

## Structure and properties of electrically conducting composites consisting of alternating layers of pure polypropylene and polypropylene with a carbon black filler

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### ABSTRACT

Electrically conducting composites consisting of alternating polypropylene (PP) and carbon black (CB)-filled polypropylene (PPCB) layers were prepared by multilayered coextrusion. The co-continuous structure with selective location of CB in PPCB layers was controllable by changing the number of multiplying elements, and decreased the percolation threshold and electrical resistivity of multilayered composites because of the double percolation effect. This double percolation could be achieved in a single polymer matrix using multilayered coextrusion, whereas it can only be produced in two different polymeric matrices by conventional approaches. Results showed that the dispersion of CB aggregates in PPCB layers was greatly affected by the shearing forces induced by the horizontal spreading flow and vertical recombination occurring during the multilayered coextrusion. The electrical resistivity, positive temperature coefficient effect and mechanical properties of multilayered composites depended strongly on their number of layers. A brittle–ductile transition occurred in PPCB layer compared with the conventional composites. The interesting positive and negative temperature coefficient effects occurred during crystallization and depended on the number of layers. A mechanism is proposed to explain these phenomena.

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### 1. Introduction

Most polymer materials are electrically insulating for their low values of dielectric constants. Nevertheless, some level of electrical conductivity is required for antistatic or semiconductive applications. Although some intrinsically conductive polymers such as polyaniline [1] offer desired conductivity, their applications are limited by high cost and lack of mechanical strength. Conductive polymer composites offer an economic alternative, whereby polymers are combined with conductive fillers, e.g., metal powder or fibers, graphite particles, and carbon nanotubes to name a few.

Carbon black (CB) with its low cost and chemical stability is one of the most common fillers for improving the electrical conductivity of polymers. However, many of the desirable properties, especially tensile elongation at break of the polymer matrix are either compromised or lost for the high filled content of CB.

Therefore, to decrease the percolation threshold is a big challenge [2].

Many reports showed that the formation of a perfect conductive network in single-component polymer matrix was crucial to the desired conductivity at lower CB content. Tai [3] reported a substantial approach to 1D electrically conductive composites which was based on the thermodynamic analysis of electric field induced particle alignment in a nonpolar thermoplastic polymeric matrix. The percolation threshold decreased greatly to 1.2 vol% CB in the electric field of 500 V/mm. Recently, Ou [4] claimed that, with the mechanical mixing method, a segregated structure was produced with polymethyl methacrylate (PMMA) particles forming faceted grains with CB particles aligning to form a network of 3D-interconnected nanowires. This microstructure allowed the percolation to occur at a low volume fraction of 0.26 vol% CB. However, these ways are seldom used in actual application due to their complicated preparation.

Up to now, one of the most common ways to decrease the percolation threshold and electrical resistivity at a relatively low CB content is to use two-component polymer blends as matrix based on the “double percolation” effect, i.e. the percolation of electrical

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conductivity in such an immiscible blend depends on the continuity of CB-rich phase or the interface as well as the percolation of CB in CB-rich phase or at the interface. By the preferential localization of CB particles in a special region, such as a phase of a dual continuous phase blend [5–11] or interface between two phases [12], the effective CB content was significantly higher than its nominal value, hence the percolation threshold reduced greatly. Gubbels [10] prepared the co-continuous polyethylene (PE) and polystyrene (PS) composites with a low percolation threshold of 3 wt% CB through CB particles selectively located in PE phase. Another common “double percolation” approach to reduce percolation threshold is to build up a continuous conductive network at the interfaces of immiscible multi-phase polymer blends. In this manner, Gubbels [12] prepared an electrical conductive co-continuous PE/PS blend with 0.4 wt% CB. Recently, conductive microfibrillar of polyethylene terephthalate (PET)/PE/CB composite with a lower percolation threshold was fabricated by Dai [13] through selectively locating CB particles at the surfaces of the PET microfibrils.

It is clear that the double percolation depends strongly on the structure and morphology of multi-component polymer matrix. The region where CB particles were selectively located must be a continuous phase in the composites for forming a continuous conductive network. But this desirable structure is hardly controlled through the conventional blending approaches because it is influenced by many rigorous conditions, such as processing parameters, ratios of volume, viscoelasticity and interfacial tension of two polymers in molten state. Therefore, the designable and controllable co-continuous structure becomes a target for double percolation studies in either scientific or applied field.

The microlayered coextrusion technology, similar to the conventional coextrusion process [14,15], was employed to prepare the multilayered composite tape with alternating polymer A and B layers as shown in Fig. 1 for improving the mechanical, optical properties or studying the rheology of multilayer systems [16–26].

Polymers A and B were first extruded from two extruders, respectively, then combined and controlled in a feedblock as two parallel layers, finally sliced and combined by a series of multiplying elements. The number of layers could be up to thousands with the increase of number of multiplying elements, and each layer was continuous along extrusion direction. Hence, this novel processing method provided not only the perfectly designable and controllable co-continuous structure but also advanced mechanical properties [27], especially elongation at break, the latter steered clear of the disadvantage of CB filled polymer composites.

In this work, we prepared electrically conducting composites consisting of alternating polypropylene (PP) and carbon black (CB)-filled polypropylene (PPCB) layers with the similar structure

as shown in Fig. 1 where polymers A and B were replaced by PP and PPCB, respectively, using the multilayered coextrusion system designed in our lab. It was very clear that this structure gave layered PP/PPCB conductivity anisotropy. Conductive channel was cut off by the insulated layers (PP) in Z direction. Because CB particles were only dispersed in the continuous conductive layers (PPCB) and the matrixes of conductive and insulated layers were all PP, the double percolation was only realized in the extrusion direction, furthermore, in a single polymeric matrix. This special double percolation cannot be obtained by the conventional blending approaches.

## 2. Experimental

### 2.1. Materials

The main materials used in this work included electrically conductive filler CB, grade E900 and PP, grade EPS30R. CB was obtained from Sichuan Zhenghao Special Carbon Technology Co. Ltd, with a dibutyl phthalate (DBP) absorption of  $260 \text{ cm}^3/100 \text{ g}$ , a density of  $1.8 \text{ g/cm}^3$ , and an original volume resistivity of  $0.2 \text{ } \Omega \text{ cm}$ , as given by the manufacturer. PP was a commercial copolymer of propylene and ethylene with an ethylene content of 6.5 wt% from Dushanzi Petroleum Chemical Company Ltd, with a volume resistivity of  $1.3 \times 10^{16} \text{ } \Omega \text{ cm}$ , a melt flow index of  $1.5 \text{ g/10 min}$ , and a melting point of about  $165 \text{ } ^\circ\text{C}$ . CB was dried at  $110 \text{ } ^\circ\text{C}$  in an oven for 12 h prior to blending.

