

STUDIES ON THE MECHANICAL PROPERTIES AND CRYSTALLIZATION BEHAVIOR OF POLYETHYLENE COMPOSITES *

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ABSTRACT

The effects of interfacial modifier on the mechanical, dynamic mechanical properties and crystallization behavior of the polyethylene composites were investigated in the present paper. It was found that the interfacial modifier significantly improved the mechanical properties, influenced the dynamic mechanical spectra and slightly changed the crystallization behavior. The results showed that the interfacial modifier changed the dispersion state of dispersed phase of the composites, resulting in different phase structure, which was the major reason leading to different mechanical and crystallization properties.

INTRODUCTION

Recently, rigid-particle strengthened and elastomer toughened thermoplastics have drawn great attention widely. In principle, incorporation of rigid particle is intended to improve the strength, hardness and high heat distortion temperature of the materials^[1-2], but generally results in increased brittleness^[3]. On the other hand, addition of a rubber component often increases the toughness^[4-5] but reduces the rigidity of composite. As a result, there is increasing interest in the use of multicomponent thermoplastics (matrix)/rubber/filler polymer composites because of the possibility of increasing both the strength and toughness of the materials^[6-9]. Carbon black has obtained wide application because it could improve the strength^[10] and conductivity^[11] of the material. The possible presence of matrix/filler, matrix/rubber and rubber/filler interfaces in the

* This work was supported by a Fund for Young Scientist from the National Advanced Materials Committee of China (NAMCC)

Received January 8, 1994

ternary composite results in the complexity of phase structure^[9] and corresponding variation of the composite properties. We think that it is beneficial to both the strength and toughness of the composite to insert a rubber interlayer between the filler and matrix, i. e., to form a core-shell dispersed phase structure with filler as a core and rubber as a shell. Based on this consideration, the self-made interfacial modifier (IM) was employed in the high density polyethylene (HDPE)/ethylene propylene diene monomer rubber (EPDM)/carbon black (CB) ternary composites and a material with high strength and high toughness was obtained.

In the present paper, the effects of interfacial modifier on the mechanical and dynamic mechanical properties of the composites from the viewpoint of phase structure and the corresponding variation of the composite crystallization behavior were examined.

EXPERIMENTAL

1. Materials

The polymers used in the work were high density polyethylene (HDPE), ethylene propylene diene monomer rubber (EPDM) and ethylene-vinyl acetate copolymer (EVA). The filler was carbon black (CB) with surface area $74.7\text{ m}^2/\text{g}$. The interfacial modifier was maleic anhydride-styrene copolymer (MAH-co-ST) prepared in this Laboratory.

2. Sample preparation

HDPE-rubber-filler composites were all prepared by melt extrusion using a Brabender twin screw extruder ($35\text{ mm}\phi$) at 30rpm. The interfacial modifier was extruded with other materials at the same time without pretreating carbon black surface.

3. Mechanical testing

Instron 1122 was employed to measure the tensile strengths and the flexural moduli of the composites. Izod impact strength was measured on XJ-40A impact tester.

4. DMA analysis

Perkin-Elmer DMA-7 was used to measure the dynamic mechanical spectra of the composites, with the load manner of three point bend, the frequency of 1Hz, the heating rate of $5^\circ\text{C}/\text{min}$ and the temperature range of -80 — $180^\circ\text{C}/\text{min}$.

5. DSC analysis

The DSC analysis was carried out on a Perkin-Elmer DSC-7, with the

heating and cooling rate 10°C/min, and the temperature range of 20—190°C/min. The measurement process was as follows: first the sample was heated to 200°C, stayed for several minutes to eliminate the thermal history and then was cooled to observe the crystallization behavior.

6. Phase morphology

Phase morphology were determined on the cross-sectioned surfaces of different composites fractured in impact test and in liquid nitrogen using a S-530 (Japan) scanning electron microscopy. Some freeze fractured samples were etched (to etch EPDM) by n-heptane at room temperature for 15 minutes.

