

Effect of Viscosity on the Electrical Properties of Conducting Thermoplastic Composites Made by Compression Molding of a Powder Mixture*

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The viscosity of thermoplastics above T_g was found to greatly affect the room temperature electrical properties of conducting thermoplastic composites made by compression molding of a powder mixture, while the mechanical properties are essentially not affected. The electrical resistivity decreased and the electromagnetic interference shielding effectiveness increased with increasing viscosity, as shown by using (i) the same filler, namely nickel particles, in polyimidesiloxane and polyether sulfone, and (ii) the same filler and matrix at different composite molding temperatures. This effect is attributed to the flow of the low viscosity thermoplastic particles during composite fabrication tending to disturb the connectivity of the filler particles achieved prior to heating.

INTRODUCTION

Electrically conducting polymer-matrix composites are used for die attach adhesives, electrical contacts, and electromagnetic interference (EMI) shielding. The conducting filler in these composites can be particles, flakes, and fibers. The electrical properties of the composites mainly depend on the materials used, namely the matrix and the conducting filler. The effect of an electrically conducting filler (particles) on the electrical properties of polymer-matrix composites is the subject of numerous papers (1-4). Indeed, the electrical resistivity, surface chemistry, surface morphology, particle size, filler volume fraction, filler orientation, and other aspects related to the filler are all very important in determining the electrical properties of the composite. On the other hand, we found in this work that with the same filler and the same filler volume fraction, the electrical properties of the composite show significant variation with the polymer species chosen for the matrix, such that the electrical resistivity of the composite decreases and the electromagnetic interference (EMI) shielding effectiveness increases with increasing viscosity of the polymer (thermoplastic) above T_g .

MATERIALS

The electrically conducting fillers used were nickel powder (1 to 5 μm in particle size) from Atlantic Equipment Engineers in Bergenfield, N.J.

The polymers used were two thermoplastics, namely polyether sulfone (Victrex PES 4100P of ICI) and polyimidesiloxane (SIM-2030M of Occidental Chemical Corp.). The properties of these polymers are shown in Tables 1 and 2.

A major difference between these two polymers lies in the viscosity above T_g . The glass transition temperatures of polyether sulfone and polyimidesiloxane are both about 220°C. Polyether sulfone flowed above T_g (e.g., at 350°C). Polyimidesiloxane did not flow above T_g (up to at least 500°C); its powder particles just became very viscous and coalesced above T_g . At 320°C, the viscosities of polyether sulfone and polyimidesiloxane are 2.1 kPa·s and 57.6 kPa·s, respectively.

COMPOSITE FABRICATION

Nickel-filled polyether sulfone was fabricated by mixing the polymer powder and the filler and then hot pressing the mixture in a matched metal die at 4.90 MPa and 310°C (unless stated otherwise) for 20 min.

Nickel-filled polyimidesiloxane was fabricated by mixing the polymer powder and the filler and then hot pressing the mixture in a matched metal die at 5.90 MPa and 300°C for 30 min.

The fabricating conditions for both polymers were suggested by the manufacturers.

COMPOSITE CHARACTERIZATION TECHNIQUES

Electrical resistivity measurements were made on composite materials that had been cut into bars. The

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Table 1. Properties of Polyether Sulfone Polymer.

T_g	220–222°C
Density	1.37 g/cm ³
Particle size	100–150 μ m
Tensile strength	45.93 \pm 1.12 MPa
Tensile modulus	2.64 \pm 0.19 GPa
Elongation at break	(3.1 \pm 0.3)%
Electrical resistivity	>10 ¹⁰ $\Omega \cdot$ cm
Coefficient of thermal expansion	55 \times 10 ⁻⁶ /K

Table 2. Properties of Polyimidesiloxane Polymer.

