

# Morphology and Electrical Properties of Short Carbon Fiber-Filled Polymer Blends: High-Density Polyethylene/Poly(methyl methacrylate)

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**ABSTRACT:** Morphology and electrical properties of short carbon fiber-filled high-density polyethylene (HDPE)/poly(methyl methacrylate)(PMMA) polymer blends have been studied. The percolation threshold of HDPE50/PMMA50 blends filled with vapor-grown carbon fiber (VGCF), 1.25 phr VGCF content, is much lower than those of the individual polymers. The SEM micrographs verified that the enhancement of conductivity could be attributed to the selective location of VGCF in the HDPE phase. A double percolation is the basic requirement for the conductivity of the composites, i.e., the percolation of carbon fibers in the HDPE phase and the continuity of this phase in the blends, which hereby are defined as the first percolation and the second percolation, respectively. The SEM micrographs also showed that the short carbon fibers could affect the morphology of the blends. With the increase of VGCF content, the HDPE domains are elongated from spherical into strip shape, finally develop to a continuous structure. As a result, the second percolation threshold of the blends filled with 2.5 phr VGCF, 20 wt % HDPE, is lower than that of the blends filled with 1.5 phr VGCF, 30 wt % HDPE. The influence of molding temperature and time on the second percolation threshold has also been investigated. For the composites molded at a lower temperature, the second percolation threshold is shifted to a higher VGCF content, but there is little influence of molding time on the second percolation threshold. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1813–1819, 1998

**Key words:** morphology; electrical properties; selective location of filler; double percolation; short carbon fiber; polymer blends

## INTRODUCTION

It is well known that the electrical conductivity of insulating polymers filled with electrical con-

ductive particles, such as metal and carbon black, discontinuously increases at certain filler content.<sup>1,2</sup> The sharp break in the relationship between the filler content and the conductivity of the composites implies some sudden change in the dispersion state of the conductive particles, i.e., the coagulation of particles to form networks that facilitate the electrical conduction through the composites.<sup>3</sup> This phenomenon, which is usually explained by the percolation theory, has been known as “percolation.” The critical filler content

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is called the "percolation threshold," which depends not only on the types of filler and polymer, but also on the dispersion state of the filler and the morphology of the matrix.<sup>4-6</sup>

Recently, more attention has been given to incorporation of carbon particles into incompatible polymer blends, because a double percolation phenomenon can provide them with electrical conductivity at very low filler content.<sup>7-11</sup> The improvement of conductivity can be ascribed to the selective location of conductive filler in one of the two phases or at their interface. The mechanism of the heterogeneous distribution of fillers is explained by the difference in the affinity of fillers to each component of the polymer blends.<sup>12,13</sup> The electrical properties strongly depend on the double percolation, i.e., the percolation of carbon particles in the filler-rich phase and the continuity of this phase in the blends,<sup>7,12</sup> defined hereby as the first percolation and the second percolation, respectively. However, there is no report dealing with the selective location and double percolation of short carbon fiber-filled polymer blends. This may be due to the big size and small surface area of traditional carbon fibers, so that the difference in the affinity of the fibers to two polymers is not enough to draw the filler from one phase to another. Vapor-grown carbon fiber (VGCF) is a new kind of carbon fiber, which is unique in its very small size, big surface area, and excellent electrical properties. In the present work, the morphology and electrical properties of VGCF-filled high-density polyethylene/poly(methyl methacrylate) blends were studied. The selective location of short carbon fibers and the double percolation of the composites were found first.

## EXPERIMENTAL

### Composite Sample Preparation

High-density polyethylene (HDPE) (E891(C), from Nihon Sekiyu Kagaku Co.) and poly(methyl methacrylate) (PMMA) (HA, from Mitsubishi Rayon Co.) were used as matrices. VGCF (average length 10  $\mu\text{m}$ , average diameter 0.2  $\mu\text{m}$ , from Showa Denko Co.) was used as an electrical conductive filler. The polymers were first mixed on a two-roll mill at 190°C for 5 min, followed by adding the filler into the mixture and mixed for 10 min. Prior to the mixing, the polymers were dried at 80°C for 24 h, and the filler was dried at 130°C for 3 h under vacuum. The sample was held molten at 190°C for 10 min and compressed under a

pressure of 18 MPa for 15 min, followed by quenching into water to obtain films with a thickness of 0.5 mm.

