL)/poly(vinyl butyral) (PVB) blends containing carbon black (CB) were studied as a functions of the PVB content and crystallization time. Comparison of the electric properties between the two cases (PCL/PVB blends and pure PCL) provided us useful information on the origin of the positive temperature coefficient (PTC) phenomenon of the resistivity. In this article, we report the influence of the morphology and the spherulitic structure on the distribution of CB, which results in the resistivity changes. Blending a small amount (up to 5%) of PVB caused significant changes in the electric property at a constant CB content. Both the resistivity and the intensity of PTC increased with the PVB content. These changes are ascribed to the change of CB distribution. A model is proposed to explain these results using Ohe's theory. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 409–416, 1997

Key words: poly(ϵ -caprolactone); poly(vinyl butyral); polymer blend; positive temperature coefficient; carbon black

INTRODUCTION

The electric conductivity of polymeric materials is increased by incorporating conducting fillers such as carbon black (CB). The conductivity of CB-filled polymer depends not only on the properties of CB such as particle size, aggregate shape, and dispersion state, but also on the characteristics of polymers such as chemical structure, crystallinity, and processing conditions. A crystalline polymer having the critical CB content shows a sharp resistivity increase with temperature around the melting point of the polymer (positive temperature coefficient [PTC]).¹ Important industrial applications of PTC materials are self-regulating heaters, current limiters, and overcurrent protectors.²

The PTC phenomenon has attracted much in-

terest and studies during the last few decades. Although there is no satisfactory theory to explain the PTC phenomenon, there have been many contributions to elucidating its specific aspects by Kohler,³ Meyer,^{2,4} Ohe,⁵ and Narkis et al.^{1,6,7} The various factors affecting the phenomenon were also reported by Sumita et al.^{8,9} and Tang et al.¹⁰ At present, the explanation based on the tunneling effect is widely accepted. According to this mechanism, electrons pass through the thin gaps between adjacent CB particles, aggregates, and agglomerates at a practical magnitude of the electric field. The gap width dominates the electrical properties rather than the length of the particle chain since the current is an exponential function of the gap width.⁵

The miscibility of crystalline/amorphous polymer blends greatly influences the morphology of the blends. Keith et al.¹¹ reported an interesting system of poly(ϵ -caprolactone) (PCL)/poly(vinyl butyral) (PVB), where the nucleation frequency of PCL crystals is drastically reduced by adding

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only up to several percent of PVB. This allows the spherulites to grow on the order of centimeters. They also observed banded spherulites, whose structure originates from the enhancement in the regularity of the lamellar organization.^{11,12} Many studies have been reported on the PTC phenomenon of polyolefin, polyethylene (PE), and polypropylene (PP). Since the morphology of the PCL/PVB blends changed greatly by blending PVB and the dimensions of the spherulites of the blends are usually on the order of 10 μm , this system is more suitable than is PE or PP for studying the effect of morphological changes on the PTC properties.

In the present study, we discuss the effect of morphological changes on the electrical properties of PCL/PVB blends containing CB. The cooperative twist of radiating lamellar crystals is expected to influence the distribution of CB and, therefore, PTC properties. This is the first attempt to investigate the relation between morphological changes and the electrical properties of a crystalline polymer containing CB. The article is organized as follows: After a brief description of the sample preparation and experimental method, the influence of the PVB content on the PTC properties is reported. DSC thermograms of the blends are compared with those of pure PCL. Then, the influence of the lamellar twisting on the electric properties is discussed. Finally, a schematic model is presented to explain the results using Ohe's theory.

EXPERIMENTAL

Electric Resistivity Measurements

Preparation of the CB-filled blends was described in Part I.¹³ The film samples (5 mm long, 8 mm wide, and 0.1 mm thick) were placed between glass plates. Silver paste (Fujikura kasei, Dotite 500) was painted on each end of the sample surface to ensure electric contact with the electrodes. The current and the voltage between the electrodes were measured with a Keithly 480 picoammeter and a Keithly 195A digital multimeter. The power supply was a Metronix DMS 35-1.5.