T_g	220°C
Density	1.25 g/cm ³
Particle size	50–100 μ m
Tensile strength	39.5 \pm 2.0 Mpa
Tensile modulus	2.1 \pm 0.11 GPa
Elongation at break	(2.1 \pm 0.13)%
Electrical resistivity	>10 ¹⁰ ohm·cm
Coefficient of thermal expansion	74.4 \times 10 ⁻⁶ /K (30–100°C) 86.4 \times 10 ⁻⁶ /K (30–150°C)

four-probe method was used. Four specimens of each composition were tested. Four data points were obtained for each specimen.

The EMI shielding effectiveness at 1.0 to 2.0 GHz was measured by using the coaxial cable method. The sample was in the form of an annular disc. The outside diameter and the inside diameter were 97.4 and 28.8 mm, respectively. The thickness ranged from 2.82 to 2.95 mm. In order to get a continuous metallic contact between the sample and the steel shielding tester chamber, conductive silver paint was applied to the inner surface of the center hole of the sample and the outer rim of the annular disc. Two specimens of each composition were tested.

The complex viscosities of polyether sulfone (PES) and polyimidesiloxane (PISO) in the temperature range of 260 to 320°C were measured by using a Rheometrics dynamic mechanical analysis system operated in the torsion mode, with an angular frequency of 6.28 rad/s and a heating rate of 5°C/min.

PES and PISO with the same filler weight fraction (40 wt%) were examined by using a viscometer (Physica MP30) and a dynamic mechanical analysis system (Perkin-Elmer DMA-7). The viscometer used a shear deformation mechanism to measure the shear strain rate above T_g , thereby determining the viscosity. This method cannot be used for measuring the viscosity of a polymer that does not flow above its T_g . In contrast, DMA is typically useful for polymers that have high viscosities above T_g . The parallel plate method of DMA was used in this work to determine the storage modulus and complex viscosity below and above T_g . A static stress of 60 kPa and a dynamic stress of 50 kPa were applied at a stress frequency of 1.00 Hz. The storage modulus and complex viscosity were continuously measured as the temperature was scanned from 220 to 320°C at a heating rate of 5°C/min.

The specimens were tested mechanically using standard methods and a Materials Testing System

(MTS). An IBM PS/2 computer with OPUS-200 software and a data acquisition board were used for the data collection. EA-13-120LZ-120 (Measurements Group, Inc.) strain gages were applied on the specimens to measure the strain. Four specimens of each composition were tested.

Specimens after mechanical polishing were examined under a scanning electron microscope (SEM).

RESULTS

Figure 1 shows the variation of the electrical resistivities of PISO/Ni and PES/Ni composites with the nickel particle volume fraction. The resistivity of PISO/Ni dropped sharply at 5 vol% Ni, which corresponds to the percolation threshold, whereas the resistivity of PES/Ni dropped less sharply, with the drop occurring over the range from 4 to 10 vol% Ni.

Tables 3 and 4 show the experimental results on the electrical resistivity and the EMI shielding effectiveness respectively. For a similar volume fraction of the filler, the electrical resistivity was much lower for polyimidesiloxane composites than polyether sulfone composites and the EMI shielding effectiveness was much higher for polyimidesiloxane composites than polyether sulfone composites.

Figure 2 shows the variation of the complex viscosities of polyether sulfone and polyimidesiloxane at various temperatures. It can be seen that polyimidesiloxane has higher viscosity than polyether sulfone at the same temperature. For example, at 260°C, the viscosities of PISO and PES are 298.3 kPa·s and 55.9 kPa·s, respectively; at 320°C, they are 57.6 kPa·s and 2.1 kPa·s, respectively.

Figure 3 shows the variation of the storage moduli and complex viscosities of PISO/Ni and PES/Ni composites (both 40 wt% Ni) at various temperatures.