### Measurement of Electrical Conductivity

The electrical conductivity was measured in the thickness direction of the composite films. Silver paste was used to ensure good contact of the sample surface with the electrodes. Prior to the measurement, all the samples were kept in a vacuum at 40°C for 24 h, and the conductivity was measured in dry air at room temperature with a Keithley 487 picoammeter/voltage source.

### Observation of Scanning Electron Microscopy (SEM)

The surface of the samples, which was fractured in liquid nitrogen, etched with Eiko IB-3 and coated with Pt-Pd, was observed by an FE S800 scanning electron microscope.

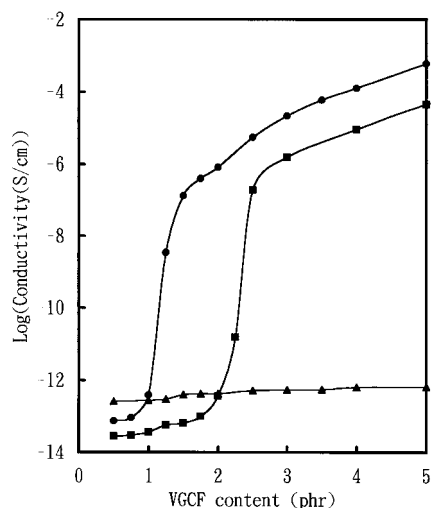
### Continuity of Two Phases

The three-dimensional continuity of HDPE and PMMA phases in the blends was analyzed by the selective extraction of PMMA phase by chloroform with a Soxhlet extractor. If the extraction left samples compact (no fragmentation into smaller pieces), the HDPE phase was considered as 100% continuous, and the degree of PMMA phase continuity was quantified as the weight fraction of PMMA that was extracted. Conversely, when samples fell apart, the PMMA phase was 100% continuous, and the degree of the HDPE phase continuity was estimated as the weight fraction of big compact pieces of HDPE released by the extraction process.

## RESULTS AND DISCUSSION

### Percolation and Selective Location

The dependence of electrical conductivity on the filler content for HDPE, PMMA, and polymer blends filled with VGCF are shown in Figure 1. The HDPE samples exhibit a percolation threshold at 2.5 phr (parts per hundred parts resin) VGCF content, whereas for the PMMA samples, there is little change in conductivity up to 5 phr VGCF content. This is due to the different filler dispersion states in the two polymers. The interfacial energy plays an important role in the conductive path formation in the loaded polymer system:



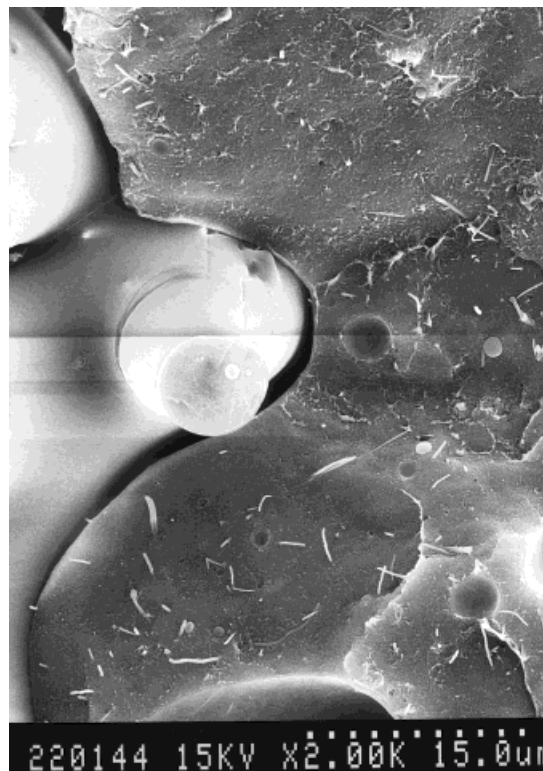
**Figure 1** Dependence of electrical conductivity on VGCF content for (■) HDPE/VGCF, (▲) PMMA/VGCF, and (●) HDPE50PMMA50/VGCF composites molded at 190°C for 15 min.