Figure 1 shows the thermal program used for the PTC measurements. Samples were heated from room temperature to 80°C at 10°C/min, annealed for 1 h, and then rapidly cooled to the crystallization temperature. After the crystallization was finished, samples were cooled in a nitrogen atmosphere to room temperature. They were

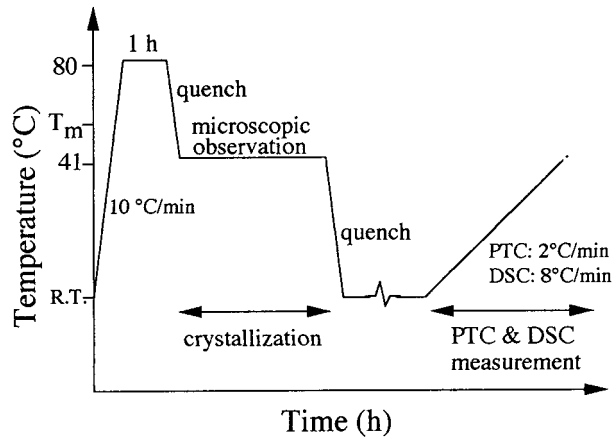


Figure 1 Thermal program for PTC and DSC measurements and optical microscopic observations.

heated again at 2°C/min to 80°C for measuring the resistivity.

Differential Scanning Calorimetry (DSC)

A Perkin-Elmer DSC-1B was used to determine the melting temperature and the degree of crystallinity of PCL crystals in the blends. The thermal program used for DSC was the same as that shown in Figure 1. The scan rate was 8°C/min.

Microscopic Observation

Polarized microscope observation was carried out for the PCL/PVB blends containing 1.3 vol % CB and 5 vol % fullerene (C_{60}). The instruments were described in Part I. Photographs were taken for each sample crystallized with the thermal program in Figure 1.

RESULTS AND DISCUSSION

Effect of PVB Blending

Figure 2 shows the temperature dependence of the resistivity ρ of a PCL/PVB blend (100 : 0) with 5 vol % CB. The samples were crystallized at 41°C with various crystallization times t_c . The resistivity–temperature curve slightly shifted upward with t_c , while the PTC intensity I_{PTC} , defined as the resistivity ratio $\rho_{\text{max}}/\rho_{\text{min}}$, was constant. Here, ρ_{max} is the maximum value of the curve and ρ_{min} is the resistivity at room temperature.

Figure 3 shows the temperature dependence of ρ of a PCL/PVB blend (99 : 1) with 5 vol % CB. The curve shift with the crystallization time was

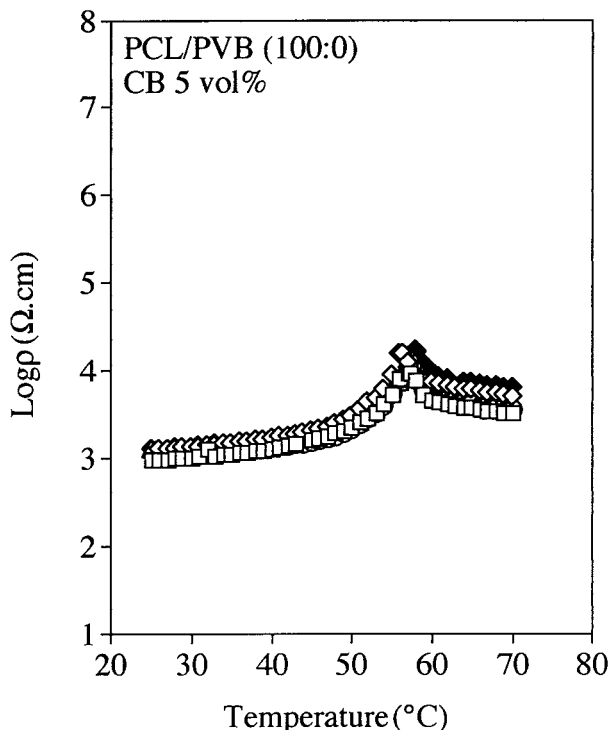


Figure 2 Temperature-resistivity curves of PCL containing 5 vol % CB with different crystallization times at 41°C: (□) quench; (◇) 0.25 h; (○) 2 h; (△) 6 h; (◆) 16 h.