RESULTS AND DISCUSSION

1. Effects of the interfacial modifier on the mechanical properties of the composites

Table 1 gives the mechanical properties of the composites. From the Table 1 it can be seen that the impact strengths of the HDPE/EPDM and

Table 1 Mechanical properties of the HDPE₂ composites

Sample	Tensile strength (MPa)	Impact strength (J/m)	Flexural modulus (MPa)
HDPE	28.6	115	576
HDPE/CB(100:10)(wt. ratio)	31.8	55	987
HDPE/CB(100:10)/IM	41.6	110	1128
HDPE/EPDM(90:10)	19.6	570	599
HDPE/EVA(90:10)	21.3	388	735
HDPE/EPDM/CB(90:10:10)	24.9	188	882
HDPE/EVA/CB(90:10:10)	25.8	198	954
HDPE/EPDM/CB(90:10:30)	30.9	50	1121
HDPE/EVA/CB(90:10:30)	31.3	27.5	1274
HDPE/EPDM/CB(90:10:10)/IM	28.3	500	732
HDPE/EPDM/CB(90:10:30)/IM	43.1	338	969

HDPE/EVA composites were much higher than that of the virgin HDPE, but a marked decrease in the tensile strength was also observed. Although the tensile strengths of HDPE/CB composites increased slightly, its impact strength decreased remarkably. The interfacial modifier had a significant improvement effect on its tensile strength and impact strength. The above results were due to the following facts: for the unmodified HDPE/CB composites, the interfacial adhesion between HDPE and CB was poor and CB-CB interaction was strong, which resulted in the agglomeration of the

CB particle. When the stress acts on the composite, stress concentration and material damage results. The interfacial modifier significantly improves the interfacial adhesion with the results of reduction of CB-CB interaction and better dispersion of the CB particles. The stress can be easily transmitted to the filler from the matrix. The stress concentration point number is significantly reduced. This is the major mechanism of increase of the tensile and impact strength. When comparing ternary composites without interfacial modifier, the composite with EVA has a higher tensile strength and flexural modulus, higher impact strength at lower CB content and lower impact strength at higher CB content than the composite with EPDM. But the difference is not significant. For both composites, at lower CB content, the tensile strength reduces slightly and the impact strength increases moderately, while at higher CB content the tensile strength increases slightly and the impact strength decreases significantly. The above results indicate that the composite with both high strength and high toughness was not obtained as expected. The self-made interfacial modifier was employed to treat the HDPE/EPDM/CB composites, the results are listed in Table 1. At lower CB content, the tensile strength is comparable with the matrix and the impact strength is much higher than that of the matrix and the unmodified ternary composites. At higher CB content, the tensile strength increases significantly while the impact strength remains comparatively high. Comparing the mechanical properties of the HDPE/EPDM/CB(90:10:30)/IM with those of the HDPE matrix, it could be seen that a composite with high strength, high modulus and high toughness was obtained. It was also found that the flexural moduli of the composites were all higher than that of the matrix, which was due to the fact that the flexural moduli of EPDM, EVA and CB were all higher than the matrix. The composite with EVA has a comparatively higher flexural modulus than that with EPDM. The fact leading to the significant increase of the tensile and impact strength of the composite with interfacial modifier may be due to the different phase structure. For the HDPE/EPDM/CB without interfacial modifier, the interaction between EPDM and CB is not strong, HDPE and CB act as independent dispersed phases with HDPE and CB separately. The existence of a large amount of HDPE/CB interface results in the deterioration of the composite properties, as observed in the HDPE/CB binary composites. Incorporation of interfacial modifier into the ternary composites results in a different phase structure, i. e., a core-shell dispersed phase structure with

filler as a core and rubber as a shell. The increase of the impact strength is due to the significant decrease of the HDPE/CB interface and the significant increase of the apparent rubber phase content resulting from the core-shell dispersed structure. The increase of the tensile strength is due to the excellent interfacial adhesion between EPDM and CB, which makes it possible to transmit the stress from the matrix to the filler through the rubber interlayer. The decrease of the flexural modulus is due to the increase of the apparent rubber phase and the corresponding decrease of the filler content while the modulus of EPDM is not as high as that of CB. The formation of core-shell dispersed phase structure in modified HDPE/EPDM/CB composite will be further confirmed by DMA observations.

2. Effects of the interfacial modifier on the dynamic mechanical properties of the composites

Fig. 1 gives the effects of the interfacial modifier on the dynamic mechanical properties of the HDPE/CB composites. For the dynamic loss spectra of the HDPE composite, α_c and γ was observed in general. From the spectra, the broad dynamic loss peak at higher temperature corresponds to the α_c , which reflects the molecular motion of the crystalline region. We

are not concerned with the situation in this region. The γ dynamic loss peak was not observed in the spectra. The dynamic loss at lower temperature is the lowest for the HDPE matrix. With incorporation of CB, the dynamic loss increases. The dynamic loss of the HDPE/CB composite with interfacial modifier is still higher than that of the HDPE/CB composite without interfacial modifier. Similar results were also observed in the composites of SiO_2 filled HDPE^[12] and CaCO_3 filled HDPE^[8]. Ideally, the dynamic loss is expected to remain the same or decrease slightly with addition of spherical particles with high modulus at these loadings. According to the research results of Maurer et al.^[13], the increase of the dynamic loss is due to the disturbed layer (interphase) of the HDPE on the filler surface. The

