Electromagnetic Interference Shielding Effectiveness and Mechanical Sliding Behavior for Electroless Nickel/Phosphorous–Poly(tetrafluoroethylene) Codeposition on Carbon Fiber/Acrylonitrile–Butadiene–Styrene Composites

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ABSTRACT: Poly(tetrafluoroethylene) (PTFE) powders were mounted on an electroless nickel/phosphorous (Ni/P) film on the surface of a carbon fiber by an electroless codeposition method. This type of carbon fiber filler, denoted FENCF, was then compounded with acrylonitrile–butadiene–styrene (ABS) for use in electromagnetic interference shielding. For the suspension of the PTFE powders, a surfactant was used. Although the adhesion between the electroless Ni/P–PTFE films and the fiber was reduced, the PTFE powders on the surface of FENCF reduced the torque values when compounded into the ABS matrix because of a self-lubricating effect. The two-step FENCF composites exhibited particularly significant advantages. The torque values for the two-step FENCF/ABS composites were about one-half of those for carbon fiber/ABS composites in compounding processes; in addition, the former had an average mean fiber length almost 2.5 times that of the latter. The multiyield phenomena in stress–strain curves of FENCF/ABS composites implied that the PTFE powders mounted on Ni/P films slid during stress–strain action. The electromagnetic interference shielding effectiveness of FENCF/ABS composites did not decrease significantly even though the PTFE powders formed a discontinuous phase on the electroless Ni/P films. The mechanical properties of FENCF composites were enhanced because of the larger fiber length. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1661–1668, 2002

Key words: electromagnetic interference (EMI); polytetrafluoroethylene (PTFE); sliding; electroless nickel; shielding

INTRODUCTION

Plastics have many advantages, such as lightness of weight, low cost, easy construction of complex shapes, and superior design capabilities. Plastics have been widely applied in electrical equipment housings and have replaced nonstructural metal materials. Nevertheless, plastics do not prevent the transmission of electromagnetic waves. For many years, electronic equipment has needed shielding to reduce interference that might abnormally affect their operation and to ensure reliable operation in an electromagnetically polluted en-

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vironment. Many technologies[1,2] have been developed to provide electromagnetic interference (EMI) shielding. These techniques could be categorized into three groups: intrinsic conductive polymers (ICPs), surface plating, and filling conductive materials. Because of their congenital properties, such as brittleness and lack of ease in forming, ICPs usually are used in electrostatic dissipative (ESD) fields or in film applications. The main problem with surface-plating methods is the adhesion between the plating films and substrates. Efficacy might be lost or other problems might be caused when plating films are scraped or peeled off. An important concern with respect to filled conductive materials is the enormous influence of physical and mechanical properties. Many studies have been aimed at this last method.[3–9] Here, we used a conductive filler in the matrix to produce conductive composites, and we chose carbon fiber (CF) to reinforce and offset the mechanical properties of those composites.

Poly(tetrafluoroethylene) (PTFE) is a solid lubricant that retains its mechanical properties over a wide temperature range.[10] It has great stability, extremely high impact strength, and a low friction coefficient. PTFE, therefore, has received much attention and is used as an internal lubricant.[11–15] Because the shear force in the blending processes would seriously break the fibers, we used PTFE powders mounted on electroless nickel/phosphorous (Ni/P) films to protect the fibers by the electroless codeposition method. The PTFE powders on the surfaces of the electroless Ni/P films not only reduced the torque of compounding significantly but also increased the average mean fiber length of fillers during the blending processes because of the self-lubricating effect. The two-step FENCF composites exhibited particularly obvious benefits (FENCF denotes a specific type of CF filler described in the Experimental section). The torque value of the two-step FENCF/acrylonitrile–butadiene–styrene (ABS) composites is just one-half that of the CF/ABS composites in compounding processes. The average mean fiber length was almost 2.5 times that of CF/ABS composites. Furthermore, PTFE powders provided sliding behavior during stress–strain action. The FENCF/ABS and two-step FENCF/ABS composites showed multiyield phenomena that could enhance the elongation of the composites. PTFE powders mounted on an electroless Ni/P matrix formed a discontinuous phase and led to increased fiber resistance. However, the results showed that the EMI shielding effectiveness (SE) did not go down significantly. This may be due to the long fibers forming a network to offset the conductive loss of discontinuity.

