

Studies on Processing Parameters and Thermal Stability of ENCF/ABS Composites for EMI Shielding

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SYNOPSIS

Electroless nickel coated carbon fibers (ENCF) were blended with acrylonitrile-butadiene-styrene (ABS) to prepare composites for electromagnetic interference (EMI) shielding. The effects of processing parameters, such as additives, temperature, and fiber loading amount, on EMI shielding effectiveness (SE) were researched. The thermal stability of EMI SE of ENCF/ABS composites was tested by heat treating composites in a drying oven at 60°C, and SE was measured at an interval of one week to consider the degradation of SE. The best SE of ENCF/ABS composites could be reached was 44 dB at optimum processing parameters. The thermal stability of ENCF/ABS composites for EMI shielding was steady without obvious degradation after 60°C heat treatment for five weeks. © 1997 John Wiley & Sons, Inc.

INTRODUCTION

Plastics, which have advantages of lighter weight, lower cost, and design freedom, are used widely to house electronic appliances. Because of the electrically insulated properties of plastics, they are transparent to electromagnetic radiation. It is very important to develop composite polymeric materials that will have good and nondegrading electromagnetic interference (EMI) performance over time.

The most economical method to enhance electrical conductivity of plastic is the incorporation of conductive fillers into the polymer matrix.¹ Nickel coated carbon fibers (NCF), which combine the high strength, low weight, high aspect ratio, and processibility of a fiber core with the conductivity and corrosion resistance of a plated nickel skin, are the best conductive filler for EMI shielding.^{2,3} In earlier work in our laboratory, Wu⁴ found that the EMI shielding effectiveness (SE) of NCF/ABS

composites was excellent (about 47 dB). However, the EMI shielding effectiveness of this composites degraded during thermal treatment at 60°C in air.

It was reported that the resistance to oxidation and corrosion of Ni-P (nickel-phosphorus) coating deposited by electroless nickel (EN) plating is better than that of nickel coating deposited by electrolytic nickel plating.^{5,6} In our previous work, Ni-P coated fibers were prepared by electroless nickel plating at different depositing conditions, and electroless nickel coated carbon fibers (ENCF) instead of NCF were blended with ABS to produce composites for EMI shielding to find the best conditions of electroless nickel plating on carbon fibers for EMI shielding effectiveness of composites.⁷ In this work, effects of processing parameters on SE and the thermal stability of SE of ENCF/ABS composites were studied. Furthermore, the authors tested the thermal stability of EMI SE of NCF/ABS composites in contrast with that of ENCF/ABS composites.

EXPERIMENTAL

Electroless Nickel Plating on the Carbon Fibers

Polyurethane (PU)-coated nickel plated carbon fibers (NCF) used in this study is MC-HTA-C3-

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Table I Formulations of Electroless Nickel Plating Baths

Nickel chloride (g/L)	30
Sodium hypophosphites (g/L)	10
Sodium citrate (g/L)	65
Ammonium chloride (g/L)	50
pH (with ammonia)	8, 9, 10
Temperature (°C)	70, 75, 80, 85, 90
Fiber workload (g/L)	2, 4, 6, 8, 10

US made by Japan Toho Rayon Co. Ltd. Carbon fibers used in this study are T300C CF & T700SC CF made by Japan Toray Co. Ltd. The electroless Ni-P alloy films were deposited on the carbon fibers, which had been catalyzed. A two-step pretreatment was used for catalyzing the carbon fibers. The fibers were immersed in the solution of sensitizer (20 g/L $\text{SnCl}_2 \cdot \text{H}_2\text{O}$ and 40 ml/L HCl) for 10 min, then were immersed in the solution of activator (0.25 g/L PdCl & 2.5 ml/L HCl) for 5 min. Ultrasonic vibrations were applied during the catalyzation treatment to facilitate uniform activation throughout the entire surface of the carbon fibers. After rinsing, electroless nickel films were then deposited from solutions at various workloads, pH, and temperatures of plating bath with air agitation. The chemical reagents were EP grade from Nippon Reagent Co. Ltd. The formulation of electroless nickel solutions was listed in Table I.

Structure Observation

The structure of Ni-P deposits were determined by X-ray diffractometry. The X-ray diffraction (XRD) pattern of Ni-P deposits was recorded at room temperature on a Siemens X-ray diffractometer with Cu K_α radiation. The step time and the step size were 0.8 s and 0.03 degrees.

SEM Micrograph

The morphology, adhesion of EN deposits on carbon fibers, and length distributions of carbon fibers which were determined after extraction from the blends by tetrahydrofuran (THF). The Ni-P coated fibers were coated with gold and viewed with a scanning electron microscope. For examination of phase morphology, the blends were immersed in liquid nitrogen and fractured, and the fracture surfaces were coated with gold and

viewed with SEM. The models of SEM were HITACH S-800 and JOE JSM-6300.