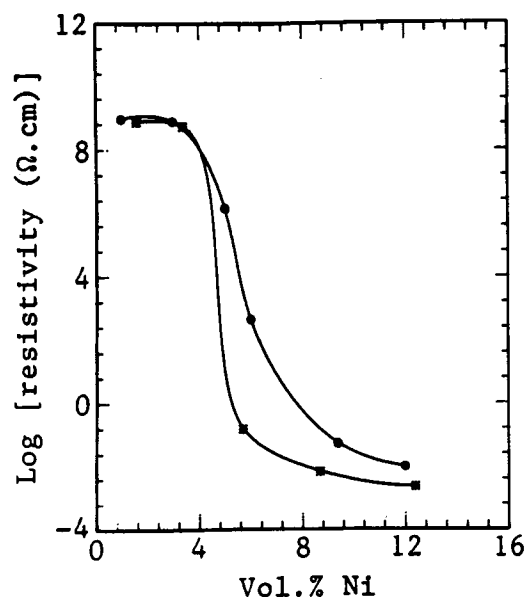


Fig. 1. Variation of the electrical resistivities of PISO/Ni and PES/Ni composites with Ni particle volume fraction. ●: PES/Ni; *: PISO/Ni.

The viscosity of PES/Ni decreased abruptly from 5.0 MPa·s at 220°C to 0.1 MPa·s at 320°C. In contrast, the viscosity of PISO/Ni changed gradually from 3.9 MPa·s at 220°C to 1.4 MPa·s at 320°C. The storage modulus of each composite varied with temperature in the same way as its complex viscosity.

Table 5 shows the tensile properties of the neat polymers and the composites. Table 6 shows the fractional increases in tensile strength and modulus due to the filler addition to the polymers. The fractional increase in strength is quite comparable for polyimidesiloxane and polyether sulfone composites of similar filler contents. The fractional increase in modulus increases with increasing filler content, as expected. This similarity in the reinforcing ability of the filler for the two polymers indicates that composites made from both polymers are similarly sound.

Table 7 shows the electrical resistivity and EMI shielding effectiveness of PES/Ni containing 9.4 vol% Ni, fabricated at different temperatures above T_g . As the fabrication temperature increased, the resistivity of the resulting composite increased while the shielding effectiveness decreased.

Tables 3, 4, and 7 all suggest that a decrease in viscosity of the polymer during fabrication increased the resistivity and decreased the shielding effectiveness. In Tables 3 and 4, PISO had a higher viscosity than PES. In Table 7, an increase in the fabrication temperature was associated with a decrease in the viscosity of PES.

Figure 4 shows SEM photographs at two different magnifications of a PES-Ni powder mixture (9.4 vol% or 40 wt% Ni) prior to compression molding. As the PES particles were much larger than the Ni particles, the mixture was naturally in the form of Ni particles surrounding the PES particles. This structure is schematically illustrated in Fig. 5a. During compression molding, a high viscosity polymer results in the

situation depicted in Fig. 5b, whereas a low viscosity polymer results in the situation depicted in Fig. 5c. The continuity of the conducting path formed by the Ni particles is highly disturbed when the viscosity is low, thus resulting in a high electrical resistivity.

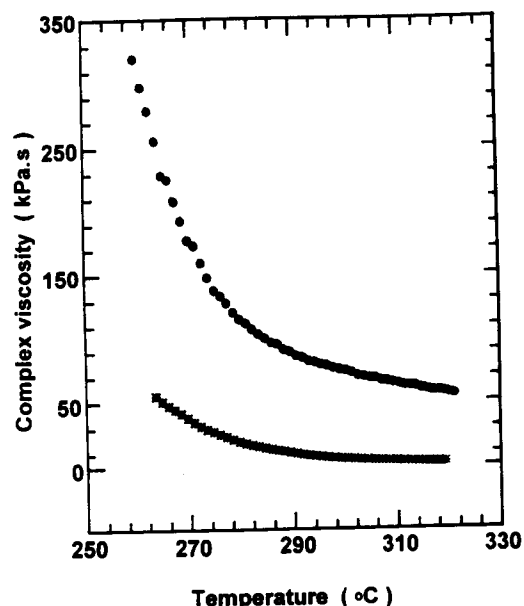


Fig. 2. Variation of the complex viscosities of polyether sulfone and polyimidesiloxane polymers with temperature. *: PES. ●: PISO.