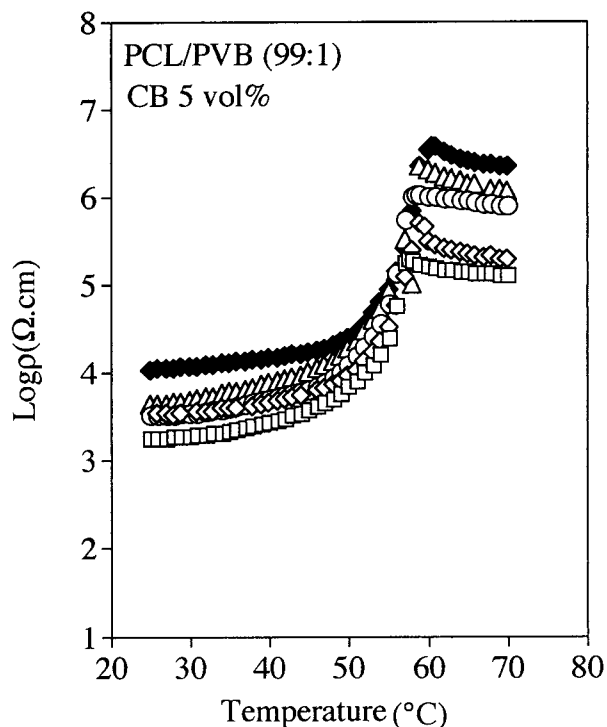


Figure 3 Temperature-resistivity curves of PCL/PVB (99 : 1) blends containing 5 vol % CB with different crystallization times at 41°C: (□) quench; (◇) 0.25 h; (○) 2 h; (△) 6 h; (◆) 16 h.

larger than that of pure PCL in Figure 2 although I_{PTC} remains almost constant for all t_c . The value of I_{PTC} for the PCL/PVB blend (99 : 1) was also larger than that for the pure PCL system. Figure 4 and Table I show the effect of the PVB blend ratio ϕ_{PVB} on the PTC properties containing the same amount of CB. Both ρ and I_{PTC} increased with ϕ_{PVB} . The value of ρ_{max} of the blend with 5% of PVB was larger than that of pure PCL by 5 orders of magnitude. Note that these samples contain the same amount of CB. However, the resistivity of the blend was already larger by 10^3 at room temperature than that of pure PCL. Such a difference in CB-filled thermoplastic polymers has been interpreted as the consequence of the thermal history of the sample. The expansion and contraction of CB-filled samples undergoing a heating-cooling cycle causes the movement of CB particles when they melt or crystallize.⁷ All the samples in Figure 4 have undergone a heating and cooling process (see Experimental section). This thermal history shifted the resistivity-temperature curve upward relative to the first run of the solution-cast sample. This effect was more profound in the blends and we discuss it in the fourth section. To verify the effect of a heating-

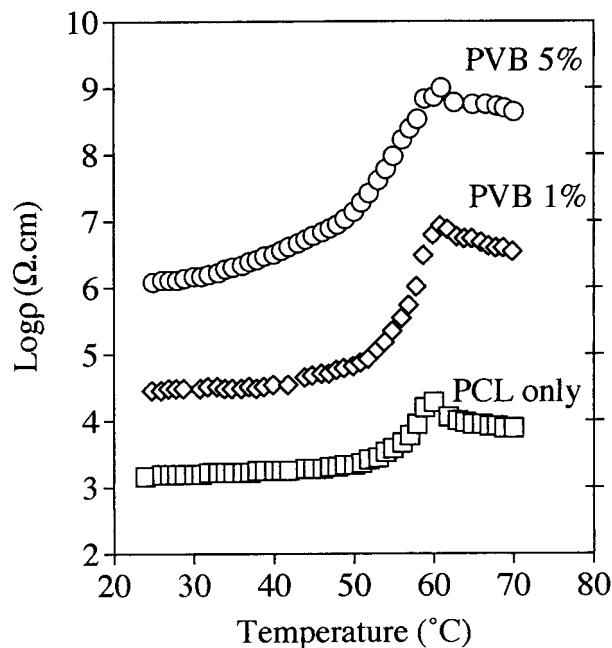


Figure 4 Dependence of temperature-resistivity curves of PCL/PVB blends containing 5 vol % CB on the PVB content. All samples have the same CB content and crystallization conditions at 41°C for 21 h: (□) pure PCL; (◇) PCL/PVB (99 : 1); (○) PCL/PVB (95 : 5).

