

FILLED POLYOLEFIN COMPOSITES PREPARED FROM *IN-SITU* POLYMERIZATION VIA A CATALYST-SUPPORTED APPROACH

I. MORPHOLOGY OF PE IN CARBON BLACK(CB)/PE *IN-SITU* COMPOSITES

Ying-wu Luo*, Xin-pei Cao and Lin-xian Feng

Institute of Polymer Science and Materials, Zhejiang University, Hangzhou 310027, China

Abstract The morphology of PE in the *in-situ* CB/PE composites prepared from *in-situ* polymerization via a catalyst-supported approach was studied by DSC. It is found that both the melting peak temperature and crystallinity of the PE shell decrease as filler level increases. The unexpected phenomena are ascribed to the strong interaction between PE and CB and the very high specific area of CB. It is suggested that the lamellar thickness should be well correlated to the PE shell thickness. A two-layer PE model is successfully used to explain the experiment results.

Key words *In-situ* composite, Filled polyolefin, Morphology

INTRODUCTION

In recent years, the field of particle-filled polymer composites has attracted considerable attention because of their widespread applications in household, automobile, and electrical industries. Inorganic fillers and/or organic fibers are incorporated into a plastic resin to improve various physical properties of the materials such as mechanical strength and modulus, or to lower the cost of polymer composite^[1]. Most recently, there is a growing interest in polymer composites prepared via *in-situ* polymerization in order to improve particle dispersion and interfacial adhesion^[2–7]. The modulus and tensile strength of *in-situ* composites were found to be distinctly higher than those of conventional melt-mixed composites^[8]. It was evident that the masterbatch of the highly filler-loaded composite could improve rheological and mechanical properties of composites because of lower surface energy and better dispersion of the highly filler-loaded composite particles^[9].

Functional polymer composites have developed rapidly due to the attractive combination of useful polymer matrix properties with those of functional fillers, which are able to impart conductivity, superconductivity, magnetic properties, piezoelectric effects. CB/Polymer composites were studied extensively^[10–31] for their important applications in rubber enhancement, toners for printing or copying, conducting polymer composites and positive temperature coefficient (PTC) devices, *etc.* Most recently, it was established that graphite/polyolefin composites synthesized by *in-situ* polymerization via a catalyst-supported approach showed some unique and interesting properties^[32, 33]. One of the authors studied CB/PE *in-situ* composites and found that the composites show special PTC properties^[34, 35]. This paper explores the morphology of the PE shell around filler particles in *in-situ* composites.

* Corresponding author: Ying-wu Luo (罗英武), E-mail: yingwu.luo@cmsce.zju.edu.cn

Current address: The State Union Key Lab. of Chemical Engineering (Polymer Reaction Engineering Branch), Zhejiang University, Hangzhou, 310027, China

Received April 22, 2002; Revised May 31, 2002; Accepted June 27, 2002

EXPERIMENTAL

Method of Preparation of the In-Situ CB/PE Composites

The *in-situ* CB/PE composites were prepared using a pre-filled polymerization mixture, which contained CB-supported catalyst particles. TiCl_4 was introduced on the surface of CB particles via CB surface hydroxyl group to form CB-supported catalyst particles, which were added to an ethylene slurry polymerization mixture.

Preparation of CB-Supported Catalyst

Prior to treatment with the catalyst systems, carbon black was pre-conditioned under vacuum at 80°C for 12 h. The pre-conditioned carbon black was then added to a sealed flask and deoxygenated. Petroleum spirit was then injected into the flask, followed by an injection of AlEt_3 whilst stirring. After twenty minutes, the CB-supported catalyst formation was completed by injecting a given amount of TiCl_4 , which was then left to react for a further twenty minutes.

Polymerization of Ethylene

Polymerization took place under anhydrous and oxygen-free conditions. The purified ethylene flowed at a constant rate through a polymerization tube immersed in a thermostat bath, where the CB-supported catalyst was suspended in petroleum spirit.

Measurement and Control of Filling Degree

The weight percentage of CB in the composites was controlled by ending the polymerization at different reaction times, so that composites with a range of filler levels were synthesized. Filling level (*i.e.* CB percentage in the composite) was determined by the gravimetric method, *i.e.*

$$p = \frac{W_1}{W_2} \times 100\%$$

where W_1 , input amount of CB; W_2 , output amount of the composite.