Table 3. Electrical Resistivity of Nickel-Filled Thermoplastics.

Thermoplastic	Filler Content (vol%)	Resistivity ($\Omega \cdot \text{cm}$)
PISO ^a	5.7	0.155 (± 0.005)
	8.7	6.75×10^{-3} ($\pm 0.74 \times 10^{-3}$)
PES ^b	5.0	1.40×10^6 ($\pm 0.33 \times 10^6$)
	9.4	5.20×10^{-2} ($\pm 0.20 \times 10^{-2}$)

^a SIM-2030M, Occidental Chemical Corp.

^b PES 4100P, Victrex, ICI.

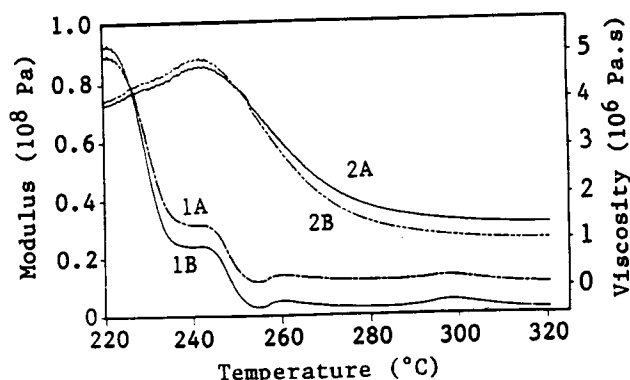


Fig. 3. Variation of the storage moduli and complex viscosities of PISO/Ni and PES/Ni composites with temperature. 1. PES/Ni. 2. PISO/Ni: A: complex viscosity, B: storage modulus.

Table 4. EMI Shielding Effectiveness (dB) of Nickel Powder-Filled Thermoplastics.

Thermoplastic	Filler Content (vol%)	Thickness (mm)	Frequency (GHz)										
			1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0
PISO ^a	5.7	2.85	42.5	40.5	39.0	37.5	38.5	37.5	39.0	41.5	43.2	45.0	44.0
	8.7	2.95	50.0	>50	>50	>50	>50	>50	>50	>50	>50	>50	>50
PES ^b	5.0	3.07	4.4	3.8	2.2	1.6	0.7	1.3	0.8	0.7	0.1	0.8	1.8
	9.4	2.80	25.5	23.2	21.5	20.1	19.8	19.5	21.2	23.5	24.9	25.8	25.5

^a SIM-2030M, Occidental Chemical Corp.

^b PES 4100P, Victrex, ICI.

Table 5. Tensile Properties of Nickel-Filled Thermoplastics.

Thermoplastic	Filler Content (vol%)	Strength (MPa)	Modulus (GPa)	Elongation (%)
PISO ^a	0	39.5 ± 2.0	2.11 ± 0.11	2.10 ± 0.13
	5.7	49.9 ± 1.5	2.67 ± 0.04	2.28 ± 0.06
	8.7	51.2 ± 1.5	2.98 ± 0.03	2.08 ± 0.09
PES ^b	0	45.93 ± 1.12	2.64 ± 0.19	3.10 ± 0.30
	5.0	56.38 ± 5.10	3.47 ± 0.16	2.27 ± 0.13
	9.4	57.13 ± 4.36	3.88 ± 0.20	1.64 ± 0.27

^a SIM-2030M, Occidental Chemical Corp.

^b PES 4100P, Victrex, ICI.