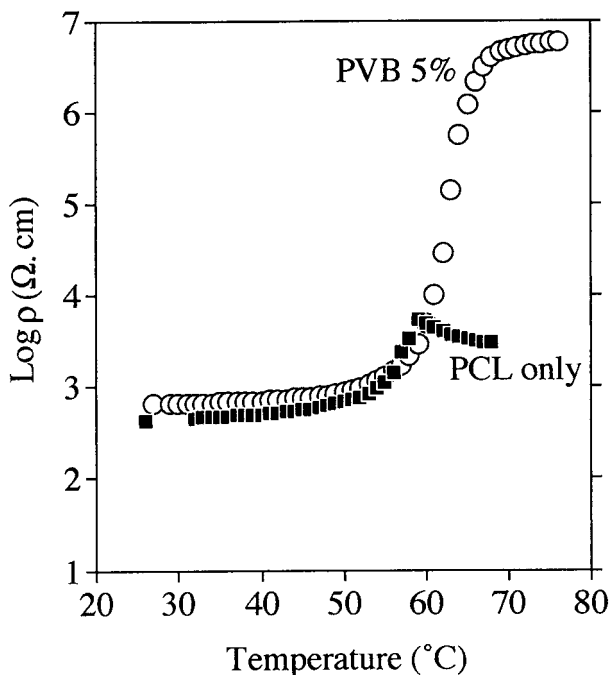


Figure 5 Dependence of temperature-resistivity curves of solvent-cast PCL/PVB blends containing 5 vol % CB on the PVB content: (■) pure PCL; (○) PCL/PVB (95 : 5).

cooling cycle, the PTC behavior of solution-cast samples was compared between a blend ($\phi_{\text{PVB}} = 5\%$) and pure PCL for the same amount of CB (5%) as shown in Figure 5. In contrast to the heat-cycled samples in Figure 4, the values of ρ_{min} of the two samples were the same. However, the I_{PTC} of the blend ($\phi_{\text{PVB}} = 5\%$) was larger than that of pure PCL. The value of ρ of the blend was still larger than that of PCL after the temperature was lowered to room temperature. This results in the difference of ρ_{min} in Figure 4.

Figures 2 and 3 show that the temperature at which the resistivity reaches the maximum ($T_{\text{max,PTC}}$) increased with t_c up to 6 h and was constant afterward (Table II). These figures also indicate that the $T_{\text{max,PTC}}$ for the PCL/PVB (99 : 1) blend is larger than that for the pure PCL system.

Table I The Values of I_{PTC} of PCL/PVB Blends Containing 5% CB; All Samples Were Crystallized at 41°C for 21 h

	PCL : PVB		
	100 : 0	99 : 1	95 : 5
I_{PTC}	12.0	324.0	673.1

PTC properties are not only dependent upon the weight fraction of CB but also on the change of the crystalline phase. Since the PTC phenomenon is caused by the volume expansion of lamellar crystals around which CB particles are distributed, the degree of crystallinity also affects the PTC properties.^{10,14} The three samples in Figure 4 had the same CB content and were crystallized under the same conditions; the difference was only the PVB content (0, 1, or 5%). As discussed in Part I, the morphology of PCL/PVB blends changed greatly with blending a small amount of PVB and this change should be one of the causes of the change in the PTC property.

DSC Analysis

Figures 6 and 7 show DSC thermograms for PCL/PVB (100 : 0) and PCL/PVB (99 : 1) blends containing 5 vol % CB crystallized at 41°C for various crystallization times. Comparison of the figures indicate that blending 1 wt % of PVB does not alter the crystalline properties of PCL, such as the crystallinity (the area of DSC melting curve) and the lamellar thickness (the endothermic peak temperature) as summarized in Table III. Such observations were reported by other researchers using a different blend system (PCL/PVC).^{15,16}

Each DSC endothermic peak temperature ($T_{\text{max,DSC}}$) increased as the crystallization time was prolonged up to 6 h and was constant after that time as in the case of $T_{\text{max,PTC}}$ in the resistivity measurement, although they do not exactly coincide with each other. Then, we can conclude tentatively that the PTC phenomenon has something to do with the melting process of the PCL crystals.