the smaller the interfacial energy between the filler and the matrix, the higher the percolation threshold. In the system that has a high matrix/filler interfacial energy, the formation of a filler/filler interface is energetically advantaged, leading to the formation of a conductive network. However, in the system where the matrix readily wets the filler, the filler particles are completely dispersed at the same level of loading. Hence, higher filler concentration is needed to achieve the state of network formation.<sup>3,14,15</sup>

It is interesting that the percolation threshold of VGCF filled HDPE/PMMA (50/50) blends is only 1.25 phr VGCF content, which is much lower than those of the individual polymers. The enhancement of conductivity can be attributed to the selective location of VGCF in the HDPE phase. Figure 2 shows the SEM micrograph of HDPE/PMMA (50/50) blends filled with 1.5 phr VGCF. We can clearly see that carbon fibers are preferentially located in the HDPE phase. The preferential accumulation of carbon fibers in the HDPE phase results in the formation of a conductive network in this phase at very low total filler content. This heterogeneous distribution of the filler between the two phases may be due to the difference in the affinity of the filler to each component of the polymer blends.<sup>12,13</sup>

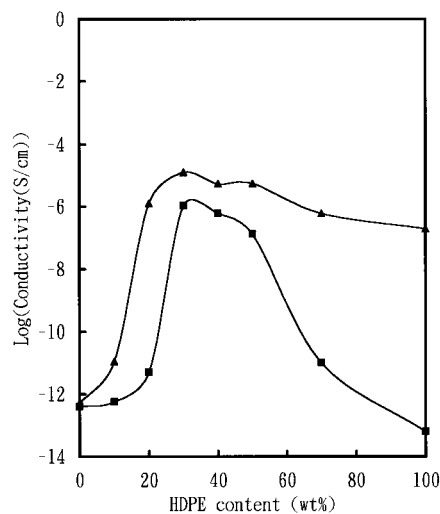
### Double Percolation and Phase Continuity

The electrical conductivity of polymer blends filled with short carbon fiber depends not only on the



**Figure 2** SEM micrograph of HDPE/PMMA (50/50) blends filled with 1.5 phr VGCF molded at 190°C for 15 min.

percolation of carbon fibers in the filler-rich phase, but also on the continuity of this phase in the blends. Figure 3 shows the dependence of electrical conductivity on HDPE content in the blends. The conductivity of the composites at a



**Figure 3** Dependence of electrical conductivity on HDPE content for HDPE/PMMA blends filled with (▲) 2.5 and (■) 1.5 phr VGCF molded at 190°C for 15 min.

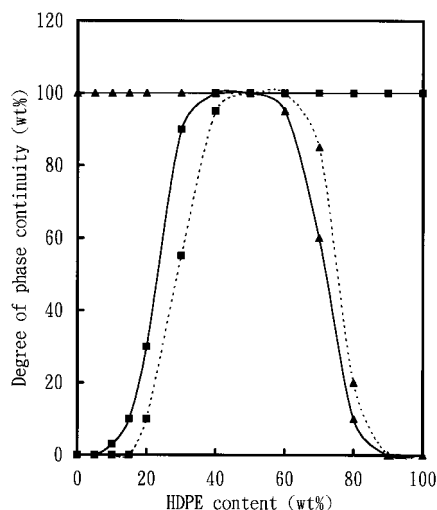
**Table I** The Degree of Two Phases Continuity for HDPE/PMMA Blends and 1.5 phr VGCF-Filled HDPE/PMMA Blends