### 2.2. Preparation of multilayered PP/PPCB composites

Prior to the microlayered coextrusion, the PPCB pellets with different amounts of CB were prepared using a twin-screw extruder. The mixing temperature gradient was varied between  $170$  and  $200 \text{ } ^\circ\text{C}$  from hopper to die. A multilayered coextrusion equipment shown in Fig. 2a, consisting of two single-crew extruders, a feedblock and some multiplying elements, was built to prepare the layered PP/PPCB composites.

PP and PPCB were extruded from extruders A and B, respectively, the feeding and rotation ratios of which were about 1:1. These two melt streams were combined and controlled in a feedblock as two parallel layers. From the feedblock the two layers flowed through a series of multiplying elements and each element doubled the number of layers as shown in Fig. 2b. In the multiplying element, the layered composites were first sliced vertically, then spread horizontally and finally recombined. An assembly of  $n$  multiplying elements produced a tape with  $2^{(n+1)}$  layers, where  $n$  was the number of multiplying elements. In this work, the largest number of layers was 64.

For the comparison with multilayered composites, the conventional CB filled PP composite tapes were also prepared using only one extruder of the multilayered coextrusion system without any multiplying element. In this paper, this conventional PPCB was referred as single-layer sample where CB particles dispersed evenly in PP matrix.

### 2.3. Thermogravimetric analysis

The CB contents of multilayered composites and conductive layers, i.e. PPCB, were determined by thermogravimetric analysis (TGA) using a WRT-2R TGA instrument. The samples were scanned from  $50$  to  $800 \text{ } ^\circ\text{C}$  in nitrogen atmosphere at a heating rate of  $10 \text{ } ^\circ\text{C/min}$ . The corresponding relationship between CB contents of multilayered composites and PPCB layers is shown in Fig. 3. The former was lower than the latter because the layered compounding of pure PP with PPCB pellets diluted the concentration of CB in multilayered composites.

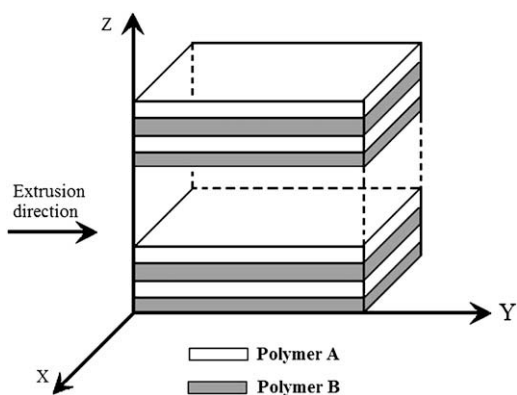


Fig. 1. Schematic of multilayered polymer composites with alternating polymer A and polymer B layers.

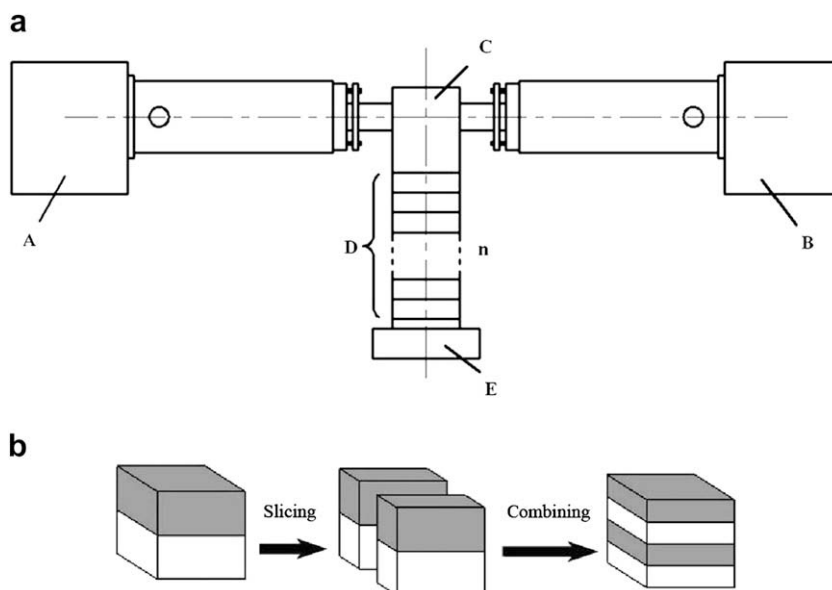


Fig. 2. Schematic of multilayer coextrusion system. A, B: Extruder, C: feedblock, D: multiplying elements, E: die.

#### 2.4. Measurement of volume resistivity

According to Fig. 1, the multilayered composites showed the electrical conductive anisotropy. Prior to measuring the electrical resistivity,  $\rho_{||}$ , along the extrusion direction, each test specimen was cut from the center portion of an extruded tape with 100.0 mm length ( $L$ ), 10.0 mm width ( $w$ ) and about 2.0 mm thickness ( $h$ ). Contact faces were polished and coated by copper paste for eliminating the contact resistance between the sample edges and the electrode of the conduction tester. The measurement of electrical resistivity was conducted on a programmable insulation resistance tester (YD9820A) consisting of a multivoltage source and a resistance meter. The constant voltage applied to samples was fixed 50.0 V unless otherwise specified.  $\rho_{||}$  was calculated by the following equation.

$$\rho_{||} = R_v \frac{wh}{L} \quad (1)$$

Where  $R_v$  is the electrical resistance. A minimum of five specimens were tested and the average value was calculated.