There are three possibilities for the changes of PTC properties: (a) the changes of the weight

Table II $T_{\text{max,PTC}}$ of PCL/PVB Blends Crystallized at 41°C with Different Crystallization Times; Crystallization Temperature and CB Content Were Kept Constant

Sample	$T_{\text{max,PTC}}$ (°C)				
	0 h (Quench)	0.25 h	2 h	6 h	16 h
PCL/PVB (100 : 0)	57	56.8	57	57.7	58
PCL/PVB (99 : 1)	57.5	59	58.4	61	61

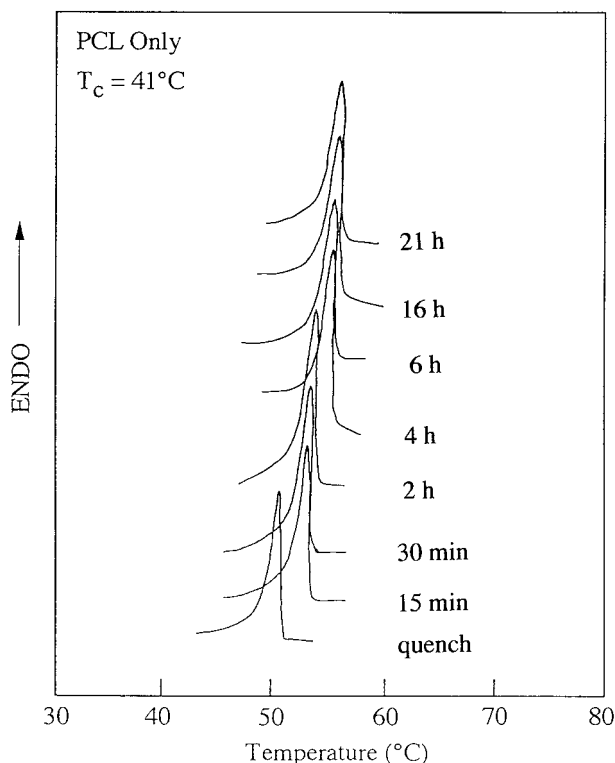


Figure 6 DSC thermograms for PCL containing 5 vol % CB with different crystallization times at 41°C. Heating rate was 8°C/min.

fraction of CB, (b) the changes of the crystalline properties between pure PCL and the blends, and (c) the morphological changes induced by blending PVB. Since the CB content is unchanged in Figures 2–5, we can exclude the first possibility. No variation of the DSC melting curve between pure PCL and PCL/PVB blends excludes the second possibility. Only the third explanation is left in question.

The Conducting Path and Twisted Lamellae

It is reasonable to assume two possibilities for the CB distribution, i.e., the conducting path, in the samples: (a) along the boundary of the spherulites and (b) along the lamellae. If CB is excluded to the growth front of spherulites during crystallization, the final distribution of CB is substantially different from the initial distribution for both PCL and PCL/PVB blends. The observations using atomic force microscopy (AFM) in Part I showed, however, that most of the CB remains in the spherulites and that only a small number of tiny CB aggregates and particles are expelled on the boundaries. We can therefore exclude the first possibility: the rejection of CB on the growing

front of the spherulite. The path along the lamellar crystals is the most possible distribution.

The growth front of the spherulites of the blend containing CB was clearly observed in Part I. However, we were not able to observe the extinction rings because of the CB aggregates in the spherulites. To confirm whether the samples containing CB have extinction rings or not, the blends containing a reduced amount of CB and the fillers having a smaller particle size than that of CB were investigated by polarizing optical microscopy.

Figure 8 shows polarized optical micrographs of PCL/PVB (99 : 1) containing (a) 1.3 vol % CB and (b) 5 vol % fullerene (C_{60}) crystallized at 41°C for 24 h. The particle sizes of CB and C_{60} are about 30 and 1 nm, respectively. In Figure 8(a), extinction rings are observed although the regularity is more reduced than that of the blends without CB. For specimens containing 5 vol % C_{60} , we can clearly see more regular rings as shown in Figure 8(b). Therefore, the PCL/PVB blend containing CB must have twisted lamellae disturbed by the presence of CB.