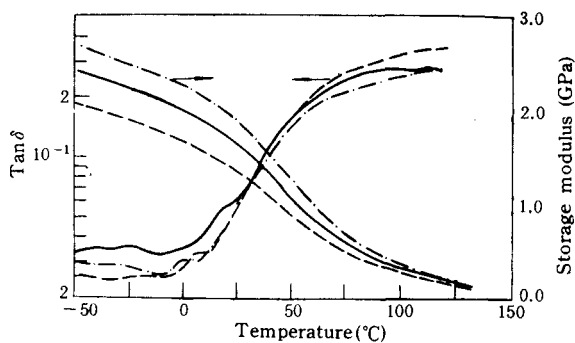


Fig. 1 Dynamic mechanical spectra for
 --- HDPE
 - · - HDPE/CB
 — HDPE/CB/Interfacial modifier

interfacial modifier changed the interphase structure of the composite, resulting in the still increase of the dynamic loss. According to Fig. 1, the storage moduli of the HDPE/CB composites with and without interfacial modifier were all higher than that of the matrix, with that of the composite without interfacial modifier the highest. This is due to the following facts: the higher storage modulus of the filler and the agglomeration of the filler due to filler-filler interaction are all beneficial to the increase of the storage modulus of the composite. The interfacial modifier reduces the filler-filler interaction and better dispersion of the filler results. The effect of the filler is consequently restrained. The dynamic mechanical spectra for the HDPE/EPDM/CB composites were given in Fig. 2. Similarly, the broad dynamic

loss peak at higher temperature corresponds to α_c . From the Fig. 2, we can discern a dynamic loss peak at about -25°C which does not appear in the HDPE/CB composites. This corresponds to the rubber glass transition.

According to the Fig. 2, the dynamic loss of the HDPE/EPDM is the highest, with that of the HDPE/EPDM/CB composite with interfacial

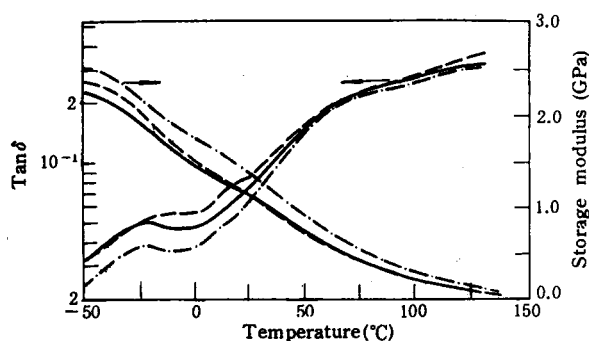


Fig. 2 Dynamic mechanical spectra for
 ---HDPE/EPDM
 - · - HDPE/EPDM/CB
 — HDPE/EPDM/CB/Interfacial modifier

modifier higher than that of the composite without interfacial modifier. The glass transition temperature of the rubber is nearly unchanged. The storage modulus is the highest for the HDPE/EPDM/CB composite without interfacial modifier, while that of the HDPE/EPDM composite higher than that of the HDPE/EPDM/CB composite with interfacial modifier. In the literature^[12], Scott et al. reported the dynamic mechanical spectra predicted by the extended van der Poel model for multiple component HDPE/EPDM/filler composites with the rubber as a uniform layer around the filler particle or as separate inclusions in the matrix. The presence of a core-shell dispersed phase structure is expected to enhance the size of the dynamic loss peak and reduce the storage modulus as compared with the separate dispersed phase structure for the rubber and filler. The phenomenon was observed in the HDPE/EPDM/ CaCO_3 composites^[8]. From our dynamic

mechanical spectra, it could be concluded that the core-shell dispersed phase structure was really formed in the HDPE/EPDM/CB composites with the interfacial modifier. The conclusion will be further confirmed by the SEM observation.