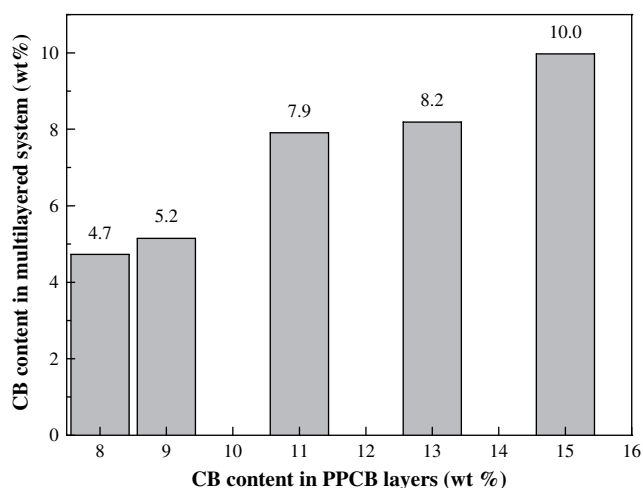


Fig. 3. Corresponding relationships between CB contents of multilayered composites and PPCB layers.

The same way was used to investigate the temperature dependence of the electrical resistivity. The measured sample was put into a temperature-controlled chamber at a heating or cooling rate of 2 °C/min.

#### 2.5. Measurement of mechanical properties

Tensile specimens were cut from the middle of coextrusion tapes paralleled to the coextrusion direction. Tests were performed on a SANS CMT4104 testing machine at a strain rate of 50 mm/min and measurements were made on at least three specimens of each sample.

#### 2.6. Morphological observation

In order to observe the dispersion of CB in conductive layers, the specimens were quenched in liquid nitrogen and cryogenically ruptured to obtain sections along the extrusion direction. The freshly broken surfaces were sputter coated with Au before scanning electron microscope (SEM) observation and then observed in a JEOL JSM-5900LV SEM. The polar light microscope (PLM) observation was performed using an Olympus BX51 polarizing microscope with an attached camera, and the sample thickness was approximately 20  $\mu$ m.

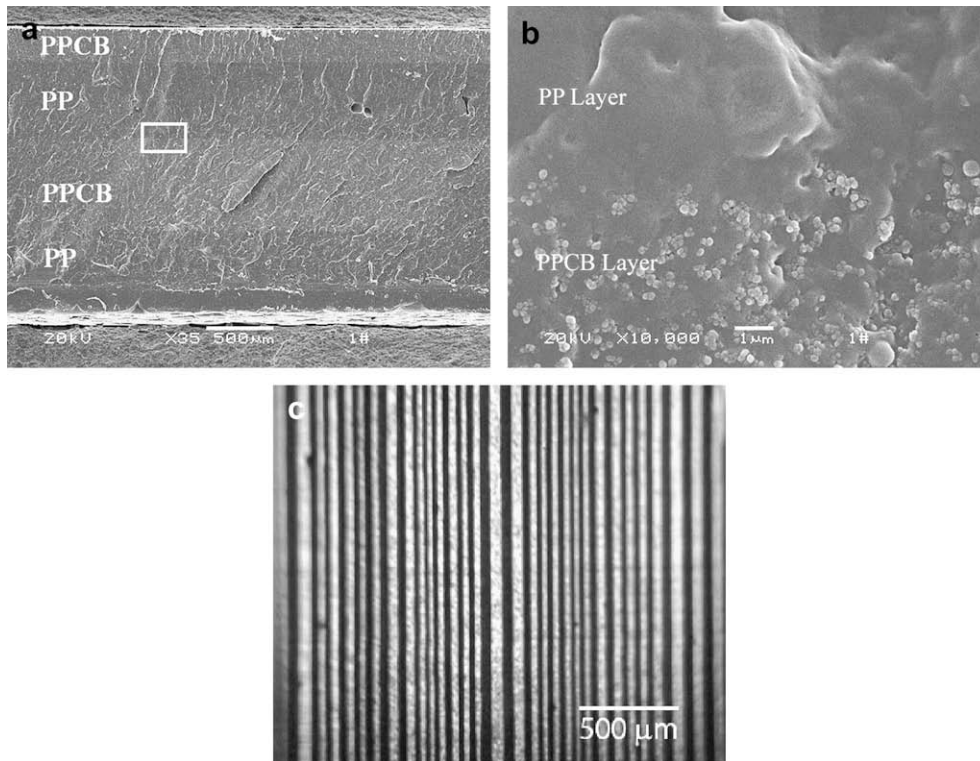
#### 2.7. Differential scanning calorimetry (DSC) measurement

DSC measurements were performed using a Netzsch DSC 204F1 to investigate nonisothermal crystallization in the cooling mode from the molten state. All tests were performed in nitrogen atmosphere. For each test, the sample was heated from 50 to 190 °C at a rate of 10 °C/min and then maintained at 190 °C for a period of 5 min to ensure an identical thermal history. The specimen was subsequently cooled down to 50 °C at a cooling rate of 10 °C/min. The exothermic crystallization peak and crystallizing curves were recorded.

### 3. Results and discussion

#### 3.1. Structure of multilayered PP/PPCB composites

Fig. 4 shows micrographs of 4- and 64-layer PP/PPCB composites' section along extrusion direction with different magnification



**Fig. 4.** Micrographs of PP/PPCB multilayered composites. (a) and (b) SEM micrographs of 4-layer composites. (b) The magnified micrograph of the rectangular region in (a). (c) PLM micrograph of 64-layered composites.

times. It was found from Fig. 4a and c that the structure of multilayered PP/PPCB composites fabricated through multilayered coextrusion accorded with that of model shown in Fig. 1. Alternating PP and PPCB layers were parallel and continuous along extrusion direction. And Fig. 4b revealed clearly that CB particles were only located in the PPCB layer through multilayered coextrusion.

The comparison of nonisothermal crystallization curves of pure PP, conventional single-layer and multilayered composites with the CB content of 15 wt% in PPCB is illustrated in Fig. 5.

Only one crystallizing peak appeared at around 108 and 122 °C for the pure PP and conventional single-layer composites, respectively, indicating that the CB aggregates were evenly dispersed in the conventional single-layer composites. But for the multilayered composites, there were two crystallizing peaks, corresponding to the crystallizing temperatures of PP and PPCB, respectively. The presence of two crystallizing temperatures in multilayered composites also indicated clearly that CB aggregates were selectively located in the specified region of PP matrix. The higher crystallizing temperature, 122 °C, of PPCB layer was due to the heterogeneous nucleation action of CB particles. The lower one of PP layer shifted from 110 to 117 °C with the increase of number of layers. The induced crystallization of CB at interfaces between PP and PPCB layers led to a higher crystallizing temperature of PP layer compared with pure PP. Consequently, the larger the number of layers (interfaces), the higher the crystallizing temperature of PP layer.