HDPE (wt %)	PMMA (wt %)	Without VGCF		With 1.5 phr VGCF	
		Continuity of HDPE Phase (%)	Continuity of PMMA Phase (%)	Continuity of HDPE Phase (%)	Continuity of PMMA Phase (%)
0	100	0	100	0	100
5	95	0	100	0	100
10	90	0	100	3	100
15	85	0	100	10	100
20	80	10	100	30	100
30	70	55	100	90	100
40	60	95	100	100	100
50	50	100	100	100	100
60	40	100	100	100	95
70	30	100	85	100	60
80	20	100	20	100	10
90	10	100	0	100	0
100	0	100	0	100	0

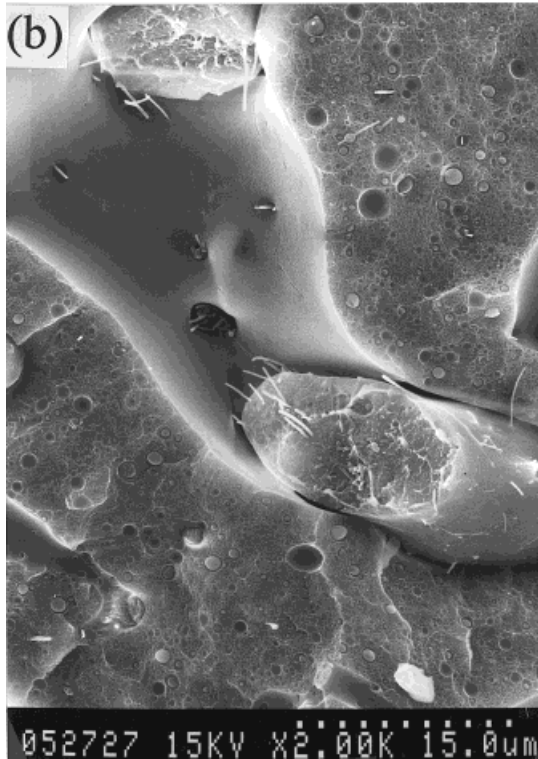
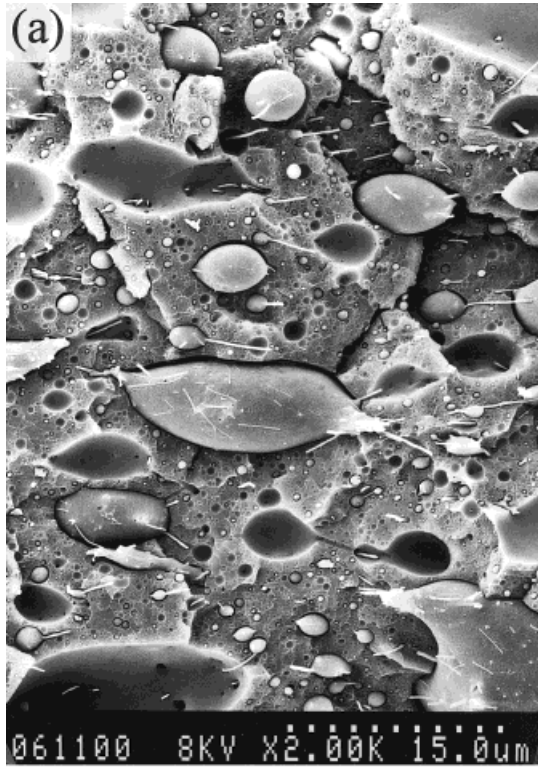
given VGCF content changes with the composition in a rather complex manner. Clearly, a double percolation effect takes place in the blends containing 30 wt % HDPE when the total VGCF loading is 1.5 phr in the blends. The dramatic change in conductivity corresponds to the change in the HDPE phase continuity in the blends. As shown in Table I and Figure 4, the degree of HDPE phase continuity is 90% when the HDPE concentration

reaches 30 wt %. This implies that the continuous structure of HDPE phase in the composites has been formed. Whereas, when the HDPE content in the blends is below 30 wt %, most of the HDPE domains are dispersed in the PMMA phase, the conductive pathway throughout the sample cannot be formed, even if the filler concentration in the HDPE phase is above the percolation threshold. The result of Figure 4 is in agreement with the observation of SEM micrographs (Fig. 5).