EXPERIMENTAL

Materials

The main resin was D-180 ABS pellets manufactured by the Grand Pacific Petrochemical Corp. (Taiwan). The CF conductive filler (yard mode) was T-700SC made by Toray Co. (Japan). To prevent the oxidation of the ABS resin and reduce the shear force in compounding processes, we added 0.5 phr antioxidant (Irganox 1076) and 2.0 phr calcium stearate.

Electroless Deposit

Three types of conductive CF fillers were produced by electroless methods. The first type was denoted ENCF: an ordinary electroless Ni/P film was coated on the surface of the CF. The second filler was coated by codeposited Ni/P–PTFE film and was named FENCF, and the third filler was coated by both electroless Ni/P and Ni/P–PTFE films and was named two-step FENCF. The deposition time for all these fillers was 20 min. The two-step FENCF was deposited by electroless Ni/P for 5 min and then was immediately deposited on electroless codeposited Ni/P–PTFE films for 15 min. The compositions of the electroless Ni/P and Ni/P–PTFE baths are listed in Table I.

Compounding Processes

The ABS pellets were dried in an oven at 80°C for 4 h. After drying, 45 g of ABS pellets, 2 phr calcium stearate, 0.5 phr Irganox 1076, and 20 phr conductive filler (i.e., CF, ENCF, FENCF, or two-step FENCF) were added to a Haake Buchler Rheomix Mixer-600. The blending temperature was set at 220°C. The rotation rate was 20 rpm for 7 min. The variation of the torque during the blend processes was recorded.

Compression Molding

The composites obtained from the compounding processes were placed in the cores and were molded to prepare a variety of specimens for testing. The hot-compression-molded processes were

Table I Compositions of Electroless Ni/P and Ni/P–PTFE Baths

Composition	ENCF Electroless Bath	FENCF Electroless Bath	Two-Step FENCF Electroless Bath	
			Bath I	Bath II
$NiSO_4 \cdot 6H_2O$ (mol/L)	0.1	0.1		0.1
$NiCl_2 \cdot 6H_2O$ (mol/L)			0.125	
CH_3COONa (mol/L)	0.1	0.1		0.1
$Na_3C_6H_5O_7 \cdot 2H_2O$ (mol/L)			0.2	
$C_4H_6O_5$ (mol/L)	0.1	0.1		0.1
$NaH_2PO_2 \cdot H_2O$ (mol/L)	0.3	0.3	0.1	0.3
NH_4Cl (mol/L)			1	
pH[a]	5	5	9	5
Temperature (°C)	60	60	75	60
PTFE powder (g/L)		1		1
Surfactant[b] (ppm)		300		300
Deposited time (min)	20	20	5	15

[a] pH adjusted with NaOH.
[b] Surfactant: $C_{215}H_{424}O_{101}$.

kept at 220°C and were subjected to three step pressures—0, 4.9, and 9.8 MPa—applied at 5, 3, and 3 min, respectively. Then, the specimens were cooled down with water.

Testing of EMI SE and Mechanical Properties

The flanged circular coaxial transmission line method, ASTM Standard D 4935-99, was used to test the EMI SE. The test frequency was between 30 and 1000 MHz,[16] although the holder was a modified evaluator, with a dynamic test frequency of up to 1.5 GHz. The SE was obtained by subtraction of the background value. Following ASTM Standard D 638-99, we tested the mechanical properties for these composites.

RESULTS AND DISCUSSION

Morphology of FENCF and Energy Dispersive Spectrometry (EDS)

T-700SC CF had a very smooth surface [Fig. 1(a)]. After treatment by electroless depositing; a uniform Ni/P film was coated on its surface [Fig. 1(b)]. Because PTFE is a hydrophobic material, it is hard to disperse and suspend well in an aqueous solution. To overcome this problem, we used a surfactant. Figure 1(c,d) shows that PTFE powders, the mean diameter of which was less than 0.2 μm, were mounted on electroless Ni/P films. However, because of the surfactant, the adhesion between the electroless Ni/P–PTFE films and fiber declined. Figure 2 shows the results of EDS component analysis. The weight percentages of Ni, P, and F on CF are listed in Table II. They support the idea that the PTFE powders had mounted uniformly onto the ENCF surface successfully. Because of the lubricative effect of PTFE, the torque and average mean fiber length of fillers in the composites showed remarkable changes.

