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A Self-Assembled Electric Conductive Network in Short Carbon Fiber Filled Poly(methyl methacrylate) Composites with Selective Adsorption of Polyethylene

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Introduction. Recently conductive polymer composite materials (CPCMs) have been fabricated based on the heterogeneous distribution of carbon black (CB) in polymer blends.[1−7] The selective location of CB in one phase or at the interface of two polymers causes a decrease of the percolation threshold to a very low level. Both the conductive network of CB in the filler-rich phase and the continuity of this phase in the composites are basic requirements for maintaining a conductive network through the composites. This has been designated as the concept of double percolation.[2] Since the electrical properties of such CPCMs strongly depend on the behavior of the double percolation, much effort has been devoted toward controlling the location of CB and the phase morphology. Sumita et al.[1,8] proposed that interfacial energy was the main factor determining the heterogeneous distribution of the fillers in polymer blend matrices. Gubbels et al.,[4] on the other hand, suggested that a substantial increase in polymer viscosity arising from selective location of the CB played a crucial role in controlling the phase morphology. Both the stability and continuity of the polymer phase could be improved by a high loading of CB.

Our preliminary interest has been on the contribution of filler geometry toward selective location and phase continuity in polymer blend matrices. Usually, a composite filled with a fiber or flake has a lower percolation threshold than one filled with spherical conductive particle.[9] Fillers with high aspect ratio may also increase the tendency to form the co-continuous phases in polymer blend matrixes.[10] A detailed study on phase continuity in short carbon fiber filled composites let us notice that the percolation threshold could be reduced not only by the double-percolation effect but also by a selective adsorption of polymer at the ends of fibers where the filler-rich phase is no longer continuous.

In the present paper, vapor-grown carbon fiber (VGCF) was used as filler. The morphology and electrical properties of VGCF/PMMA composites with addition of 1 and 5 wt % HDPE were studied. It is known that VGCF is one of the developing short carbon fibers which was commonly grown through the pyrolysis of hydrocarbon gases in the presence of metal catalysts.[11] In comparison with other carbon fibers, VGCF offers the highest thermal conductivity and improved electrical properties, providing a great potential for application in advanced materials.[12] Few results have been reported so far concerning electrical properties of polymer or polymer blends compounded with VGCF.

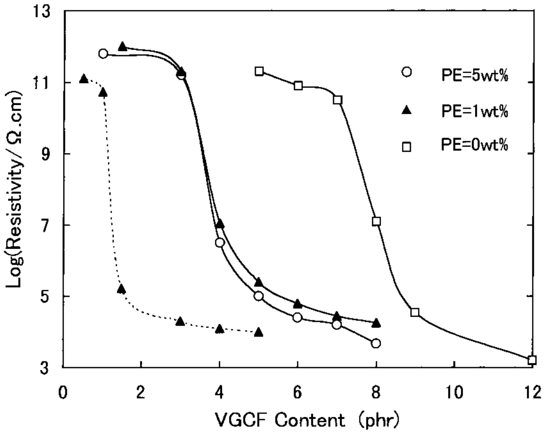

Figure 1. Influence of VGCF content on electrical resistivity of VGCF/PMMA composites containing different amount of HDPE (solid line, molded at 190 °C for 15 min; dash line, further annealed at 220 °C for 30 min).

Experimental Section. High-density polyethylene (E891(C); Nihon Sekiyu Kagaku Co., $T_m = 129$ °C), poly(methyl methacrylate) (HA; Mitsubishi Rayon Co.), and vapor-grown carbon fiber (average length 10 μm, diameter 0.2 μm, Showa Denko Co.) were dried at 80 °C for 24 h under vacuum oven before using. The PMMA was first mixed with HDPE using a two-roll mill at 220 °C for 5 min, followed by addition of the filler to the mixture and mixed for 10 min. The composites were compression molded at 190 °C for 15 min under the pressure of 20 MPa and finally quenched in water. The thickness of the molded sheet was about 0.5 mm.

The morphology of the films was determined by means of a field emission type scanning electron microscopy (FE S800, HITACHI). The specimens for SEM measurements were annealed at 220 °C for 30 min under a nitrogen gas atmosphere. To clarify the HDPE domain, the PMMA was selectively extracted by chloroform at room temperature for 72 h. The extracted residue was then dispersed into small particles in isopropyl alcohol by ultrasonic microwaves.