DSC Measurement

Melting process and crystallinity were determined by using a Perkin-Elmer DSC-7 at a heating rate of 10 K/min. Before measurement, a sample was heated up to 165°C at 40 K/min and held at 165°C for five minutes, and then cooled down to 30°C at a cooling rate of 10 K/min. Crystallinity was calculated by

$$x = \frac{\Delta H_f}{\Delta H_f^\circ}$$

Extraction of CB/PE Composites

An amount of the dry CB/PE composite was Soxhlet extracted with xylene for 24 h.

RESULTS AND DISCUSSION

When DSC measurement was carried out with a series of the *in-situ* composites with different filler levels, some unexpected phenomena were observed and are illustrated in Figs. 1 and 2. From Fig. 1, it is apparent that the melting peak temperature (T_{mp}) of the composites decreases with increasing filling level to a limiting value of 121°C at 80% *W/W* filler. From Fig. 2, it is also apparent that the crystallinity of the composites varies in a similar manner to that of the T_{mp} data with the crystalline content reaching a limiting value of 15% at a slightly lower filler level than was observed in the T_{mp} data.

The phenomena were unexpected as the samples examined had the same thermal history. Variation in molecular weight caused by differences in polymerization time^[36] (which controls the filler content) are not considered to be great enough to cause such large changes in T_{mp} and crystalline content. In addition, molecular weight variation does not explain the attainment of limiting values of T_{mp} and crystalline content at high filler levels.

It is well-known that the thickness of polymer lamellae is related to the melting point by the equation^[37]

$$T_m = T_m^0 \left(1 - \frac{2\sigma_e}{\Delta H_f l}\right) \quad (1)$$

that means the thickness of PE lamellae is a function of filler level according to the above experimental observation, *i.e.*,

$$l = F(W_p) = C(W_p) W_p / (d_p A_c) = \frac{C(W_p)}{d_p A_c} \frac{1-p}{p} \quad (2)$$

where the terms have the following meanings: l , thickness of PE lamella; $C(W_p)$, coefficient factor; W_p , mass of polymer per gram CB in the composite; A_c , specific surface area of CB; d_p , polymer density; p , filling degree, weight percentage of CB in the composite.

At the first approximation, we have

$$W_p / (d_p A_c) \approx l_p \quad (3)$$

Combining (2) and (3) gives

$$l \approx C(W_p) l_p \quad (4)$$

where l_p is thickness of PE shell in the composite and C is a function of filling degree.

On the other hand, substituting Eq. (2) into (1), we have

$$T_m = T_m^0 \left(1 - k \frac{p}{1-p}\right) \quad (5)$$

where

$$k = \frac{2\delta_e d_p A_c}{\Delta H_f C(W_p)}$$

In Fig. 1, the solid line represents the best fitting line of the melting peak temperature with $\frac{p}{1-p}$. It is clearly shown that Eq. (5) is in good agreement with the experiment results when $\frac{p}{1-p} < 5$ and k , *i.e.* C , is constant instead of a function of W_p . From Eq. (4), it is clear that the thickness of PE lamellae is proportional to that of the PE shell. It is concluded that the decrease of the melting peak temperature with increase of filling degree is attributed to the limitation of PE shell thickness, as a result of very high specific area shown later. On the other hand, the leveling-off of melting peak temperature when $\frac{p}{1-p} > 5$ is due to the nanometer voids on the surface of the CB aggregate, as is reasoned in the following section.

The unusual variation of the morphology in the PE shell of the composites should be attributed to the special structure of CB and the strong interfacial adhesion arising from *in-situ* polymerization. Generally speaking, the minimum dispersible unit of CB is an aggregate of CB particles. An aggregate (as shown in Fig. 3), which has an aciniform morphology, consists of a number of particles, which become fused together during CB synthesis^[14] The properties of carbon black used in our experiment are listed in Table 1. A surface area of 75 m²/g is obtained by calculation based on measured diameter from TEM images. If a small loss of surface area from fusion of particles together is taken into account, there is an approximate agreement between the surface area value obtained by electron microscopy and that obtained by gas adsorption measurements, which is an indication of the lack of micro-porosity in the primary CB particles.