The Effect of Lamellar Twist on the PTC Effects

We now explain the relation between the change of the distribution of CB and the PTC properties

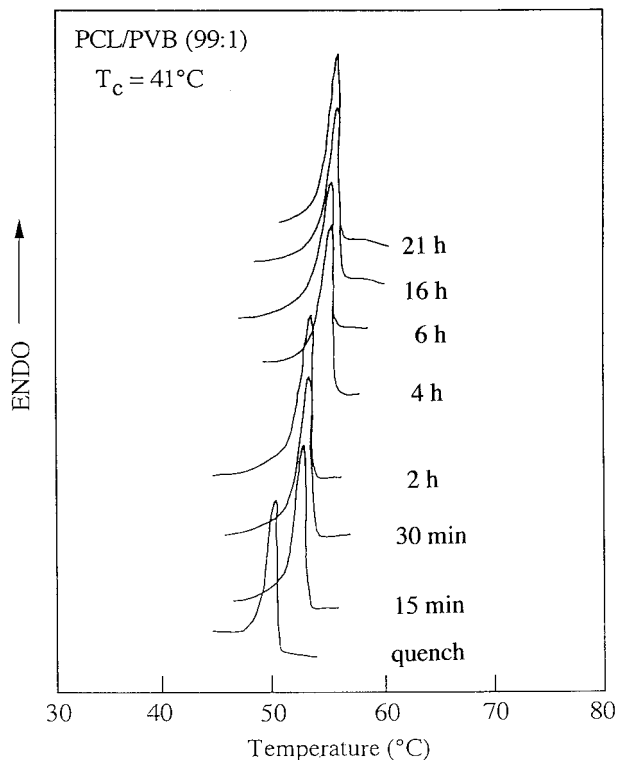


Figure 7 DSC thermograms for PCL/PVB (99 : 1) blends containing 5 vol % CB with different crystallization times at 41°C. Heating rate was 8°C/min.

Table III DSC Endothermic Peak Temperature ($T_{\max, \text{DSC}}$) of PCL/PVB Blends Crystallized at 41°C with Different Crystallization Times^a

Sample	$T_{\max, \text{DSC}}$ (°C)					
	0 h (Quench)	0.25 h	2 h	4 h	6 h	16 h
PCL/PVB (100 : 0)	51.4	52.7	52.9	53.4	54.9	54.9
PCL/PVB (99 : 1)	50.4	52.9	52.9	52.9	54.9	54.9

^a The PVB content did not alter $T_{\max, \text{DSC}}$. The crystallization temperature and the CB content were kept constant.

using Ohe's equivalent circuit model.⁵ The resistivity of PTC materials is composed of a large number of low-resistivity elements of CB particles,

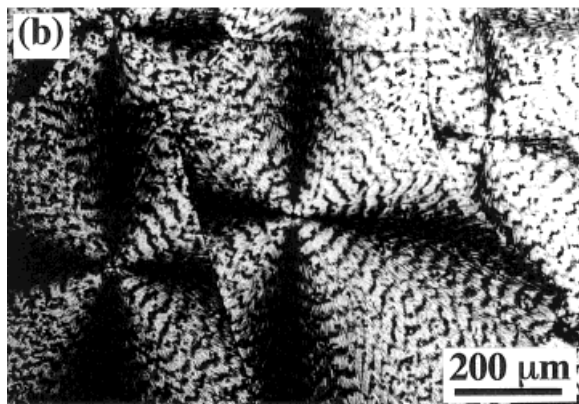
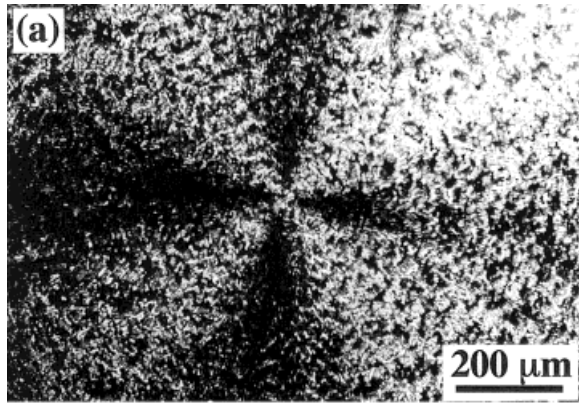