Figure 6 shows SEM photographs of polished sections of PISO/Ni and PES/Ni composites. PISO/Ni had more or less circular conducting paths, because PISO did not flow, whereas PES/Ni had conducting paths that were not circular because of the significant change in shape of the PES particles during compression molding. As a result, the conducting paths were more continuous in PISO/Ni than PES/Ni.

Figure 7 shows SEM photographs of polished sections of PES/Ni composites (9.4 vol% Ni) fabricated at 260 and 330°C. The higher fabrication temperature was associated with a lower viscosity, thereby causing more discontinuity in the conducting paths.

DISCUSSION

The experimental results show a large difference in the electrical properties between polyimidesiloxane and polyether sulfone composites, though the mechanical properties are similar. This difference is attributed to the difference in viscosity of the polymers

Table 6. Fractional Increases in Tensile Strength and Modulus Resulting from Filler Addition to PISO or PES.

Thermoplastic	Filler Content (vol%)	Fractional Increase	
		Strength	Modulus
PISO ^a	5.7	26%	27%
	8.7	30%	41%
PES ^b	5.0	23%	31%
	9.4	24%	47%

^a SIM-2030M, Occidental Chemical Corp.

^b PES 4100P, Victrex, ICI.

Table 7. Electrical Resistivity and EMI Shielding Effectiveness of PES/Ni Particle Composites (9.4 vol% Ni) Fabricated at Different Temperatures Above T_g .

Fabrication Temperature (°C)	Complex Viscosity of Neat Polymer (kPa · s)	Electrical Resistivity ($\Omega \cdot \text{cm}$)	Shielding Effectiveness (dB)							Thickness (mm)
			Frequency (GHz)							
			1.0	1.2	1.4	1.6	1.8	2.0		
260	55.9	1.22×10^{-2}	31.2	32.0	27.8	28.9	31.8	32.0	2.91	
280	17.8	2.15×10^{-2}	28.3	26.0	23.7	24.4	23.8	28.8	2.90	
300	5.5	3.36×10^{-2}	27.6	25.0	22.6	23.4	26.0	27.2	2.74	
330	2.1 ^a	5.14×10^{-2}	25.5	23.4	21.0	21.7	21.1	24.9	2.70	

^a Viscosity at 320°C.

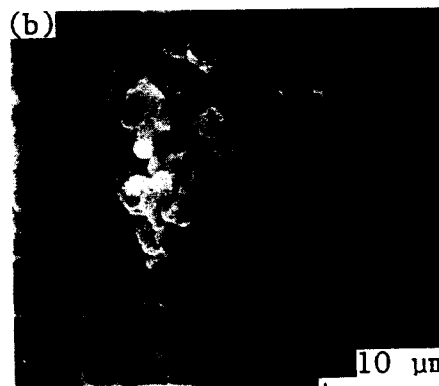
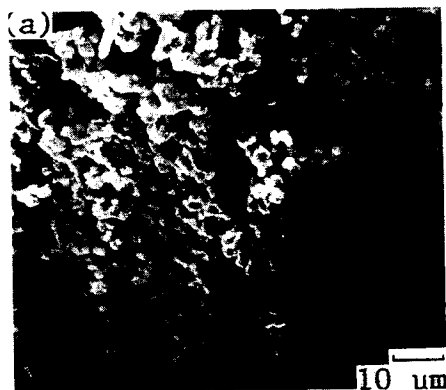


Fig. 4. SEM photographs at two different magnifications of a PES-Ni powder mixture (9.4 vol% or 40 wt% Ni) prior to compression molding.