It is convenient to represent the aggregates as spheroids of a certain bulkiness, as shown in Fig. 3, and the DBP value represents the volume of the voids both within and between these equivalent spheres when they are

close-packed^[14]. As the diameter of the primary particles of CB is of nanometer size, it is inferred that the voids on the surface of the CB aggregates are also of nanometer size. Actually, in Table 1, if the DBP value is divided by the BET value, a void size of 27 nm is obtained.

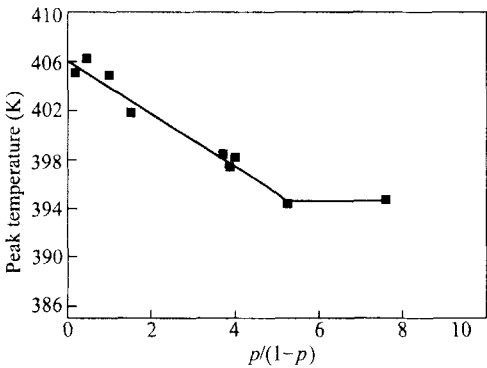


Fig. 1 Effects of filling level on the melting peak temperature
— Best fitting line; ■ Experimental data

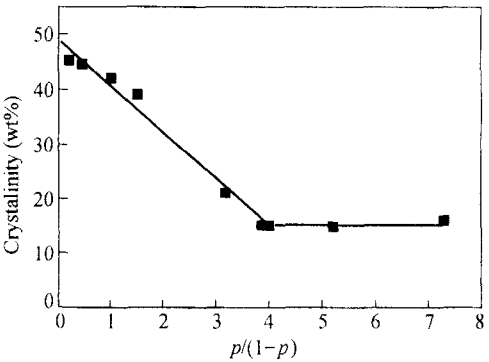


Fig. 2 Effects of filling level on the crystallinity of PE shell
— Best fitting line; ■ Experimental data

Table 1. Properties of CB used in the present experiments*

Diameter (nm)	BET (m ² /g)	I ₂ (mg/g)	DBP (cm ³ /g)
42	63	70	1.7

* Data measured by Qilu Petrum-Chemical Company

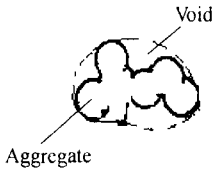


Fig. 3 The schematic drawing of a CB aggregate

The morphology of the CB discussed above provides an explanation for the unexpected morphology of the PE shell. For the *in-situ* PE composites, it was established that PE lamellar crystallites envelop the filler particles, and the bases of the lamellae are parallel to the filler^[138]. The CB specific surface area as high as 63 m²/g as well as the strong interaction between PE and CB offered by *in-situ* polymerization make most of polymer molecules strongly fixed on the surface of CB, which was indicated by the solvent extraction experiment (which will be described in the following part). As a compensation for this interaction, some meta-stable lamellae are formed instead of stable lamellae. The thicker the PE shell, the less the overall interactions, and the more stable lamellae form.

From the morphology of the CB, it is clear that those molecules in the nanometer void will have the strongest interaction with CB surface because of the highest contacting area. Furthermore, from Fig. 2 it is seen that at higher filler level the crystallinity is very low and keeps constant. It is reasonable to propose that the PE shell is composed of two layers: the interface layer and bulk layer in terms of the interaction between PE macromolecules and CB. At the very high filling level, almost all PE macromolecules are fixed on the surface of CB so that only the interface layer exists. PE macromolecules in the interface layer are greatly hindered from crystallizing. With increase of the PE amount, more and more PE macromolecules stay away from the surface of CB. These PE macromolecules are not prevented from crystallizing and constitute the bulk PE layer. It is clearly reasonable to assume that (1) thickness of the interface layer is constant where there exists a bulk PE layer, (2) PE crystallinity in the interface layer is constant, (3) PE crystallinity in the bulk layer is constant.

