

Studies on the Comprehensive Performance of Graphite and Additives Filled High Density Polyethylene Composites

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ABSTRACT: The comprehensive performance of graphite and additives filled high-density polyethylene (HDPE) composites is studied in this article. Four graphites with different particle diameters are used as conductive fillers in HDPE/graphite. Plasticizer, nucleator, and certain particle diameter graphite are employed to prepare HDPE composite. The behavior of crystallization and the distribution of graphite are also studied by means of SEM. An orthogonal design experiment is taken to optimize the content of the filler. The experimental results indicate that the positive temperature coefficient (PTC) effect is related to the

particle diameter of graphite. And the bending strength of HDPE/graphite composite with the plasticizer and nucleator is two times less than that of HDPE-graphite blends. Meanwhile, the high PTC intensity (the ratio of peak resistivity to room temperature resistivity) is also preserved. An excellent comprehensive performance conductive composite is prepared. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 4000–4004, 2008

Key words: additives; blends; composites; conducting polymers; melting point; PTC effect

INTRODUCTION

Polymer materials exhibit the effect of positive temperature coefficient (PTC) when filled conductive fillers (CB, graphite, metal oxide, etc.). It was first discovered by Frydman in 1945.¹ PTC effect can describe as sudden increase in resistivity with temperature. The resistivity can boost several orders of magnitude when temperature approached the melting point of polymer matrix. Polymer PTC materials have been studied extensively in academic and commercial fields over the past two decades because of their numerous properties, such as light weight, low cost, ease of processing, and corrosion resistance.^{2,3} Up to now, these conductive composites are being put to good use in a number of applications, such as heating elements, temperature-dependent resistors and sensors, self-limiting electrical heaters, and switching devices, etc.^{4–7}

The electric conduction theory of the polymer materials has been studied for many years, but there is still not a uniform explanation for PTC effect. Kohler⁸ proposed that the PTC effect is caused by thermal expansion in 1966. He suggested that conductive fillers form a network of conducting chains at ambient temperature. The expansion of polymer matrix broke up the conducting

chains, which resulted in the consequent anomalous increase in the resistivity. In contrast, Ohe and Natio⁹ assumed that the interparticle gaps existed everywhere and the electron tunneling can take place at a low temperature. The particles distribute randomly and the gaps were too large to allow electron tunneling when temperature near polymer matrix melting point. Meyer¹⁰ supposed that thin crystalline films of the polymer were significantly better conductors than amorphous films of the polymer. Conductive particles were initially spread through the polymer in the amorphous areas. The anomalous rise of the resistivity near melting point was attributed to the phase change of these crystallites. However, most of mechanisms remain controversial.

Graphite is frequently used for improving the electrical conductivity, antistatic properties, and thermal conductivity of plastics because it is abundant in natural resources and inexpensive. In the present work, the physical behavior, electrical conductivity, and bending strength of graphite and additives filled high-density polyethylene (HDPE) were investigated. It was found that the graphite size and the additives have significant influence on the comprehensive performance of graphite filled HDPE composites.

EXPERIMENTAL

Materials

HDPE (melting index = 0.090 g min⁻¹, density = 0.954 g cm⁻³) provided from Tsilu Petrochemical

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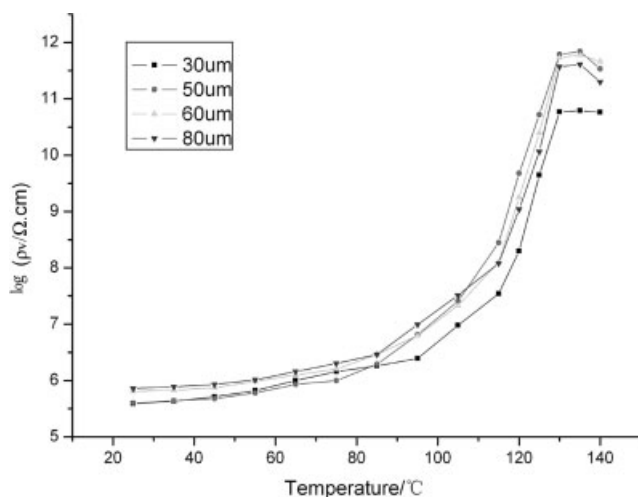


Figure 1 Effect of different graphite size on PTC characteristic for HDPE/graphite.