Figure 8 Cross-polarized optical micrographs describing the extinction rings of PCL/PVB spherulites crystallized at 41°C for 21 h: (a) CB 1.3 vol %; (b) fullerene (C_{60}) 5 vol %. To observe the extinction rings in the spherulite, the CB content was reduced for (a) and a finer filler was used for (b).

high-resistivity elements of interparticle gaps, and much higher resistivity elements of polymeric matrices. The last elements have so high a resistivity that they do not contribute to the total value. Therefore, the resistivity depends mainly on the interparticle gap width. According to the theory,⁵ the resistance of the interparticle gaps is governed by the tunneling effect through the polymeric insulators. The distribution of the interparticle gaps become more random as the temperature increases. The resistance of some gaps increases extremely and others may decrease with increase of the temperature, especially around the melting point. The resistivity of a PTC composite material is expressed by the following equation:

$$R = \left(\frac{N}{M} \right) \frac{h^2 s_0}{a^2 e^2 \sqrt{2m\Phi}} \times (1 + \beta s_0 \sigma) \exp \left(\beta s_0 + \frac{\beta^2 s_0 \sigma^2}{2} \right) \quad (1)$$

where N/M is the constant depending on the network of conductive particles in the system; a , the cross-sectional area of the conductive particle; e , the electron charge; h , the Plank constant; m , the electron mass; s_0 , the average width of the interparticle gap; σ , the distribution factor of the gap distance; β , $2m\phi[(4\pi)/h]$; and ϕ , the conductive particle–insulator work function.

Equation (1) indicates the strong contribution of σ to the resistivity, i.e., the resistivity changes by several factors of 10 via the change of σ only by a factor of 10 even if the average width of the interparticle gaps is unchanged. Thus, the PTC phenomenon has a strong relation with σ and, therefore, the distribution of CB particles.

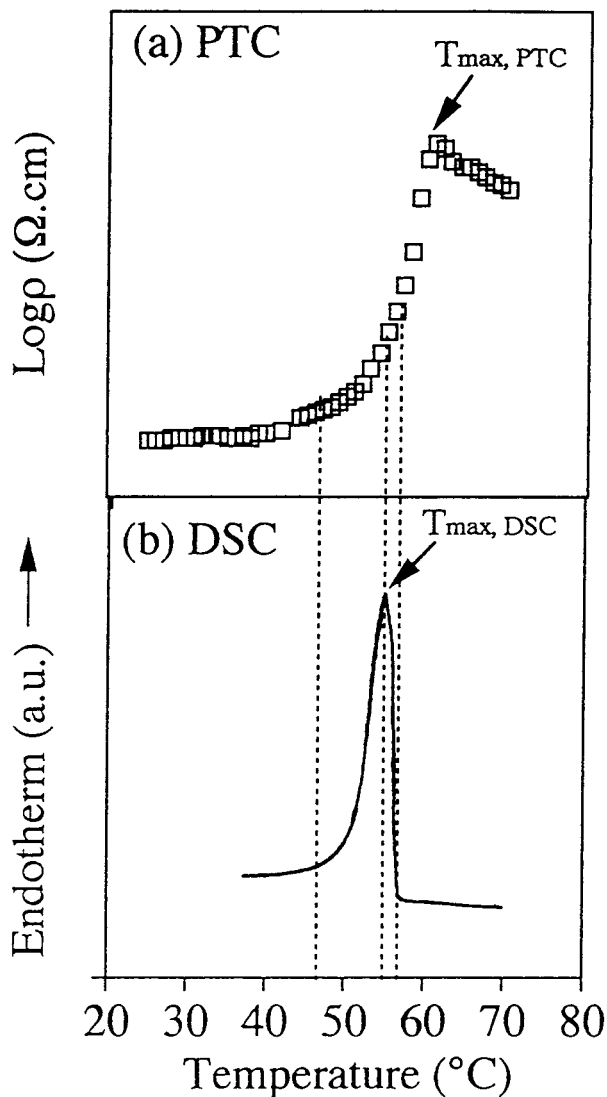


Figure 9 Comparison between an experimentally obtained PTC curve and a DSC melting curve. Crystallization conditions and the CB content were kept constant for the two samples ($T_c = 41^\circ\text{C}$ for 21 h and 5 vol % of CB).