Based on the above two-layer model, a mass balance gives

$$x = x_1w_1 + x_2(1 - w_1) = x_2 + (x_1 - x_2)w_1 \qquad p < p_c \tag{6}$$

where the terms have the following meanings, x , overall crystallinity of PE shell; x_1 , crystallinity of PE in the interface layer; x_2 , crystallinity of PE in the bulk layer; w_1 , weight fraction of PE of the interface layer among the total PE; p_c , critical filler level, *i.e.*, the filler level at which the thickness of the PE shell is equal to that of the interface layer.

From assumption (1), at $p < p_c$, the amount of PE of the interface layer should be equal to that at $p = p_c$

$$w_1(1 - p) = p \frac{(1 - p_c)}{p_c} \tag{7}$$

Rearrangement gives

$$w_1 = \frac{(1 - p_c)}{p_c} \frac{p}{(1 - p)} \tag{8}$$

Substituting of Eq. (8) into Eq. (6) gives

$$x = x_2 + (x_1 - x_2) \frac{(1 - p_c)}{p_c} \frac{p}{(1 - p)} \qquad p < p_c \tag{9}$$

where x_1 , x_2 , and p_c are constant. Eq. (9) suggests that the crystallinity be linearly proportional to $\frac{p}{1 - p}$ where $p < p_c$. In Fig. 2, the solid line represents the best fitting line of the overall crystallinity of PE shell with $\frac{p}{1 - p}$. It

is clearly shown that Eq. (7) fits the experiment results well. Comparison of the experimental data with the theoretical predication supports the hypothesis that the PE shell consists of two layers. From the mathematical fit to the experimental data, the following can be obtained: $x_1 = 50\%$, $x_2 = 15\%$, and $p_c = 80\%$. From the p_c value of 80%, a value of interface thickness of 4 nm can be obtained.

When the filler level is greater than 80%, there is no bulk layer, so the overall crystallinity is equal to that of the interface layer and keeps constant. In view of the low crystallinity (15%), it is considered that ordered domains exist instead of true lamellar crystallites, that account for the exothermic peak in the DSC spectrum. That is why the melting peak temperature can remain constant at high filler levels greater than p_c .

Table 2. Extraction results of CB/PE composites

System	Extracted PE percentage (%)
PE//CB	100%
PE/CB88	15%
PE/CB87	19%
PE/CB79	58%
PE/CB50	60%

* PE//CB: composite by melt-blending; PE/CBnn: composite by *in-situ* polymerization, nn represents percentage filling degree

In order to further verify the above assumptions, a solvent extraction experiment was carried out. The experiment results are listed in Table 2. It is evident that not all of the PE can be extracted away from the *in-situ* composites, whereas PE is completely extractable from the conventionally produced composites. It is therefore concluded that chemical attachment of PE macromolecules to the CB surface hinders chain folding and hence crystallization. This effect ultimately leads to an interface layer with a significantly reduced crystalline content.

CONCLUSION

The morphology of the PE shell was studied in CB/PE *in-situ* composites. It is suggested that this shell should consist of two layers: a bulk PE layer and an interface layer. The crystalline content of the latter is very low, due

were successfully developed to explain the variation of melting point and crystallinity.

The effect of the above morphological features on the properties of the *in-situ* composites will be reported in the next paper.