Technology, China. The graphite supplied from Tsingdao Carbon Company (its average size is 40–50 μm , special surface area = $0.288 \text{ m}^2 \text{ g}^{-1}$, and density = 2.85 g mL^{-1}), China. Dioctyl-Phthalate (DOP) (relative molecular weight = 390.57 and density = 0.976 g mL^{-1}) was used as plasticizer from Shanghai Lingfeng Chemical Reagent, and talc powder (relative molecular weight = 379.29) was used as nucleator from Tianjin Tianda Chemical Reagent.

Preparation of the sample

Screen four grades of graphite by using standard sieves. The diameters of graphite particle were 30, 50, 60, and 80 μm , respectively. HDPE and graphite (or contain additives) were melt-mixed in a Brabender for 15 min at 200°C , then kneaded on two-roll mill for 5 min at 180°C . The samples were compression molded at 200°C for 10 min, then holding at 120°C for 120 min, and slowly cooled to room temperature, respectively. The two sides of the samples were bonded with aluminum foil to reduce the contact resistance.

Measurements of the sample

The samples were put in the chamber to measure the electrical properties at various temperatures. The volume resistivities of the composites were measured by a digital multimeter when electrical resistance is lower than $2 \times 10^7 \Omega$, and ZC-36 type megger was used when the resistance exceed $2 \times 10^7 \Omega$. The heating rate was $10^\circ\text{C min}^{-1}$.

The bending strength of the samples was tested by using an Instron 4465 tensile tester at a speed of 2 mm min^{-1} .

RESULTS AND DISCUSSION

Effect of graphite size on PTC intensity

Figure 1 displays the effect of different graphite size on PTC characteristic. It is obvious that four grades of graphite filled HDPE have the significant PTC effect. It implies that conductive fillers form a network of conducting chains which result in the low resistivity at room temperature. The resistivity increases with the temperature and it increases more rapidly near the crystalline melting temperature because of the thermal expansion of polymer matrix.⁸ The transformation from the crystalline phase to the amorphous phase produces a significant volume expansion,¹¹ which increases the interparticle distances of graphite and reduces the number of conductive paths, resulting in high resistivity of the materials.

All conductive composites can present the obvious PTC intensity. And it can be found that the graphite size plays an important role in the PTC composite. The room temperature resistivity increases with the graphite size. As shown in Figure 2, the composite with the graphite whose average diameter is 50 μm exhibit the highest PTC intensity and the composite with 30 μm graphite present the lowest PTC intensity. The PTC intensity of the conductive composite with 50 μm graphite exceeds six orders of magnitude. It is 0.5 orders of magnitude higher than that of 80 μm and one order of magnitude higher than that of 30 μm . The PTC intensity of composite with 60 μm graphite presents near six orders of magnitude.

Figure 3(a–d) displays SEM images of the samples filled with graphite of different particle diameters. As depicted in these micrographs, the reason for this difference in the PTC intensity lies on the fact that

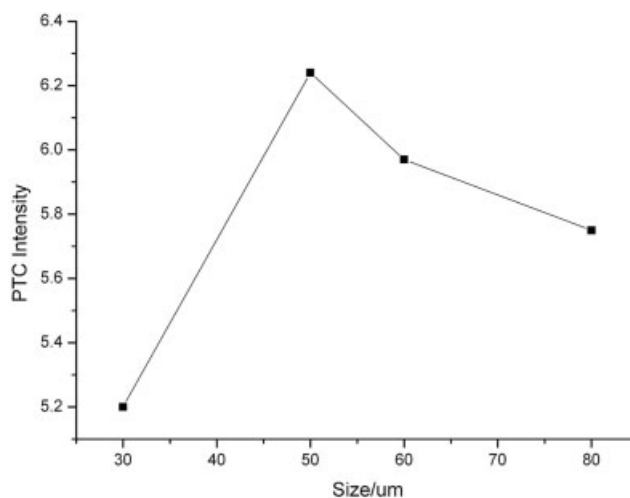


Figure 2 Effect of different graphite size on PTC intensity for HDPE/graphite.