The electrical resistivity was measured by a Keithley 487 picoammeter in the perpendicular direction of the molded sheets. Silver paste was used to ensure good contact of the sample surface with the copper electrodes. Due to no observable deviation from the four-terminal measurements, data in this work were measured using the two-terminal technique. The resistivity of samples was found to be time-dependent. Therefore, the room-temperature resistivity was measured after a wait of 2 min in order to obtain the stationary value. The temperature dependence of the resistivity measurement was carried out by a computer-controlled system under a test voltage of 1 V. All values of resistivity reported in this work are values of dc resistivity.

Results and Discussion. The influence of VGCF loading on the room-temperature resistivity of VGCF/PMMA composites containing 1 and 5 wt % HDPE (weight percent of total polymer matrix) is shown in Figure 1. It was found that the percolation threshold of VGCF/PMMA composites reduced remarkably from 8.0 phr (per hundred parts of matrix) to 4.0 phr with addition of only 1 wt % HDPE. A much lower threshold (1.5 phr) was obtained after the specimens were an-

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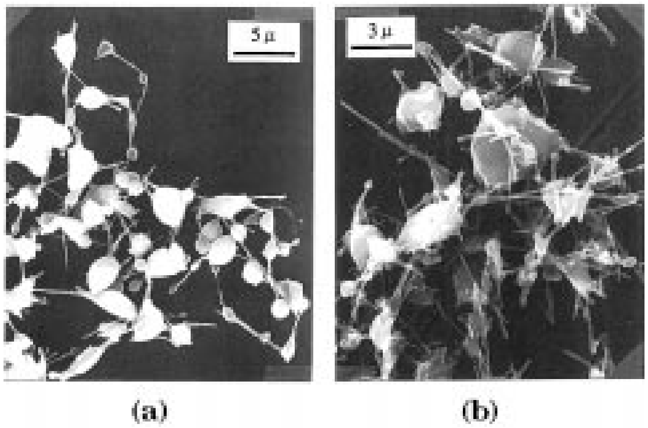


(a) (b)

Figure 2. SEM micrographs of PMMA-extracted VGCF/PMMA composites containing 5 wt % HDPE and (a) 1.5 phr VGCF and (b) 2.5 phr VGCF.

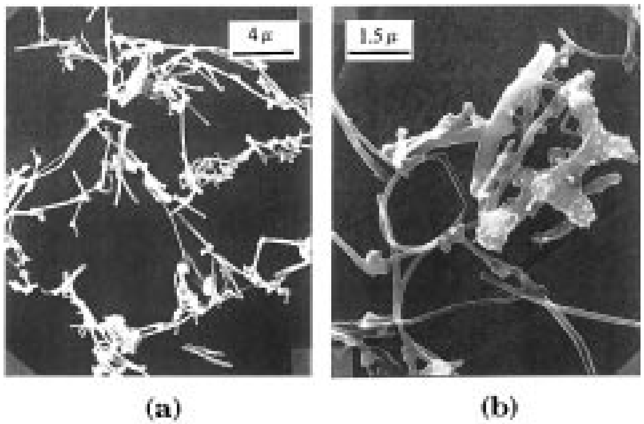
nealed at 220 °C for 30 min. The increase of HDPE content from 1 to 5 wt % was found to cause little change of the percolation threshold.

The concept of double percolation might be adopted to account for the decrease of the percolation thresholds. Gubbels et al.[4] reported that 5 wt % HDPE could maintain the double percolation in CB/HDPE/PS composites by loading 4.0 wt % CB. In fact, we have observed the selective location of VGCF in the HDPE phase and found that the double percolation could adequately describe the electrical properties of VGCF/HDPE/PMMA composites with the content of HDPE range from 20 to 100 wt %.[13] Furthermore, the postannealed specimen containing 1 or 5 wt % HDPE and 1.5 phr VGCF was found to keep compact after the extraction of PMMA by chloroform for 72 h, suggesting that the extracted residue remained continuous even if the content of HDPE was reduced to 1 wt %.

However, further investigation by SEM revealed that the continuity of the extracted residue was not related to the continuity of HDPE phase. Figure 2 shows the structure of PMMA-extracted composites containing 5 wt % HDPE. The micrographs show that the HDPE domains in VGCF/PMMA composites having 1.5 phr VGCF (Figure 2a) and 2.5 phr VGCF (Figure 2b) were isolated from each other. The continuity of extracted specimens seems to be constructed in such a pattern with carbon fiber as a skeleton and HDPE a clamp holder. Carbon fibers were found to be connected by HDPE. Further, the HDPE was selectively adsorbed at cross parts or the end parts of VGCF filaments.