REFERENCES

- 1 Nielsen, L.E., *Mechanical Properties of Polymers and Composites*, Marcel Dekker, New York, 1974
- 2 Volfson, S.A., "Composite Polymeric Materials Today and Tomorrow", Ser. Khim (in Russian), Moscow, Znanie, 1982
- 3 Kojima, Y., Usuki, A. and Kawasumi, M., Kurauchi, T., Kamigaito, O., *J. Polym. Sci.*, 1993, A31, 1755
- 4 Lipscomb, R. De W., E. I. Du Pont de Nemours and Company, 1976, Patent USA 3950303
- 5 Goettler, L.A. and Neff, W.J., *Polym. Comp.*, 1986, 7: 383
- 6 Qu, Y., Yu, Z., Feng, Y. and Fang, X., *Chinese J. Polym. Sci.*, 1993, 11: 31
- 7 Kojima, Y., Usuki, A., Kawasumi, M., Okada, A., Kurauchi, T. and Kamigaito, O., *J. Polym. Sci.*, 1993, A31: 983
- 8 Kyu, T., Zhou, Z.L., Zhu, G.C., Tajuddin, Y. and Qutubuddin, S., *J. Polym. Sci.*, 1996, B34: 1761
- 9 Kyu, T., Zhou Z.L., Zhu, G.C., Tajuddin, Y. and Qutubuddin, S., *J. Polym. Sci.*, 1996, B34: 1769
- 10 Lakdawala, K. and Salovey, R., *Polym. Eng. Sci.*, 1987, 27: 1035
- 11 Medalia, A.I., *Rub. Chem. Technol.*, 1978, 51: 437
- 12 Ayala, J.A., Hess, W.M., Kistler, F.D. and Joyce, G. A., *Rub. Chem. Technol.*, 1991, 64: 19
- 13 Clason, C. and Kubat, J., *J. Appl. Polym. Sci.*, 1975, 19: 831
- 14 Sichel, E.K., Ed., *Carbon Black-Polymer Composites*, Marcel Dekker, New York, 1982
- 15 Meyer, J., *Polym. Eng. Sci.*, 1973, 13: 462
- 16 Meyer, J., *Polym. Eng. Sci.*, 1974, 14: 706
- 17 Reboul, J.P. and Mossalli, G., *Int. J. Polym. Mater.*, 1976, 5: 133
- 18 Buche, F., *J. Appl. Phys.*, 1973, 44: 532
- 19 Norman, R.H., *Conductive Rubbers and Plastics*, Elsevier, Amsterdam, 1970
- 20 Narkis, M., Ram A. and Flashner, F., *J. Appl. Polym. Sci.*, 1978, 22: 1163
- 21 Narkis, M., Ram, A. and Flashner, F., *Polym. Eng. Sci.*, 1978, 22: 649
- 22 Narkis, M., Ram, A. and Stein, Z., *Polym. Eng. Sci.*, 1981, 21: 1049
- 23 Kost, J., Narkis, M. and Foux, F., *Polym. Eng. Sci.*, 1983, 23: 567
- 24 Obliego, G. and Herrman, U., *Kunststoffe*, 1984, 74: 97
- 25 Balta, F.J., Ezquerro, T.A., Rueda, D.R. and Alonso-Lopez, J., *J. Mater. Sci. Lett.*, 1984, 3: 165
- 26 Miyauchi, S., Sorimachi, Y., Mitsui, M., Akihida, H. and Ohkita, E., *J. Appl. Polym. Sci.*, 1984, 29: 5251
- 27 Narkis, M. and Vaxman, A., *J. Appl. Polym. Sci.*, 1984, 29: 1639
- 28 Yacubowicz, J. and Narkis, M., *Polym. Eng. Sci.*, 1986, 26: 1568
- 29 Benguigui, L., Yacubowicz, J. and Narkis, M., *J. Polym. Sci.*, 1987, B25: 127
- 30 Yacubowicz, J., Narkis, M. and Benguigui, L., *Polym. Eng. Sci.*, 1988, 28: 1581
- 31 Yacubowicz, J., Narkis M. and Benguigui, L., *Polym. Eng. Sci.*, 1990, 30: 459
- 32 Shevchenko, V.G., Ponomareko, T. and Klason, C., *Smart. Mater. Struct.*, 1995, 4: 31
- 33 Ponomareko, T., Shevchenko, V.G., Klason, C. and Pristpa, A. L., *Smart. Mater. Struct.*, 1994, 3: 409
- 34 Cheng, J., Wang, L. and Feng, L., *Petroleum Chemical Engineering*, (in Chinese), 1995, 24(5): 211
- 35 Cheng, J., Wang, L. and Feng, L., *Petroleum Chemical Engineering*, (in Chinese), 1995, 24(5): 299
- 36 Boor, J., *Ziegler-Natta Catalysts and Polymerizations*, Academic Press, New York, 1979, 488
- 37 Wunderlich, B., *Macromolecular Physics*, Vol. 3, Academic Press, New York
- 38 Minkova, L., Velikova, M. and Damyanov, D., *Acta Polym.*, 1991, 42(1): 8