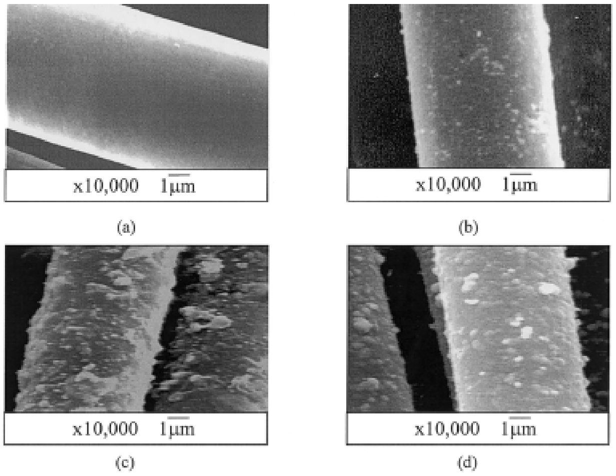
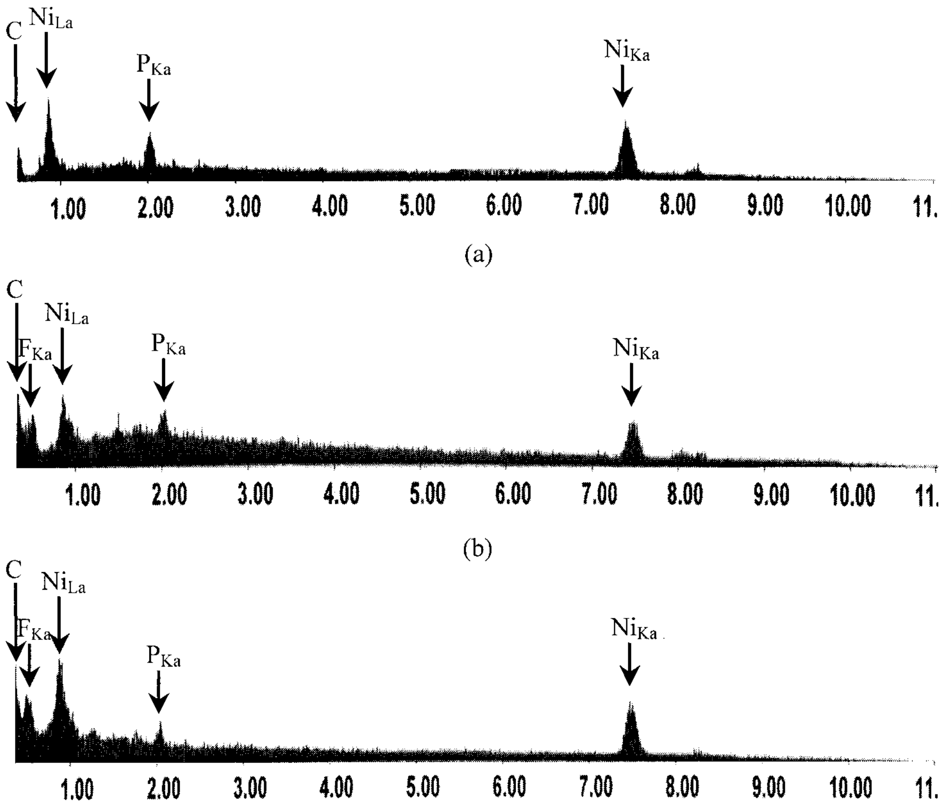


Figure 1 SEM micrographs of various CFs: (a) pure CF, (b) ENCF, (c) FENCF, and (d) two-step FENCF.