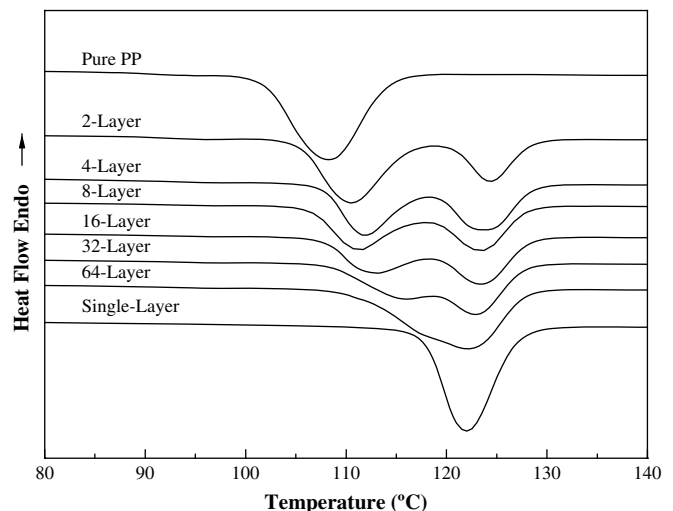
### 3.2. Electrical properties

#### 3.2.1. Dependence of room-temperature resistivity on structure of multilayered composites

Along the extrusion direction, the dependence of the room-temperature electrical resistivity on the total CB loading in

composites for the conventional single-layer and multilayered composites with 2 and 4 layers is depicted in Fig. 6.

It was obviously found from Fig. 6 that a significant decrease of volume resistivity for each curve was observed in a rather narrow concentration range of the filler, indicating that the composites exhibited a typical characteristic of percolation threshold. The percolation threshold of the multilayered composites was about 5.0 wt%, 2.0 wt% lower than that of the conventional extruded specimen. Moreover, the volume resistivity of the multilayered composites was greatly lower than that of the conventional composites at any CB content. Clearly, the lower percolation threshold and electrical resistivity for multilayered composites



**Fig. 5.** Comparison of DSC curves of conventional and multilayered composites with the same CB content of 15 wt% in PPCB layer at a cooling rate of 10 °C/min.

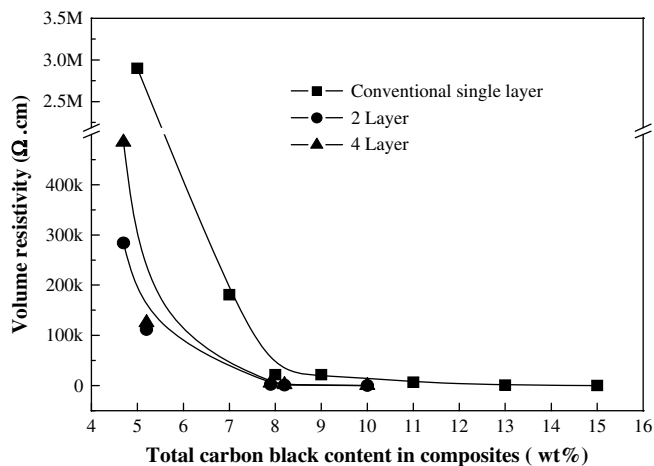


Fig. 6. Dependence of electrical resistivity on the total CB loading in composites for the conventional single-, 2-, and 4-layer composites.

were attributed to the selective location of CB particles in PPCB layers and double percolation effect caused by the particular co-continuous structure with alternating PP and PPCB layers through multilayered coextrusion system. The further comparison between 2- and 4-layer composites showed that the volume resistivity of the former was lower than that of the latter at the lower CB content, which meant that the number of layers of multilayered tapes had a large influence on the electrical conductivity.

Fig. 7 illustrated the correlation of number of layers and the room-temperature resistivity. When the number of layers was lower than 16, the electrical resistivity of multilayered composites was obviously lower than that of the conventional single-layer composites. But with the increase of number of layers, the resistivity of multilayered specimens also increased. For the multilayered composites, the same total CB content in composites led to the different electrical properties due to the variance of number of layers, depending on the morphology of CB particles in PPCB layers. In this work, the SEM was employed to observe the dispersion of CB particles in PPCB layers as shown in Fig. 8.

SEM micrographs in Fig. 8 intuitively showed that, when the number of layers was 2 and the CB content in PPCB layers was 13 wt%, many primary nanoparticles were fused together in a grape-like aggregate to form a high-structure CB. With the increase of number of layers, these high-structure CB aggregates

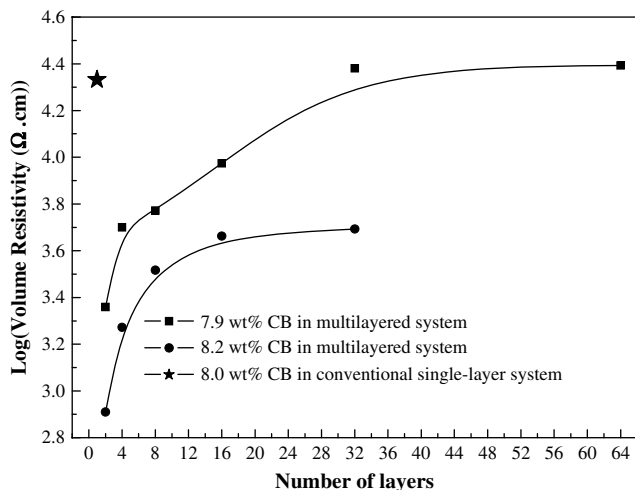


Fig. 7. Influence of number of layers on room-temperature electrical resistivity. (The CB content in this figure refers to the total one in composites.)

were broken into small size aggregates consisting of less primary nanoparticles, referred to as a low structure. The larger the layer number was, the smaller the aggregate size was. The statistical results of size distribution of CB aggregates shown in Table 1 further revealed the dependence of CB aggregate size on the increasing number of layers. The average size of aggregates,  $D_n$ , the major and largest aggregates' size incessantly decreased with the number of layers of multilayered tapes increased from 2 to 16.