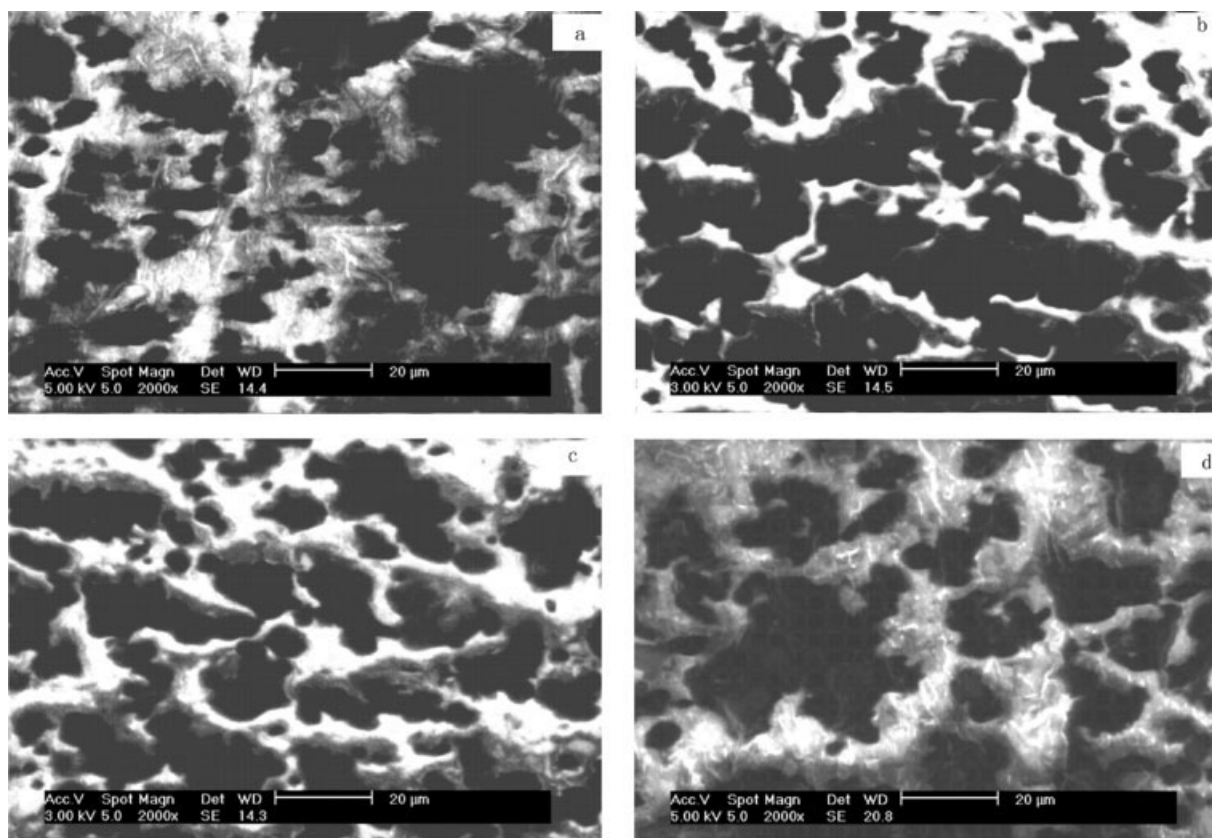


Figure 3 SEM images of the samples filled with graphite of different particle diameters. (a) 30 μm , (b) 50 μm , (c) 60 μm , (d) 80 μm .

the number of conductive pathways and the distribution of the graphite. The small-size graphite with a comparatively big specific surface area can bring about more conducting chains to the polymer matrix.¹² However, the small-size graphite is more prone to conglomeration because of van der Waals forces and the covalent bonds among some particles,¹³ which result in a minor change of the resistivity with the temperature increasing. Therefore, the composite with small-size graphite show a somewhat lower room temperature resistivity and PTC intensity. The large-size graphite can distribute randomly so that they can break up most conductive chains near the melting point. Though the composite with large particle-size graphite has a higher PTC intensity, the room temperature resistivity is usually higher which will affect the application of the composites. As mentioned earlier, a balance between the PTC intensity and the room temperature is attempted by using 50 μm graphite in the composite.