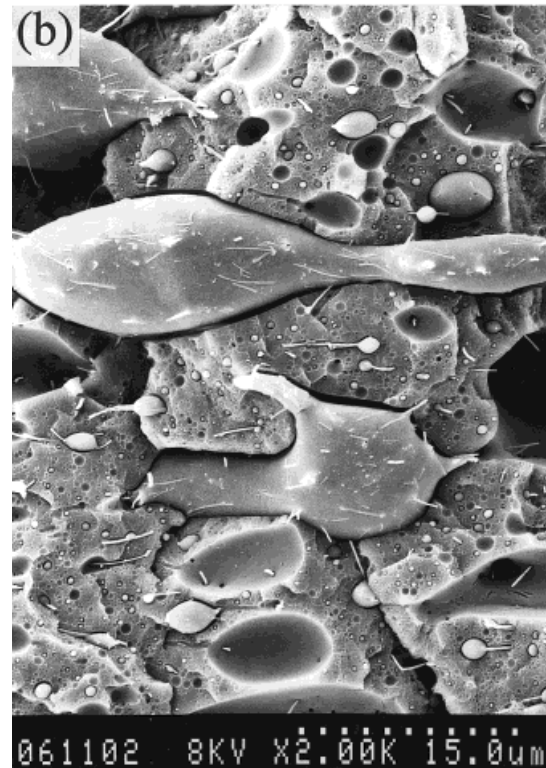
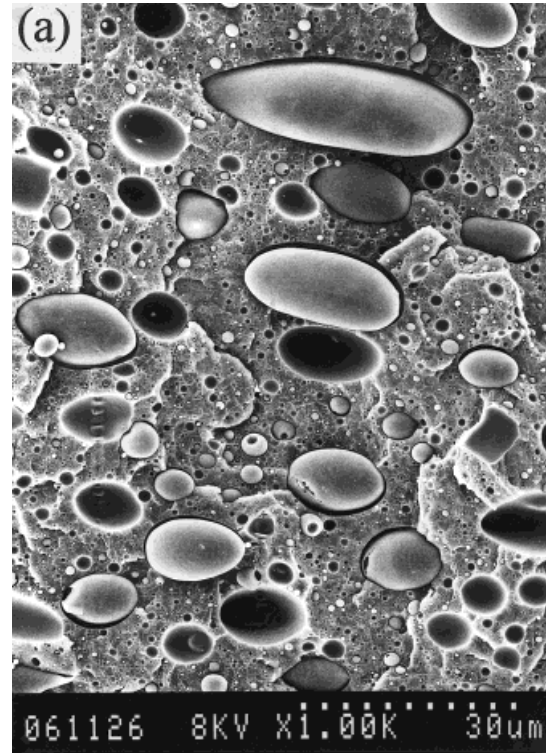
Another interesting observation is found in Figures 3 and 4, in relation to the effect of the filler content on the conductivity and the phase continuity of the composites. With the increase of VGCF content, the second percolation threshold and the formation of continuous structure of the HDPE phase are shifted to a lower HDPE content. It implies that the filler can affect the morphology of the blends. This effect is verified by SEM. Comparing Figure 5(a) with Figure 6, we can find that with increasing VGCF content, the HDPE domains become more irregular, and are elongated from spherical into strip, finally develop to a continuous structure. The explanation is that VGCF more likely increases the HDPE melt viscosity and perturbs the kinetics of the phase coalescence during the molding process.<sup>16,17</sup> As a result, the second percolation threshold of the blends filled with 2.5 phr VGCF, 20 wt % HDPE, is lower than that of the blends filled with 1.5 phr VGCF, 30 wt % HDPE.