These comparisons indicated that there were many large-size grape-like aggregates inhomogeneously distributed in PPCB layers of multilayered composites as the number of layers was low. Many researches [28–30] showed that a high-structure CB with large aggregate size promoted the formation of a conductive network, indicating a low electrical resistivity. The perfect dispersion of discrete small CB aggregates is not always necessary or even desirable because their surfaces are completely covered with polymer resin, which hold up the formation of the conductive network. Therefore, the increase in electrical resistivity with the increase of number of layers was attributed to the reduced size of CB aggregates and their overdispersion. In this work, the shearing forces, induced by the horizontal spread flow and vertical recombination when polymer melts flowed through the multiplying elements, made CB agglomerates at the interfaces of laminar flow broken into small aggregates. As a sequence, the smaller CB aggregates were achieved if melts flowed through more multiplying elements with longer-time action of shearing forces. This essential reason caused the increase of electrical resistivity with the increase of number of layers.

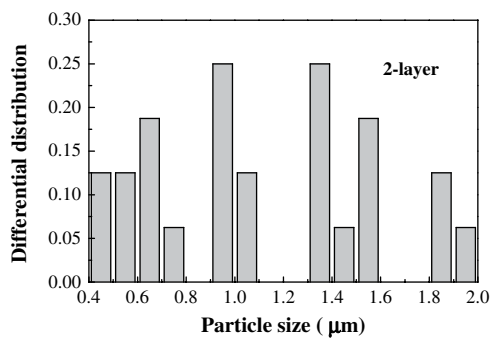
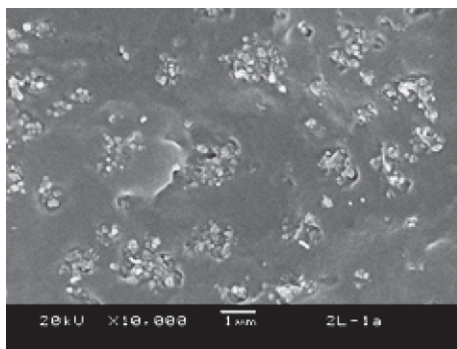
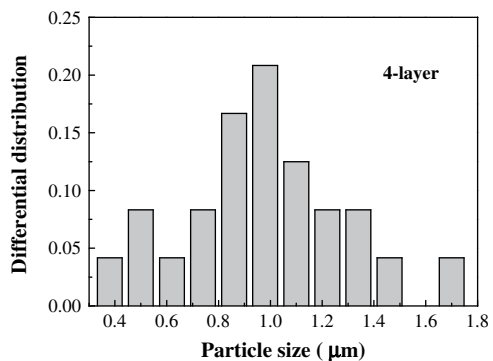
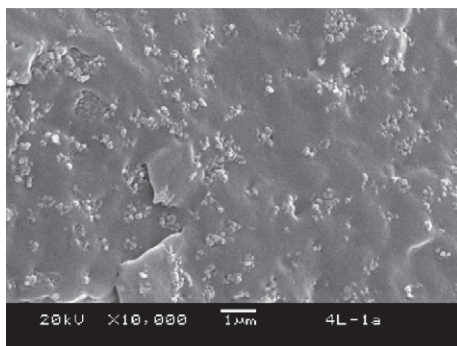
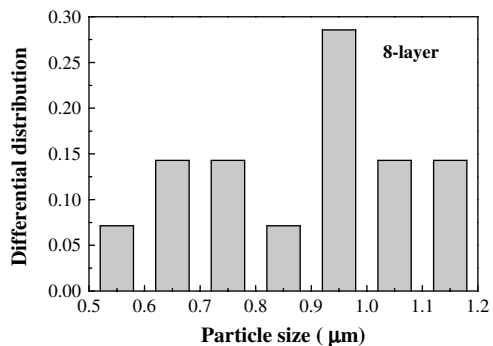
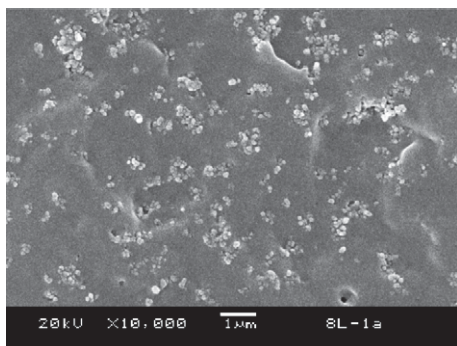
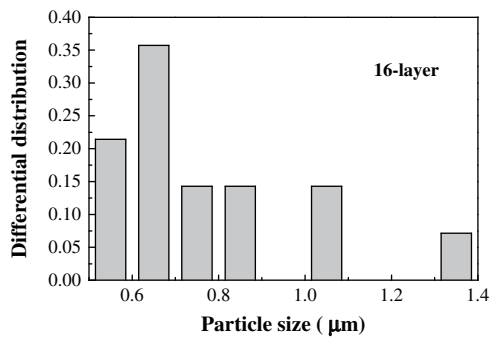
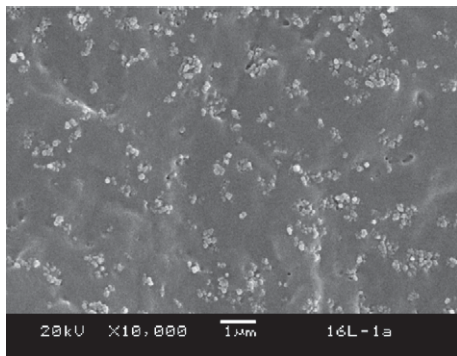
As discussed above, the multilayered coextrusion brought two inconsistent effects on the electrical resistivity of multilayered composites. The double percolation indicated that less CB was needed to form a conductive network, but the shearing force caused an opposite effect on the electrical resistivity. This disagreement was revealed by the comparison of resistivity of 8-layer and conventional single-layer composites as shown in Fig. 9.

When the CB content was too low to form a conductive network, the long-time shearing forces enlarged the interparticle distance due to their reduced size in 8-layer composites. Therefore, the electrical resistivity of 8-layer composites was higher than that of conventional single-layer composites. Once the CB content increased to the percolation threshold and the conductive network was formed, the effect of double percolation on resistivity was dominant. As a result, the 8-layer composites obtained a lower electrical resistivity compared with the conventional single-layer composites.

### 3.2.2. Temperature-resistivity properties of multilayered composites at heating

Some conductive polymer compounds showed a positive temperature coefficient (PTC) phenomenon. Polymer based PTC materials have been used as self-regulating heaters, self-resetting current limiters, over current protectors, microswitches, sensors, and other devices [31–33]. On the one hand, these materials needed the lower room-temperature resistivity to ensure sufficient electrothermal output. On the other hand, higher PTC intensity was desired to prevent materials from overheating. And this dilemma was difficult for single-polymer based composites through the conventional processing because of high CB concentration. In this work, we realized the double percolation in single PP matrix by the multilayered coextrusion and achieved a low room-temperature resistivity at low CB loading.