Electron micrographs of impact fractured surface of HDPE/EPDM/CB composites were shown in Fig. 3. It can be seen that although there all exist shear yielding bands in the HDPE/EPDM/CB and HDPE/EPDM/CB/IM composites, the cavitation is obvious in the HDPE/EPDM/CB composite and

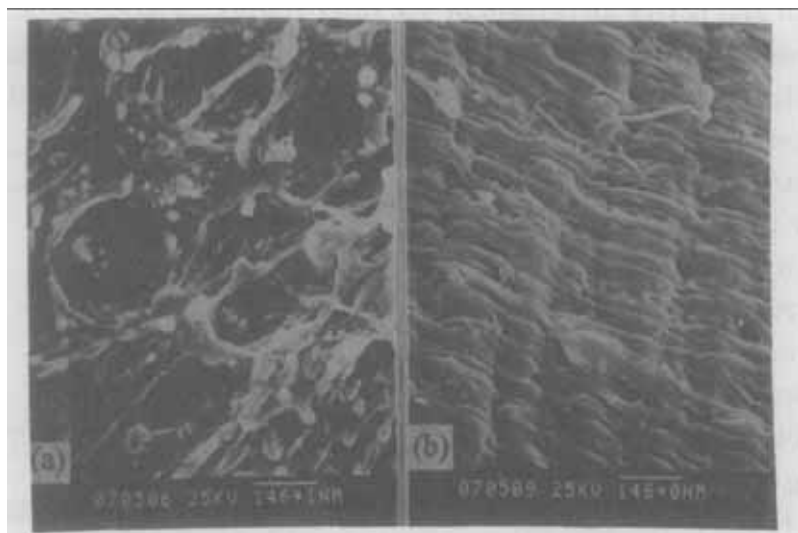


Fig. 3 SEM photographs of impact fractured surfaces

(a) HDPE/EPDM/CB composite (b) HDPE/EPDM/CB/IM composite

the filler can be clearly seen. The cavitation process becomes an important way of absorbing the energy. The existence of cavitation is due to the direct contact of filler and HDPE. On the contrary, the shear yielding band of the HDPE/EPDM/CB/IM composite is dense and the cavitation does not exist. The shear yielding is the major way of absorbing the energy and consequently the impact strength increases significantly. The above observation demonstrates that the direct contact of filler and the matrix in HDPE/EPDM/CB/IM is much less than that in HDPE/EPDM/CB. Electron micrographs of freeze fractured surface of HDPE composites were shown in Fig. 4. Comparison of the fracture surface of HDPE/EPDM/CB composite before and after etching reveals the separate dispersion of filler and rubber inclusion. The filler particles can already be clearly seen in Fig. 4(a) and the interface is clear, that is, it acts as a separate dispersed phase. After etching, as can be seen in Fig. 4(b), the only difference is the etched