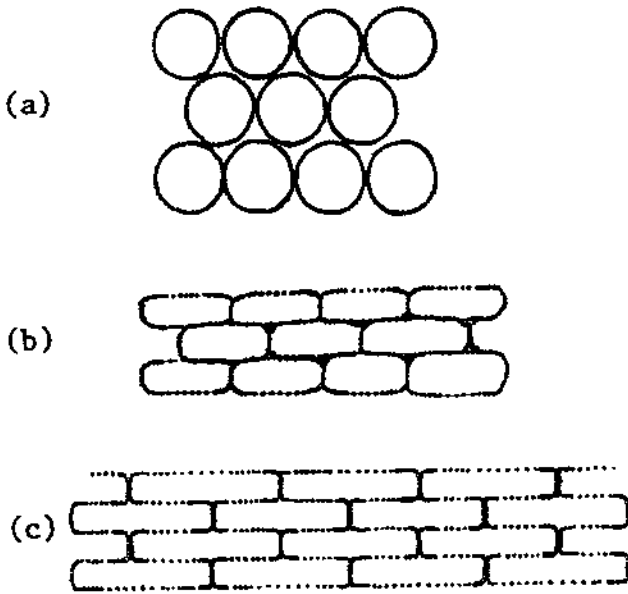


Fig. 5. Schematic illustration of a mixture of small conducting particles and large polymer particles. (a) before compression molding. (b) after compression molding for the case of a polymer with a high viscosity, (c) after compression molding for the case of a polymer with a low viscosity.

above T_g , as shown by DMA. In the composite fabrication, the mixture of polymer and filler was hot pressed above T_g . Prior to heating, the uniform distribution of the filler enhanced percolation. Upon hot pressing, the shape of polyether sulfone particles was greatly changed, thereby disturbing the filler arrangement, whereas the shape of polyimidesiloxane particles changed only slightly, thus maintaining the filler arrangement that was favorable for percolation. Similarly, the effect of the composite fabrication temperature on the electrical properties of PES/Ni particulate composites is attributed to the decrease in viscosity with increasing temperature.

For metal particle-filled polymer composite, two configurations of packing metal particles in a polymer matrix have been employed. They are "random" and "segregated" distributions (5, 6). For the case of a composite fabricated via a slurry of the filler in the liquid polymer, the random distribution applies. Previous works (7-9) reported that the critical volume fraction of the conducting filler increased with increasing viscosity of the polymer in the random distribution case. That is, the electrical resistivity of the metal filled polymer-matrix composite increased with increasing viscosity of the polymer matrix. This is mainly because of the metal-polymer surface tension and interfacial energies, which affect the critical vol-

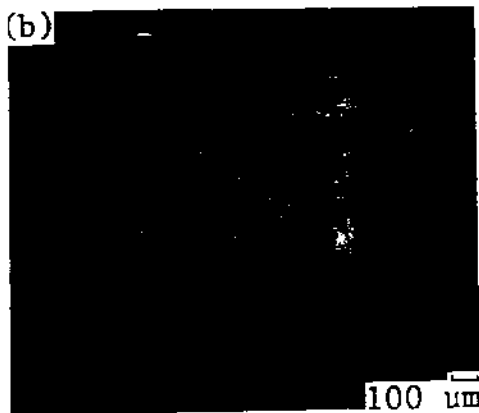
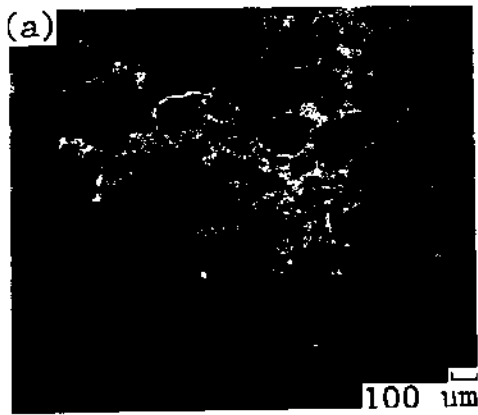


Fig. 6. SEM photographs of polished sections of (a) PISO/Ni and (b) PES/Ni particulate composites.