Fig. 10 showed the dependence of the electrical resistivity on temperature at a heating rate of 2 °C/min for composites with 11 wt% CB content in PPCB layers. It was seen that the resistivity of all composites increased slowly with the increase of temperature followed by a steep increase at 160–165 °C corresponding to the

**a** 2-layer composites**b** 4-layer composites**c** 8-layer composites**d** 16-layer composites

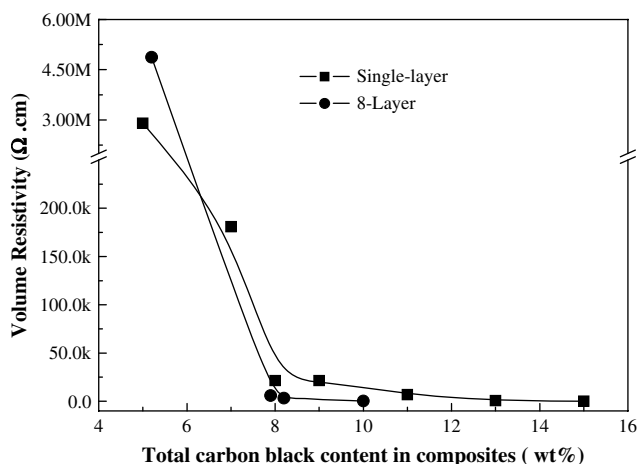
**Fig. 8.** SEM micrographs of CB aggregates and their size dispersion with 13 wt% CB content in PPCB layers. (a) 2-Layer composites, (b) 4-layer composites, (c) 8-layer composites, and (d) 16-layer composites.

**Table 1**  
Statistical results of size dispersion of CB aggregates in PPCB shown in Fig. 8

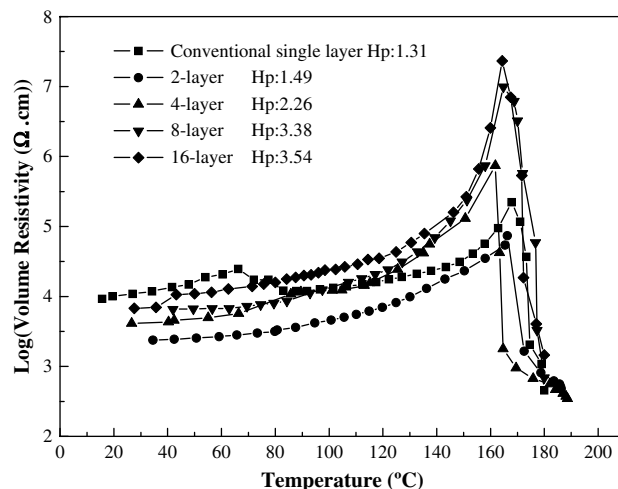
Number of layers	$D_n$ ( $\mu\text{m}$ )	Major particles		Largest particles	
		Diameter ( $\mu\text{m}$ )	Percentage (%)	Diameter ( $\mu\text{m}$ )	Percentage (%)
2	1.73	1.35, 0.95	25.0, 25.0	1.95	6.3
4	1.27	1.0	20.8	1.7	4.2
8	0.89	0.95	28.6	1.15	14.3
16	0.83	0.65	35.7	1.3	7.1

melting temperature of PP. The PTC intensity  $H_p$ , calculated according to the formula  $H_p = \log(\rho_{\text{max}}/\rho_{\text{RT}})$  where  $\rho_{\text{max}}$  and  $\rho_{\text{RT}}$  are the maximum and room-temperature resistivity, respectively, depended strongly on the number of layers. The PTC intensity was higher in the multilayered composites than the conventional single-layer ones, and increased with the increase of number of layers. Nowadays it has been accepted that the PTC at melting point was due to the volume expansion from the melting of the crystalline region in the semicrystalline polymer matrix, which enlarged the interparticle distance [34–36]. According to the tunneling theory, the tunneling probability of an electron was related to the interparticle distance. Therefore, the resistivity increased dramatically as the interparticle distance increased and exceeded the electron tunneling distance because the conductive network was deteriorated even broken up. As discussed above, as compared with the conventional single-layer PPCB composites, the aggregates of CB in multilayered PP/PPCB composites were broken into small ones by the shearing forces. As a result, the interparticle distance increased but still kept the electron tunneling distance to form the conductive network at the room temperature. Therefore, when a large thermal expansion of the polymer occurred in the vicinity of the melting point of PP, the conductive network of multilayered composites was easy to be deteriorated and broken up. And then the multilayered composites showed a much higher resistivity and PTC intensity than the conventional single ones because of the larger interparticle distance. Due to the same reason, the PTC intensity of multilayered composites increased with the increase of number of layers.

Fig. 11 showed plots of the resistivity of 2-layer composites with various total CB contents as a function of temperature. The PTC intensity depended greatly on the CB content. For a 2-layer composite with a low CB content of 5.2 wt%, a large number of the interparticle distances could be greater than the electron tunneling distance after the thermal expansion; hence, the resistivity of the composite increased greatly. With the increase of CB content, the



**Fig. 9.** Comparison of resistivity of 8-layer and conventional single-layer composites.



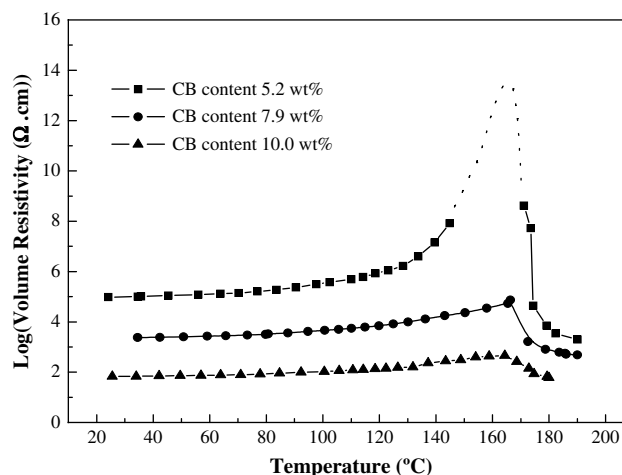
**Fig. 10.** Dependence of electrical resistivity on temperature at a heating rate of  $2^\circ\text{C}/\text{min}$  for multilayered composites with 11 wt% CB content in PPCB layers. (PTC intensity:  $H_p = \log(\rho_{\text{max}}/\rho_{\text{RT}})$ ).

interparticle distance was relatively small or the CB particles can still form a continuous conductive network owing to a higher CB content though the temperature was increased to melting point. This led to a lower PTC intensity.