Figure 9 shows the PTC and DSC melting curves of a PCL/PVB blend (99 : 1) cast from a THF solution. The PVB content and the CB content were kept constant for the two samples. The resistivity began to increase when lamellar crystals started to melt and abruptly increased when the temperature approached $T_{\max, \text{DSC}}$. It reached the maximum around $T_{\max, \text{DSC}}$ and started to decrease gradually after that temperature as a result of the reagglomeration of CB particles in the molten polymer phase (negative temperature

coefficient [NTC]).^{4,10} Thus, the resistivity change is strongly related to the melting process.

The above results indicate that the drastic PTC property change originates from the following process: The abrupt volume expansion of melting lamellae displaces CB. It changes the distribution of interparticle gaps and, hence, the resistivity of PTC materials. Figure 10 shows a schematic presentation of the situation. A conductive path is along a crystalline lamella or a fibril in a spherulite. When the PCL lamellae melt, they change the interparticle gap width and make the distribution more random. Most of the CB particles move perpendicularly to the surface of a nontwisted lamella [Fig. 10(b)], while CB close to a twisted lamella moves in almost all directions [Fig. 10(a)]. Increasing the PVB content decreases the period of the lamellar twist¹²; this increases the displacement of the CB near the lamella surface.

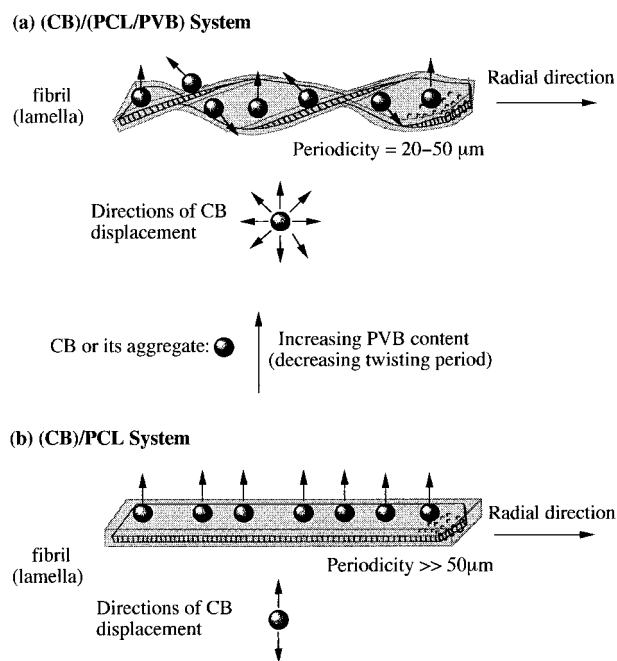


Figure 10 Schematic presentation of possible directions of the displacement of CB particles and aggregates around a lamella (or a fibril) in a PCL/PVB blend. In the melting process, the volume expansion and the molecular motion of polymer chain displace CB particles, which are located near the lamella (shaded area). Increasing the PVB content shortens the period of lamella twisting and causes more complex displacement of CB. The more random distribution of interparticle gaps is achieved for a shorter period. (a) A PCL/PVB blend, periodicity = 20–50 μm ; (b) pure PCL, periodicity $\geq 50 \mu\text{m}$.

CONCLUSIONS

1. In PCL/PVB blends containing CB, blending a small amount (up to 5%) of PVB drastically increases ρ and I_{PTC} .
2. Since blending PVB does not change the crystalline properties of PCL, the changes of the PTC property are ascribed to the morphological difference between PCL/PVB blends and pure PCL. The cooperatively twisted lamellae in the blends displace CB particles more randomly than those of pure PCL in the melting process. This is the first time that the influence of morphological changes on the PTC properties was studied and that the origin of the PTC phenomenon was explained experimentally.
3. The origin of the PTC phenomenon is the change of the distribution of the interparticle gap width of CB when the crystalline phase melts. This is explained by Ohe's equivalent circuit model.

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