(a)

(b)

(c)

Figure 2 EDS spectra of components Ni, P, and F on various CFs: (a) ENCF, (b) FENCF, and (c) two-step FENCF

Influence on the Torque of Compounding Processes

Whether or not the fillers dispersed in the composites uniformly was a key factor. In our previous research,[3] the critical fiber length needed to be greater than 200 μm; otherwise, it would lose the strength of the composites. During compounding, the ABS pellets, antioxidants, and additives melted in the mixer completely, and then the conductive fillers were added. Although the mixer provided shear force to distribute the fillers well, it also broke the fibers significantly. This implied that the higher the torque was during the blending process, the greater the damage status was of the fibers. Reducing the friction between the fibers and matrix was one feasible solution. Therefore, the electroless Ni/P method is an attractive and simple technique. It has many advantages, such as uniform deposition, good wear and abrasion resistance, high hardness, and excellent ductility, and it has been widely applied in many fields. In addition, it also provides metallic materials for conducting electrons and decreases friction a little. However, PTFE is a good solid lubricant. It possesses a low friction coefficient. Using the proper particles in an electroless solution such as PTFE and codepositing a metallic Ni/P matrix and PTFE particles on fibers would increase the conductivity and reduce the friction of fibers. Figure 3 shows the variation of torque during compounding processes. The torque values of FENCF series composites were lower than

Table II Proportion of Components Ni, P, and F for Various Electroless Ni/P–PTFE Baths

	Ni (wt %)	P (wt %)	F (wt %)
ENCF	80.13	19.87	—
FENCF	78.52	18.42	3.06
Two-step FENCF	85.15	12.26	2.59

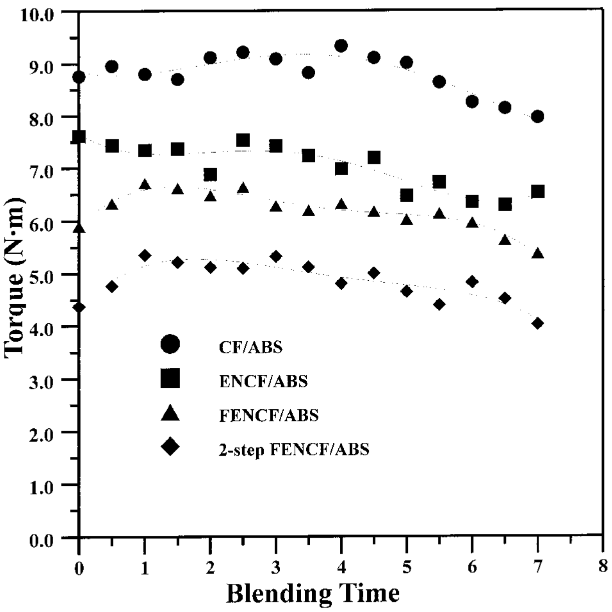


Figure 3 Torque values of various CF-type composites: CF/ABS, ENCF/ABS, FENCF/ABS, and two-step FENCF/ABS.

those of CF-type composites. When fillers were exerted with an external stress, such as the shearing force in the compounding processes, the PTFE powders, which were mounted on the electroless Ni/P films, overcame it via a self-lubricating effect. They offered CFs gliding in the molten ABS resin. Therefore, the torque decreased significantly. The torque of two-step FENCF/ABS composites, in particular, was just one-half the torque of the CF/ABS composites in compounding processes (Fig. 3).

Average Fiber Length of the Fillers in the Composites

After blending, the composites were dissolved with an acetone solvent, and the fillers were extracted and percolated from the solution with a filter. The fibers were observed with scanning electron microscopy (SEM; Fig. 4). The mean fiber length of the fillers was calculated, and statistics were inferred. Many researchers[5,7,9] have proposed that the high aspect ratio of fibers is the main factor affecting the conductivity of fiber-filled composites. The benefits of long-fiber-reinforced composites are the higher material performance on impact and flexural strength compared with those of short-fiber-reinforced composites.[17] The long fibers more easily formed networks in the composites. Because the PTFE powders in the Ni/P matrix assisted in the lubrication of the fillers and provided them with a sleek surface, the formidable shearing stresses of the mixer reduced the force to damage the fillers; the mean fiber length of two-step FENCF/ABS composites, therefore, was almost 2.5 times those of CF/ABS composites (see Fig. 5).