### 3.2.3. Temperature-resistivity properties of multilayered composites at cooling

To the best of our knowledge, most studies focused on the dependence of resistivity on the temperature during heating. In this work, we investigated the relation of the resistivity with temperature for the conventional single-layer and 8-layer composites with a CB content of 9 wt% in PPCB at a cooling rate of about  $2^\circ\text{C}/\text{min}$  from the melt. Fig. 12 showed the interesting results.

With the decrease of temperature, the resistivity of composites increased greatly at about  $136^\circ\text{C}$  followed by a sharp decrease of resistivity at about  $129^\circ\text{C}$ . These phenomena were very similar to PTC and negative temperature coefficient (NTC) occurring during heating. So, we called them the cooling PTC and NTC. Clearly, the temperature at which the cooling PTC and NTC occurred corresponded to the crystallizing point of PP, indicating the dependence



**Fig. 11.** Dependence of electrical resistivity on temperature at a heating rate of  $2^\circ\text{C}/\text{min}$  for 2-layer composites with different total CB contents in composites.

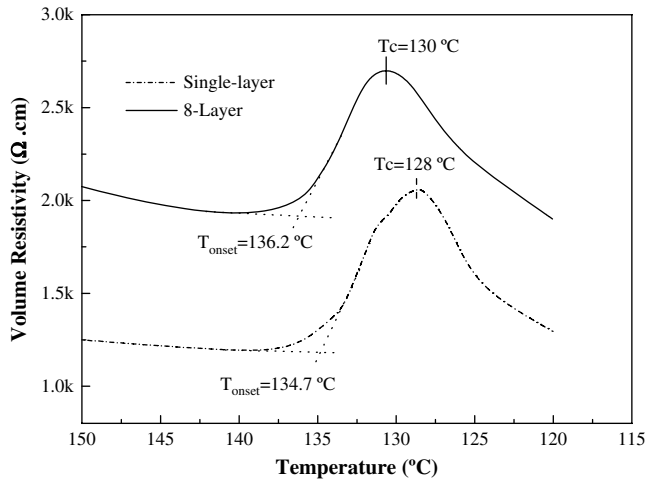


Fig. 12. Dependence of electrical resistivity on temperature at a cooling rate of 2 °C/min for 8-layer and conventional single-layer composites with CB content of 9 wt% in PPCB.

of the resistivity on the crystallization. Based on this fact, we provided a model shown in Fig. 13 to explain the cooling PTC and NTC effects.

As the temperature was higher than crystallizing point, the conductive network was formed due to the migration of CB particles in PP melts, leading to a lower resistivity. Once the temperature decreased to the onset temperature ( $T_{\text{onset}}$ ) of about 136 °C, corresponding to the onset point of crystallizing temperature for DSC measurement, the appearance of lots of tiny crystalline grains induced by the heterogeneous nucleation action of CB particles blocked the migration of CB particles and cut off the partial conductive pathways of network, resulting in an increase of resistivity. Once the temperature was lower than crystallizing peak temperature ( $T_c$ ), 128–130 °C, the growth of crystalline grains with the decrease of temperature removed CB to the noncrystalline interlamellar and interspherulitic regions [37], and thereby recovered the conductive network with the decreasing resistivity. Compared with the conventional single-layer composites, it was found from Fig. 12 that the curve of 8-layer composites shifted to the high temperature with higher  $T_{\text{onset}}$  and  $T_c$ . The shearing forces

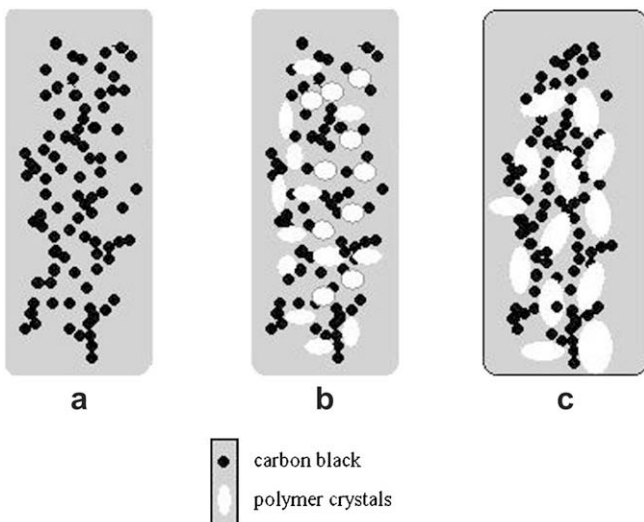


Fig. 13. Schematic of a mechanism provided to explain the cooling PTC and NTC effects.

Table 2

Dependence of the elongation at break on CB content in conventional single-layer composites

CB content (wt%)	0	9	11	13	15
Elongation at break (%)	760	84	66.5	42	12

induced during the multilayered coextrusion caused the smaller and more CB aggregates in the PPCB layers of 8-layer composites than those in the conventional single-layer composites, which produced more obvious heterogeneous nucleation action and made the cooling PTC and NTC effects occur at a higher temperature for 8-layer composites according to the mechanism stated above.

### 3.3. Mechanical properties

The incorporation of conductive fillers had a complex influence on the final electrical and mechanical properties. The addition of CB increased the electrical conductivity of polymers, but the mechanical properties were dramatically deteriorated, especially the elongation at break [38,39]. On the one hand, CB acted as a stress concentrator and thus supplied the composites with potential sites for crack growth. On the other hand, the presence of CB restricted the molecular movement of PP, leading to a brittle fracture. The data listed in Table 2 showed that the elongation at break of the PPCB composites decreased sharply compared to neat PP, and the higher the CB content was, the lower the elongation at break was.