Effect of additives on PTC intensity and mechanics performance

In the present investigation, the additives which affect PTC intensity and mechanics performance are

plasticizer, nucleator, and certain particle diameter graphite. An orthogonal design L_9 (3^4) is used to optimize the PTC intensity and mechanics performance. Weigh up 100 g HDPE and corresponding additives. Preparation and measurement of the samples are stated earlier. The various parameters and levels thus selected are presented in Table I. Factor *A* means graphite content, factor *B* means DOP content, and factor *C* means talc powder content. The results and analysis of the experiment were listed in Tables II and III. In the orthogonal test, *K* is the sum of PTC intensity or bending strength of every level and by comparing to *K*, the optimal level of variables can be confirmed. $R = \max\{k_1, k_2, \dots, k_n\} - \min\{k_1, k_2, \dots, k_n\}$, and *R* scales the effect of variables on the result. High *R* value of variable means that this variable has strong effect on the result.

TABLE I
Experimental Design Combinations for the Factors and Levels

Parameters	Level 1	Level 2	Level 3
A. Graphite content (g)	40	50	60
B. DOP content (g)	10	25	45
C. Talc powder content (g)	8	12	16

TABLE II
The Experiment Results of the Orthogonal Design $L_9(3^4)$

Experiment	Graphite content (g)	DOP content (g)	Talc powder content (g)	Vacancy array	PTC intensity	Bending strength
1	40	10	8	1	5.60	7.41
2	40	25	12	2	5.48	4.50
3	40	45	16	3	3.52	3.14
4	50	10	12	3	5.91	7.50
5	50	25	16	1	5.76	4.60
6	50	45	8	2	3.84	3.50
7	60	10	16	2	6.62	6.20
8	60	25	8	3	6.47	4.80
9	60	45	12	1	4.88	3.80
PTC intensity						
K_1	4.867 ^a	6.043	5.303	5.413		
K_2	5.170	5.903	5.423	5.313		
K_3	5.990	4.080	5.300	5.300		
R	1.123 ^b	1.963	0.123	0.113		
Bending strength						
K_1	5.017	7.037	5.237	5.270		
K_2	5.200	4.633	5.267	4.733		
K_3	4.933	3.480	4.647	5.147		
R	0.267	3.557	0.620	0.537		

^a $K_i^A = \Sigma$ the amount of PTC intensity at A_i .

^b $R_i^A = \max\{K_i^A\} - \min\{K_i^A\}$.

From Table II, it is clear that the influence of every factors on PTC intensity are $B > A > C$ on the basis of the value of R . And the influence on bending strength are $B > C > A$. Factor B is the main factor which affects the comprehensive performance of the composites. Concerning factor B , the K value of every level is that $K_1 > K_2 > K_3$, and the value of K_1 is almost equal to that of K_2 . Taking into account bending strength, the K value of every level is that $K_1 > K_2 > K_3$. Though factor B adopting the value of B_3 can improve the bending capacity, the PTC intensity is too low. So, the value of B_2 is the best choice to the factor B considering the PTC intensity and the bending strength; Table III shows that the variance analysis of orthogonal test on optimization of the content of the filler. It has no distinct difference among the levels of three factors. For factor A , the K value of every level is that $K_3 > K_2 > K_1$ according to the R value of PTC intensity, so the best value of factor A is A_3 ; The K value of factor C is that $K_2 > K_1 > K_3$ and it is not the main factor, so C_2 is chosen as the C value. Optimum content of the additives is $A_3B_2C_2$, which means to add graphite 60 g, DOP 25 g, and talc powder 12 g. Preparation of the sample filled with the optimum content additives. Repetition experiments show that the PTC intensity of the sample is 6.4 orders of magnitude and the bending strength is 3.5 MPa. While the PTC intensity of HDPE-graphite blends is 6.2 orders of magnitude and bending strength is 11.2 MPa. The plasticity of this composite is obviously improved by adding the additives and this composite has the excellent comprehensive performance.