Mechanical Properties and Stress–Strain Behaviors of the Composites

ABS is a tough material that shows a yield point and neck behavior in a stress–strain test. With added reinforced fibers, the tensile strength of ABS composites was strengthened, the elongation of the composites was reduced, and the composites became brittle, at which point the yield point disappeared (Fig. 6). Nevertheless, the composites with FENCF series fillers showed a unique multiyield phenomenon. It likely resulted from the effect of the fillers coated with lower surface-energy resins. The lower surface energy fillers gave poor mechanical properties because of the weak interactions at the interface.[18] The composites broke when the tensile stress was increased gradually. If the bonding status was good enough, the fillers against the main stress and the com-

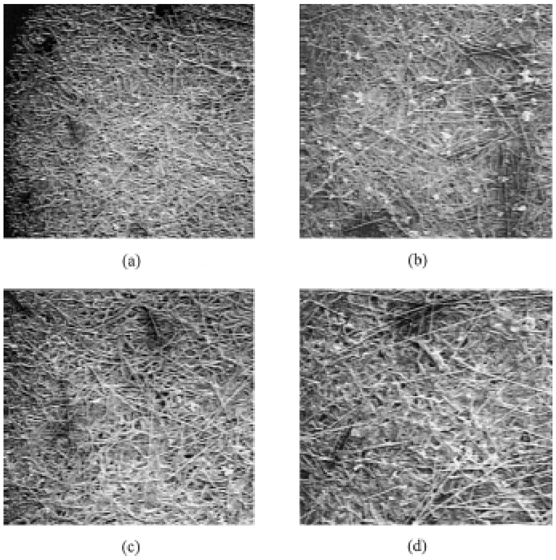


Figure 4 SEM micrographs of various fibers extracted from various composites: (a) CF/ABS, (b) ENCF/ABS, (c) FENCF/ABS, and (d) two-step FENCF/ABS.

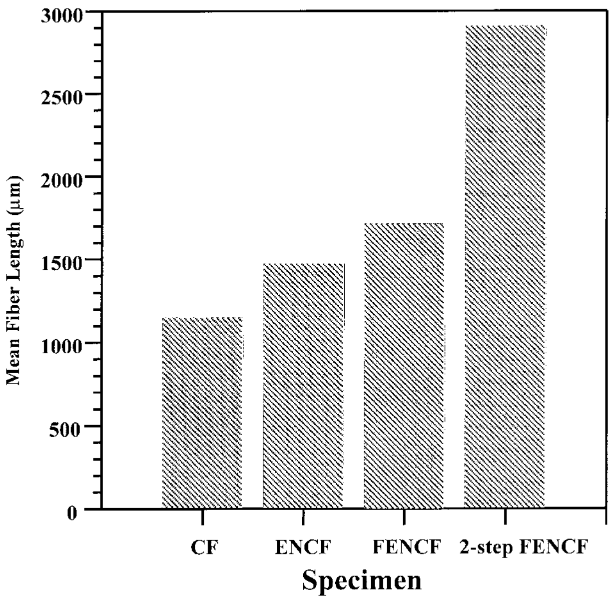


Figure 5 Average fiber lengths of various CF-type/ABS composites.

posites achieved a reinforcement effect. On the contrary, the CFs broke and were dragged out from the matrix. The PTFE powders on the ENCF films caused sliding behavior and might have broken pieces (Fig. 7). This macroscopic behavior explains the unique multiyield phenomena during the stress–strain testing (Fig. 6) for all the specimens of the FENCF series composites. It also brings the elongations to absorb the mechanical energy.

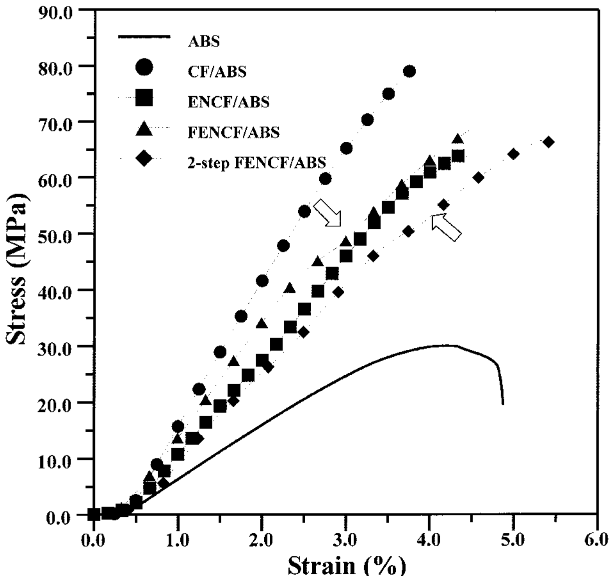


Figure 6 Tensile strengths and elongations for various CF-type/ABS composites.