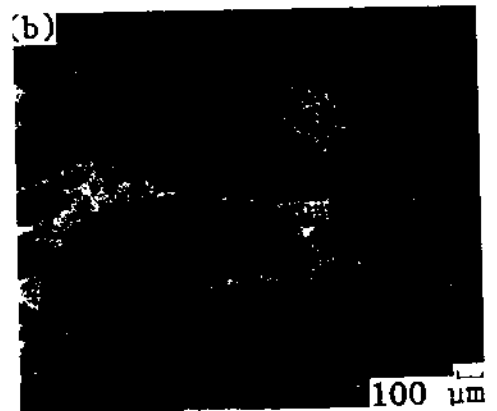


Fig. 7. SEM photographs of polished sections of PES/Ni particulate composites fabricated at (a) 260°C and (b) 330°C.

ume fraction corresponding to the percolation threshold. For the case of a composite fabricated by hot pressing a dry mixture of a metal filler and a polymer powder, as in this investigation, however, the segregated distribution model is followed. In the segregated distribution, network formation is governed by restricting the volume that any metal particle can occupy from the entire field of view to only the interproximal contacts or the interstices of the polymer particles (10). In contrast to the wet mixture mentioned above, a high viscosity helps maintain the percolation arrangement attained by the filler particles. This can be supported by the geometric structure schematically illustrated in Fig. 5b and 5c. It was also indicated by the SEM photographs of Fig. 6 and Fig. 7.

The viscosity of the metal-filled polymer-matrix composite during fabrication can be described as being in either of two categories, namely "local" viscosity and "macroscopic" viscosity. The local viscosity is determined by the polymer matrix, which depends on the temperature only. However, the macroscopic viscosity, the viscosity of the filled polymer, is governed not only by the polymer matrix but also by the filler. It is well known that the viscosity of filled polymers increases rapidly with the filler content. For polyether sulfone and polyimidesiloxane polymers, the local viscosities are 2.1 kPa·s and 57.6 kPa·s at 320°C, respectively, whereas the macroscopic viscosities of the filled polymers (both 40 wt% Ni) are 100 kPa·s and 1400 kPa·s, respectively. The viscosity of the filled polymer was indeed increased by the presence of the filler. However, large differences still exist between the local viscosities of these two neat polymers and between the macroscopic viscosities of these two filled polymers. Therefore, the local viscosity plays a more important role than the macroscopic viscosity in affecting the electrical properties of the composites fabricated by dry mixing and compression molding.

A higher pressure (5.90 MPa) was applied to fabricate PISO/Ni composites than that (4.90 MPa) for PES/Ni composites. If these two polymers had the same viscosity at high temperatures ($>T_g$), the shape of polyimidesiloxane particles would have undergone larger changes than that of polyether sulfone. This would result in better percolation among the nickel particles on the surface of PES particles than those on the surface of polyimidesiloxane particles, and hence a lower electrical resistivity in PES/Ni. However, the electrical resistivity of PISO/Ni was actually lower than that of PES/Ni. Thus, the observed effect is clearly due to the difference in viscosity of the polymers above T_g .

It had been found that a large polymer-to-filler particle size ratio enhanced the electrical continuity in the composite (5, 6). In this work, the ratio of the polymer particle size to the Ni particle size was actually larger for polyether sulfone than polyimidesiloxane, so that percolation should have been enhanced for polyether sulfone composites compared to polyimidesiloxane composites, if the difference in viscosity were absent.

CONCLUSION

The electrical resistivity of Ni-filled polyimidesiloxane was much lower than that of Ni-filled polyether sulfone. The EMI shielding effectiveness of Ni-filled polyimidesiloxane was much higher than that of Ni-filled polyether sulfone. This difference is attributed to the difference in viscosity of the two polymers above T_g . Consistent with this result, the resistivity increased and the shielding effectiveness decreased with increasing compression molding temperature (i.e., decreasing viscosity) for PES/Ni. Therefore, the viscosity of a polymer plays an important role in affecting the electrical properties of a particulate polymer-matrix composite containing an electrically conducting filler.

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