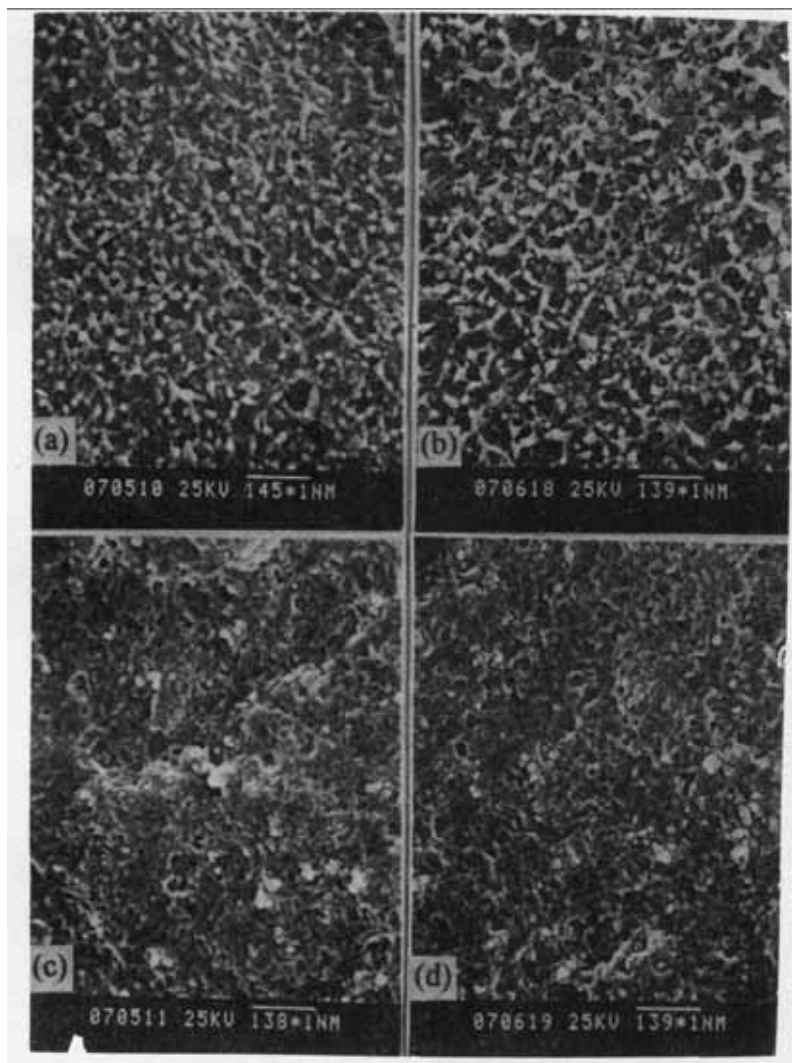


Fig. 4 SEM photographs of freeze fractured surfaces

- (a) HDPE/EPDM/CB composite (b) etched HDPE/EPDM/CB composite
(c) HDPE/EPDM/CB/IM composite (d) etched HDPE/EPDM/CB/IM composite

away separate EPDM, while the filler dispersion changes little. On the contrary, the filler can be hardly seen in HDPE/EPDM/CB/IM composite, as shown in Fig. 4(c). Those particles that can be seen have no clear interface with the matrix. After etching the EPDM, the gap between the filler and the matrix becomes obvious and many particles that have not appeared before etching can now be clearly seen, as shown in Fig. 4(d). This is due to the formation of core-shell dispersed phase structure. The direct freeze fracture does not reveal many filler particles due to the

inclusion of filler in the rubber. The existence of clear gap after etching is the result of etched thin interlayer of rubber. Moreover, the appearance of many filler particles after the etching of EPDM further confirms the existence of core-shell dispersed phase structure.

4. Effects of the interfacial modifier on the crystallization behavior of the composites

Because the crystallization state is generally a crucial factor in determining the material properties for the semicrystalline polymers, the nonisothermal crystallization behavior of the composites was investigated. The results are listed in Table 2. In the table, T_p denotes the temperature where the crystallization exotherm shows the peak, which reflects the supercooling of the sample, T_{onset} denotes the temperature of the onset of

Table 2 Crystallization behavior of the HDPE composites

Sample	T_p (°C)	T_{onset} (°C)	$T_{onset}-T_p$ (°C)	A/m (J/kg)	$\Delta\omega$
HDPE	116.2	121.6	5.4	201000	1.1
HDPE/CB(100:10)(wt. ratio)	118.3	121.7	3.4	218000	0.9
HDPE/CB(100:10)/IM	117.6	121.4	3.8	172000	1.2
HDPE/EPDM(90:10)	115.5	118.6	3.1	199000	0.7
HDPE/EVA(90:10)	115.5	118.7	3.2	219000	0.7
HDPE/EPDM/CB(90:10:10)	118.3	121.5	3.2	198000	0.8
HDPE/EVA/CB(90:10:10)	117.6	121.5	3.9	213000	0.9
HDPE/EPDM/CB(90:10:10)/IM	116.8	120.3	3.5	189000	1.0

material crystallization, $(T_{onset}-T_p)$ reflects the overall crystallization rate of the sample, the lower the $(T_{onset}-T_p)$, the higher the overall crystallization rate, $\Delta\omega$ denotes the half-width of the crystallization peak after normalization of the peak to constant HDPE component, which reflects the crystallite size distribution, A/m denotes the enthalpy after normalization to the constant HDPE component, which reflects the degree of crystallinity of the matrix. Gupta et al.^[14] made a detailed explanation of the above parameters. According to Table 2, the overall crystallization rates of all components were all higher than that of the virgin HDPE. This is due to the heterogeneous phase nucleation effect of the added disperse phase. The composite with EVA has a higher crystallization rate, higher degree of crystallinity and similar crystallite size distribution as compared with the corresponding composite with EPDM. Whether for HDPE/CB or HDPE/EPDM/CB composites, addition of interfacial modifier changed the

crystallization behavior, increasing the supercooling rate and decreasing the crystallization rate. The above results may be due to the following facts; the addition of the interfacial modifier improves the interfacial adhesion between the disperse phase and the matrix. In the course of the crystallization, the folding of the molecular chain of HDPE was restrained, resulting in the decrease of crystallization rate. Addition of the interfacial modifier also decreases the degree of crystallinity and broadens the crystallite size distribution. This may also be the result of the variation of matrix-filler-rubber interaction and the corresponding variation of the phase structure with addition of the interfacial modifier. The overall results are as follows: although the incorporation of interfacial modifier results in a slightly different crystallization behavior of the matrix, the different mechanical properties may not be the result of this. The different phase structure is probably the major mechanism of the improvement of the properties of the composite.

Keywords:

HDPE; Interfacial modifier; Mechanical property; Crystallization behavior

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