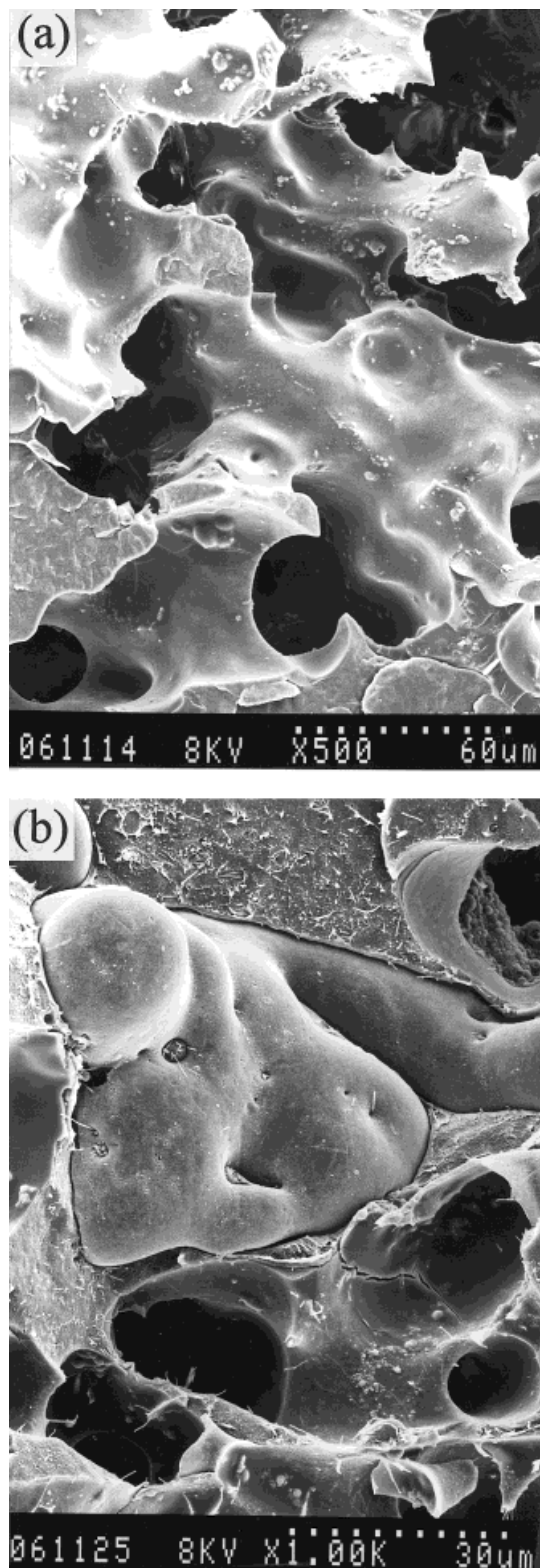
**Figure 4** Dependence of degree of (■) HDPE and (▲) PMMA phase continuity on HDPE content for HDPE/PMMA blends (broken line) and HDPE/PMMA blends filled with 1.5 phr VGCF (solid line) molded at 190°C for 15 min.



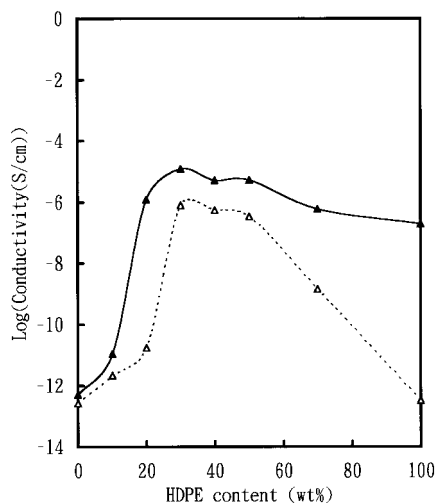
**Figure 5** SEM micrographs of HDPE/PMMA (a) 20/80 and (b) 30/70 blends filled with 1.5 phr VGCF molded at 190°C for 15 min.



**Figure 6** SEM micrographs of HDPE/PMMA (20/80) blends (a) without VGCF and (b) filled with 2.5 phr VGCF molded at 190°C for 15 min.