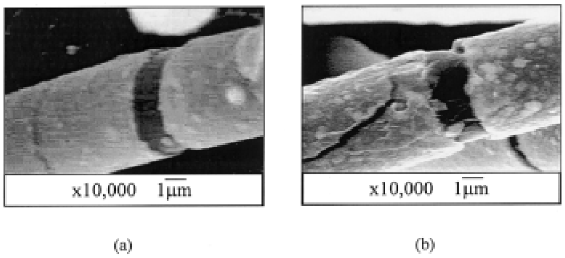


Figure 7 SEM micrographs of CF/ABS composites: (a) FENCF/ABS and (b) two-step FENCF/ABS.

Influence of the PTFE Particles on the EMI Shielding

When electrons or electromagnetic waves travel in a material or a composite, a continuous metal path provides a good conductive path. Because the PTFE powders were mounted onto Ni/P films, there was a discontinuous phase in the electroless Ni/P films, and the transport of electrons was resisted. Lu et al.[7] showed the relationship between the resistivity and EMI SE. When the re-

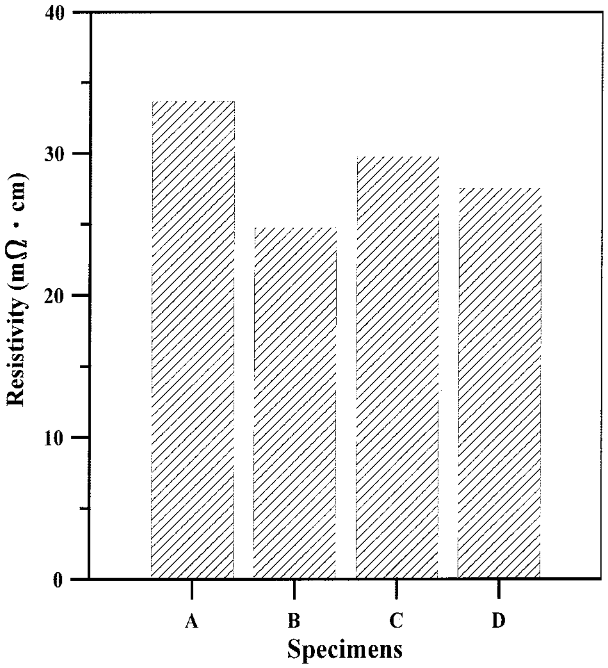


Figure 8 Resistivities of various CF-type/ABS composites: (A) pure CF, (B) ENCF, (C) FENCF, and (D) two-step FENCF.

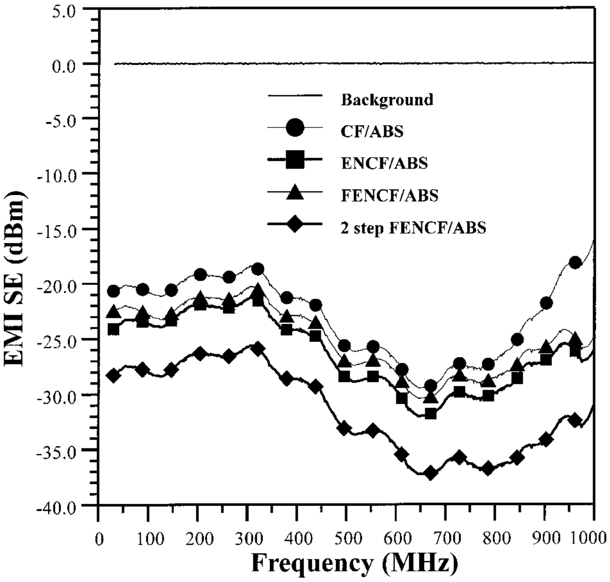


Figure 9 EMI SE of various CF-type/ABS composites.