Figure 4 displays the SEM images of the sample with optimized formulation additives. The conductive particles initially spread in the amorphous areas.¹⁴ It is believed that the crystallinity of polymer matrix is decreased with the additives added. Then the amorphous areas enlarged and this decreased the concentration of graphite. Therefore, the content of graphite must be increased in order to obtain a distinct PTC effect. According to our research, the percolation concentration of graphite is about 40 wt %. By adding small amount of additives, the PTC intensity is enhanced when compared with HDPE-graphite blends. According to previous works,¹⁵⁻¹⁷ we suggest that talc working as nucleator makes heterogeneous nucleation in polymer matrix and new phase nucleation takes place on the surface of the talc. The interfacial energy and nucleation energy decrease in this process, which make the nucleation

TABLE III
The Variance Analysis of $L_9(3^4)$ Orthogonal Test on Optimization of the Content of the Filler

Factor	SS ^a	df ^b	MS ^c	F	P
A	2.026	2	1.013	0.042	>0.05
B	7.199	2	3.600	0.150	>0.05
C	0.030	2	0.015	0.001	>0.05
Error	48.10	2			

$F_{0.05}(2,2) = 19$, $F_{0.01}(2,2) = 99.0$.

^a Sum of squares.

^b Degrees of freedom.

^c Mean square.

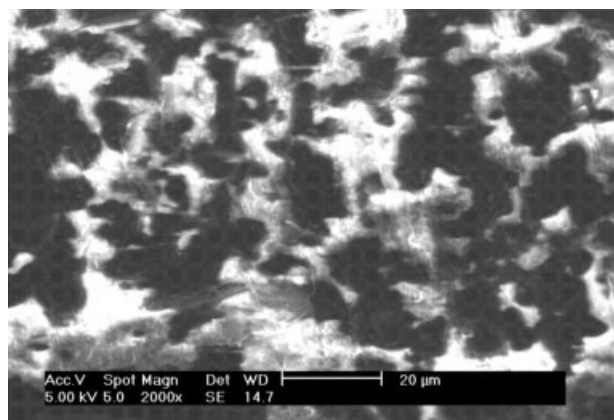


Figure 4 SEM images of the sample with optimized formulation additives.

much easier. After the stable nuclei appear, the crystals begin to grow up. The decrease of bending strength major arises from the plasticization of DOP. And DOP also adsorbs around the nuclei and restrains the growth of the crystals, which makes grains refine as homogenize the distribution of the graphite. The crystal area is easy to melt and this can result in the breaking up of the neighborhood conductive chains when temperature is near the melting point of polymer matrix. The PTC effect depends strongly on the graphite movement in the matrix. Consequently it can also present an obvious PTC effect even the crystallinity of polymer matrix is reduced. And the graphite form conductive chains around the crystal boundary. A good adhesion between the matrix and the fillers will decrease the bending modulus due to the homogeneous distribution of the graphite.

It can be seen (from Table II) that the bending strength is decreasing with the additives content. But the melting point (T_m) and the crystallinity of polymer matrix can drastically decrease when the additives content exceeds the critical amount. This has a great influence on the PTC effect. The room temperature resistivity and the PTC intensity are also reduced. For the reasons presented earlier, there is a limit to the amount of the additives content. And a balance between the PTC intensity and the

mechanics property can be achieved by using the optimum content of additives in the composite.

CONCLUSION

Our results show that graphite filled HDPE also had the high PTC intensity. An appropriate graphite size is found to be very important to obtain high PTC intensity. The best size of graphite is 50 μm . The composite with it has a balance between the PTC intensity and the room temperature. A drastic improvement of the comprehensive performance is achieved by using the orthogonal design experiment. The optimum content is that the graphite content is 60 g, DOP is 25 g, and talc powder is 12 g. The bending strength of this composite is two times less than that of HDPE-graphite blends. And the PTC intensity is also preserved.

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