Figure 3a shows the morphology of the PMMA-extracted composite having 1 wt % HDPE and 4.0 phr VGCF. A regular but effective continuous network was observed. The magnified picture (see Figure 3b) illustrated clearly that VGCF filaments were connected by HDPE. These results demonstrate that the "phase" continuum does not derive from HDPE, but from the self-assembled architecture between VGCF and HDPE.

A large positive temperature coefficient (PTC) resistivity effect can be expected near the melting temperature of HDPE if the conductive network is assembled by selective adsorption of HDPE, as the melting of HDPE will cause a sudden volume expansion and thereby break the conductive network.[14,15] The temperature dependence of resistivity with one heating−cooling cycle (rate: ±1 °C/min) is shown in Figure 4. To remove the effect of processing history, three cycles were run before the test. The VGCF/PMMA composite containing 1 wt % HDPE showed a large PTC anomaly near 120 °C, whereas the VGCF/PMMA composite alone exhibited a gradual increase of resistivity. A more pronounced PTC effect within similar temperature range was found for specimens containing 5 wt % HDPE. The large anomaly of PTC resistivity near the melting temperature of HDPE of 120 °C as measured by DSC should correspond to the melting process of selectively adsorbed HDPE. It is observed in Figure 4 that the high-temperature resistivity (above 100 °C) of 1 wt % HDPE containing composites is much higher than that of the VGCF/PMMA system. This might be due to the higher resistivity of HDPE bridging between fibers and more drastic breaking of conductive networks compared with PMMA matrix system. It should also mentioned that the melting temperature of HDPE in the composite (120 °C) was much lower than that of pure HDPE (129 °C). The lower temperature might correspond to the reduced mobility of the polyethylene chains and difficulty of crystallization due to the adsorption of HDPE on the VGCF surface.[16] These results confirm that HDPE is located at the connection part of VGCF and conductive network is maintained by HDPE domains.



(a) (b)

Figure 3. SEM micrographs of PMMA-extracted VGCF/PMMA composite containing 1 wt % HDPE and 4.0 phr VGCF with different magnification.

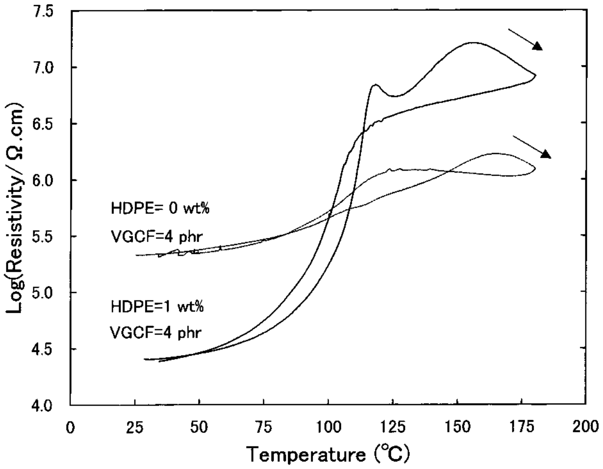


Figure 4. Temperature dependence of resistivity for VGCF/PMMA composites containing different amounts of HDPE. The specimens have been further annealed at 220°C for 30 min. Arrows indicate the direction of heating−cooling cycling.

Finally, we should point out that the self-assembled VGCF/HDPE conductive network does not mean that the HDPE should always act as a conductive bridge. The room-temperature measurements of ac conductivity for these systems with VGCF loading higher than percolation threshold revealed that the conductivity was independent of frequency up to 10^7 Hz, indicating that the conductivity is maintained by the conductor-like contact of VGCF. In other words, HDPE in these cases does not act as a conductive bridge but only as a mechanical bridge. It is supposed that the reduction of the percolation threshold might arise from the change of filler dispersion: the selective adsorption of HDPE at cross parts and the end of VGCF rearranges the dispersion of VGCF in a more effective way to form the conducive network.

In conclusion, with addition of 1−5 wt % HDPE, the percolation threshold of VGCF/PMMA composites was reduced from 8.0 to 4.0 phr. Annealing at 220 °C for 30 min further reduced to 1.5 phr. The drastic decrease of the percolation threshold does not derive from the double-percolation effect, but from the architecture of self-assembled conductive network constructed by selective adsorption of HDPE in VGCF/PMMA composites. The preferential adsorption of HDPE on VGCF filaments implies that there is a special affinity between VGCF and HDPE. The mechanism of selective adsorption of HDPE on VGCF and the process of assembling conductive network will be described in a future paper.

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