sistance of a composite decreased, the EMI SE of the composite increased. The different volume resistances of the composites are compared in Figure 8. Because of PTFE, the volume resistance of the composites with FENCF and two-step FENCF was larger than that of the ENCF. Despite this disadvantage, PTFE particles could provide a filler with suitable protection, reducing friction and preventing breakage by shear stress. It is well known that long fibers can help conductive composites to form networks and to reach transmitted electromagnetic waves. Therefore, although there were discontinuous phases of PTFE, the EMI SE was not significantly reduced (Fig. 9). Furthermore, the two-step FENCF/ABS composites increased the EMI SE because of the long-fiber-formed network structure in the composite. Sherman et al.[19] showed that there are three physical processes—percolation, quantum mechanical tunneling, and thermal expansion—for the electron-transport processes in conductor-filled polymers. Arcioni et al.[20] indicated that parallel conducting planes would trap the electromagnetic energy. This is a phenomenon of electromagnetic coupling. When electromagnetic coupling occurs, the frequency response is a δ function of the distance between the parallel planes. In this investigation, the composites contained numerous conductive fibers embedded in the matrix. Because the fillers were probably parallel or perpendicular or linked to one another, they formed networks to transmit electromagnetic waves. The fibers in the matrix formed a trap to restrict EMI waves. Because the parallel chinks between fibers could change, the δ function of electromagnetic coupling was broadened. The results of EMI SE showed an apparent notch between 600 and 700 MHz (Fig. 9).

CONCLUSIONS

With their self-lubricating effect, PTFE powders not only reduced the torque but also increased the average mean fiber length of fillers during the blending processes. The torque of two-step FENCF/ABS composites decreased by half in comparison with the CF/ABS composite; moreover, the average mean fiber length of the two-step FENCF/ABS composites was almost 2.5 times longer than those of the CF/ABS composites. Because PTFE powders on the ENCF films offered lubrication effectiveness, they provided sliding behavior during stress–strain action and caused macroscopic multiyield phenomena. Therefore, the elongation and energy absorption increased effectively. Because PTFE powders were mounded and formed discontinuous second phases on the ENCF films, they were disadvantageous for electron transmission. However, PTFE powders provided suitable protection for the fillers, resulting in long fibers and increased network linking. Therefore, the EMI SE of the composites was increased markedly.

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REFERENCES

1. Huang, J.-C. Adv Polym Technol 1995, 14, 137.
2. Mallory, G. O.; Hajdu, J. B. Electroless Plating: Fundamental and Applications; American Electroplaters and Surface Finishers Society: Orlando, FL, 1990.
3. Huang, C.-Y.; Pai, J.-F. J Appl Polym Sci 1997, 63, 115.
4. Huang, C.-Y.; Pai, J.-F. Eur Polym J 1998, 34, 261.
5. Huang, C.-Y.; Chiou, T.-W. Eur Polym J 1998, 34, 37.
6. Huang, C.-Y.; Wu, C.-C. Eur Polym J 2000, 36, 2729.

7. Lu, G.; Li, X.; Jiang, H. Compos Sci Technol 1996, 56, 193.
8. Fu, X.; Chung, D. D. L. Cem Concr Res 1996, 26, 1467.
9. Jana, P. B.; Mallick, A. K.; De, S. K. J Mater Sci 1993, 28, 2097.
10. Henry, J. Metal Finishing, Oct., 15, 1990.
11. Chiang, W.-Y.; Huang, C.-Y. J Chin I Ch E 1991, 22, 291.
12. Chiang, W.-Y.; Huang, C.-Y. Eur Polym J 1992, 28, 583.
13. Chiang, W.-Y.; Huang, C.-Y. Angew Makromol Chem 1992, 196, 21.
14. Chiang, W.-Y.; Huang, C.-Y. J Appl Polym Sci 1993, 47, 577.
15. Huang, C.-Y.; Chiang, W.-Y. Eur Polym J 1993, 29, 834.
16. Wilson, P. F.; Ma, M. T. IEEE Trans Electromagn Compact 1988, 30, 239.
17. Rosenow, M. W. K.; Bell, J. A. E. Mater Process Afford: Keys Future 1998, 43, 854.
18. Tian, J.; Xue, Q. Tuliao Gongye 1997, 4, 16.
19. Sherman, R. D.; Middleman, L. M.; Jacobs, S. M. Polym Eng Sci 1983, 23, 36.
20. Arcioni, P.; Bressan, M.; Broggi, F.; Conciauro, G.; Perregrini, L.; Pierini, P. Nucl Instrum Methods Phys Res Sect A 1995, 358, 108.