Some additives were conventionally employed to compensate for brittleness [40], but this effectiveness was usually less pronounced. Many references proved that the layered structure endowed the composites with the high toughness [16,27,41]. Fig. 14 showed typical stress–strain curves of the conventional single-layer and 8-layer composites with the same CB content of 11 wt% in PPCB.

It was found that the elongation at break of conventional single-layer composites was very low. But for 8-layer composites, the stress linearly increased till to a yielding value with the increase of strain, and then maintained a constant value till a high elongation at break. This tensile behavior was very similar to that of the homogeneous polymer, indicating that the deformations and breakages of PP and PPCB layers in multilayered composites were concurrent as a whole body. This synergism was due to that when subjected to a stress, the high-toughness PP layers impelled

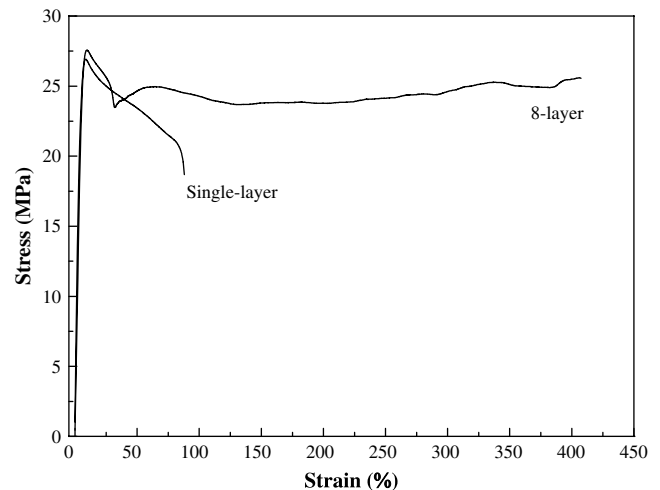
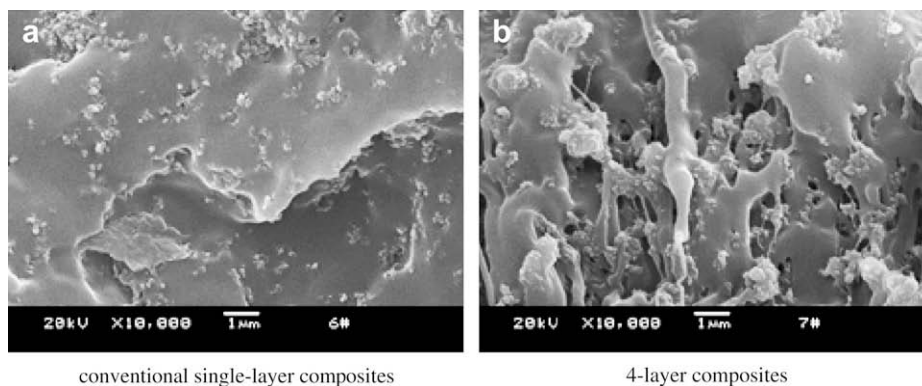


Fig. 14. Stress–strain curves of 8-layer and conventional single-layer composites with 11 wt% CB content in PPCB.





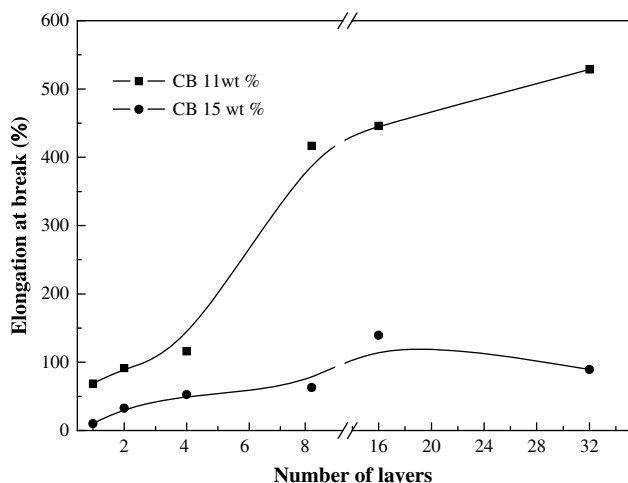
**Fig. 15.** SEM photographs for tensile fracture surface of conventional single-layer and 4-layer composites with the same CB content of 11 wt% in PPCB. (a) Conventional single-layer composites and (b) 4-layer composites.

the molecules of PPCB layers to move through the strong interfacial adhesion between PP and PPCB layers. In addition, the decrease in the size of CB aggregates induced by multilayered coextrusion decreased the stress concentration effect of CB and thus also improved the toughness of PPCB layers in multilayered composites.

SEM photograph of tensile fracture surface is usually employed to judge the tensile failure behavior of materials. Fig. 15a exhibited a smooth fracture surface of the conventional single-layer composites with 11 wt% CB, indicating a brittle failure. For the 4-layer composites with the same CB content in PPCB layers, the failure behavior of PPCB layer was ductile with the coarse fracture surface as shown in Fig. 15b.

This brittle–ductile transition was attributed to the layered structure and small size of CB aggregates. Therefore, the number of layers of multilayered composites would affect obviously the toughness of PPCB layer. Fig. 16 showed that the elongation at break of composites with the CB content of 11 and 15 wt% in PPCB increased as the layer number increased.

This increase was due to more interfaces between PP and PPCB layers, which made the molecular movement of PP in PPCB layer easier, and smaller size of CB aggregates with the increase of layer number. Even when the number of layers of multilayered composites with the CB content of 11 wt% in PPCB layers increased to 32, its elongation at break amounted to around 530%, close to that of neat PP.



**Fig. 16.** Effect of number of layers on elongation at break of multilayered composites. (The CB content in this figure refers to the one in PPCB.)

#### 4. Conclusions

- (1) The multilayered electrically conducting composites with the selective location of CB in PPCB layer were endowed with low percolation threshold and electrical resistivity because of the especial double percolation in the single polymer matrix.
- (2) The conductive network was formed along the extrusion direction with the increase of CB content in PPCB layers, but cut off due to the presence of insulated layers (PP).
- (3) The SEM photographs showed that the size of CB aggregations decreased with the increasing number of layers. As a result, the electrical resistivity, PTC intensity and elongation at break of multilayered composites depended strongly on their number of layers.
- (4) The interesting cooling PTC and NTC phenomena occurring during the crystallization of PP depended on the formation and growth of crystalline grains. All that can induce the crystallization of PP caused the cooling PTC and NTC to occur at a higher temperature.

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