**Figure 7** SEM micrographs of HDPE/PMMA (70/30) blends (a) without VGCF and (b) filled with 1.5 phr VGCF molded at 190°C for 15 min (PMMA was extracted by chloroform).



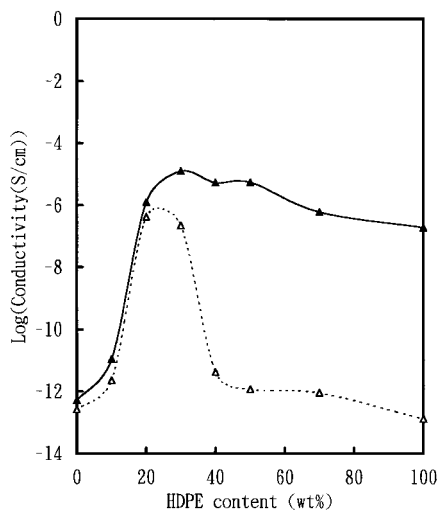
**Figure 8** Dependence of electrical conductivity on HDPE content for HDPE/PMMA blends filled with 2.5 phr VGCF molded at (▲) 190°C and (△) 170°C for 15 min.

An inverse effect is found for the PMMA phase. Figure 7 shows SEM micrographs of the samples containing 30 wt % PMMA. For the sample without filler, the PMMA phase is continuous in the blends, and is extracted by the solvent, whereas for the blends filled with 1.5 phr VGCF, there are still some PMMA domains dispersed in the HDPE phase. The observation of SEM is in agreement with the result of Figure 4. The composition at which the PMMA phase starts to be continuous is shifted to a higher PMMA content for the blends filled with 1.5 phr VGCF.

#### Influence of Molding Temperature on the Second Percolation

The above results show that the electrical conductivity of HDPE/PMMA blends filled with VGCF is affected by both the aggregation state of VGCF in the HDPE phase and the continuity of this phase in the blends. We can expect that the preparation condition of the samples, which affects the dispersion state of the fillers and the morphology of the blends, will have an influence on the conductivity of the composites.

Figure 8 illustrates the dependence of electrical conductivity on HDPE content for the blends filled with 2.5 phr VGCF molded at different temperatures. According to Paul and Barlow,<sup>18</sup> the phase continuous structure is difficult to be formed in the case of high viscosity, so the second percolation threshold is shifted to a higher HDPE content at a lower molding temperature.



**Figure 9** Dependence of electrical conductivity on HDPE content for HDPE/PMMA blends filled with 2.5 phr VGCF molded at 190°C for (▲) 15 min (△) 1 min.

### Influence of Molding Time on the Second Percolation

Figure 9 shows the dependence of electrical conductivity on the HDPE content for the blends filled with 2.5 phr VGCF molded for different molding time. It seems that there is little influence of molding time on the second percolation threshold, indicating a stable effect of the filler on the morphology of the blends. This result is in agreement with that of Gubbels's. According to his explanation, the filler more likely increases the viscosity of HDPE phase and perturbs the kinetics of the phase coalescence.<sup>17</sup>

### CONCLUSIONS

1. The percolation threshold of VGCF filled HDPE50/PMMA50 blends, 1.25 phr VGCF content, is much lower than those of the individual polymers. The enhancement of electrical conductivity can be attributed to the selective location of VGCF in the HDPE phase.
2. A double percolation is the basic requirement for the conductivity of the composites, i.e., the percolation of carbon fibers in the filler-rich phase and the continuity of this phase in the blends.
3. Carbon fibers can affect the morphology of the HDPE/PMMA blends. With the increase of VGCF content, the HDPE domains become more irregular, and are elongated from a

spherical shape into strip shape, finally develop into a continuous structure.

4. The molding temperature has a strong influence on the second percolation. For the composites molded at a lower temperature, the second percolation threshold is shifted to a higher HDPE content, but there is little influence of molding time on the second percolation threshold.

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