Compounding

Acrylonitrile-butadiene-styrene (ABS), as stabilized pellets (general purpose grade 1000), is made by Taiwan Talta Chemical Co. Ltd. ABS pellets were dried in a heating oven for 2 h for 80°C. ENCF and ABS pellets with lubricant (calcium stearate) and antioxidants (TNPP & Irganox 1076) were blended in a Brabender Platsticorder Torque Rheometer, PLE-330, at 200 or 220°C, with a screw speed of 20 rpm.

Compression Molding

After being compounding, a batch of composites was hot-compression-molded and four step pressures, 0, 4.9, 9.8, and 14.7 MPa, were applied for 6, 2, 2, and 2 min. They were cooled by water at the rate of 40°C/min until the temperature fell below 100°C.

EMI Shielding Effectiveness

The SE value was measured by coaxial transmission line test method specified by ASTM ES-7-83. The SE was obtained by comparing the signals with and without the shield and measured in the range from 30 to 1000 MHz, in which the measurement limit for this equipment was 50 dB. The detail measurement method and EMI SE theory had been described by Chiang and Chiang.³

Heat Treatment of Ni-P Coated Fibers

The as-plated carbon fibers were heated in a nitrogen atmosphere at 400 or 600°C for one hour or in air at 350°C for two hours to vary the structure of Ni-P alloy and study the effects of structure on the thermal stability of composites for EMI shielding.

Heat Treatment of Composites

To examine the thermal stability of ENCF/ABS composites for EMI shielding effectiveness, each sample was heated in a drying oven at 60°C in air, and SE was measured at an interval of one week.

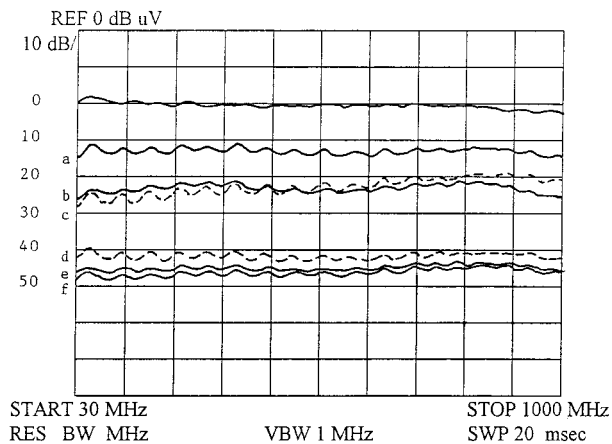


Figure 1 The effect of additives on SE of NCF (30 phr)/ABS and ENCF (30 phr)/ABS composites blending at 20°C: (a) NCF/ABS without additives, (b) NCF/ABS + Oxi., (c) ENCF/ABS without additives, (d) ENCF/ABS + Oxi. + Lub., (e) NCF/ABS + Lub., (f) NCF/ABS + Oxi. + Lub.

RESULTS AND DISCUSSION

Effects of Additives (Lubricant and Antioxidant) on SE

Figure 1 shows the EMI shielding effectiveness spectrum of ABS filled with NCF and ENCF processed with or without lubricant (Lub.) and/or antioxidant (Oxi.). The solid lines refer to NCF/ABS composite, and the dashed lines refer to ENCF/ABS composites. It was found that lubricant has an effective influence in SE of composites (compare a and e), and the antioxidant has a little influence in SE of composites (compare a and b). Adding lubricant and antioxidant simultaneously could effect the shielding effectiveness.

Because lubricants are additives, which facilitate the processing of plastics by improving flow properties and reducing the adherence of the melt to machine parts,⁸ the fiber length of composites with lubricant was longer, as shown in Figure 2. Many filler dispersion aids also function by serving as internal lubricants, promoting polymer of flow in the vicinity of the filler particle. Calcium stearate is the most useful dispersion aid.⁹ The adding of lubricants, such as calcium stearate, not only avoids breakage of fibers by reducing the viscosity of polymer but also improves dispersion of fibers. Therefore, composites with lubricant achieve outstanding electroconductivity and SE by forming a more conductive network. It is generally accepted that polymer degrade by a free radi-

cal mechanism. Most polymers are subject to attack by oxygen from air during processing. The addition of antioxidants to minimize degradation of polymer during processing could also prevent the free radical from attacking nickel coatings on fibers. Therefore, the SE of composites could be enhanced slightly by adding antioxidant. On the other hand, the fiber length of composites could not be increased effectively by adding antioxidant (Fig. 2). For this reason, the SE of composites slightly increased by only adding antioxidants into composites. The best SE of composites can be obtained by adding both lubricant and antioxidant.

From Figure 1, of the composites possessing lubricant and antioxidant, the SE of the ABS/NCF composite is better than that of ENCF/ABS composite. Of the SE of composites without additives, the SE of ENCF/ABS is better than that of NCF/ABS. The SE of the ENCF/ABS composite without additives is equal to that of the NCF/ABS composite with antioxidant. It was proposed that the resistance to oxidation of ENCF is better than that of NCF.

Effects of Processing Temperature on SE

Melt polymer blending at higher temperature generally allows use of lower torque than blending

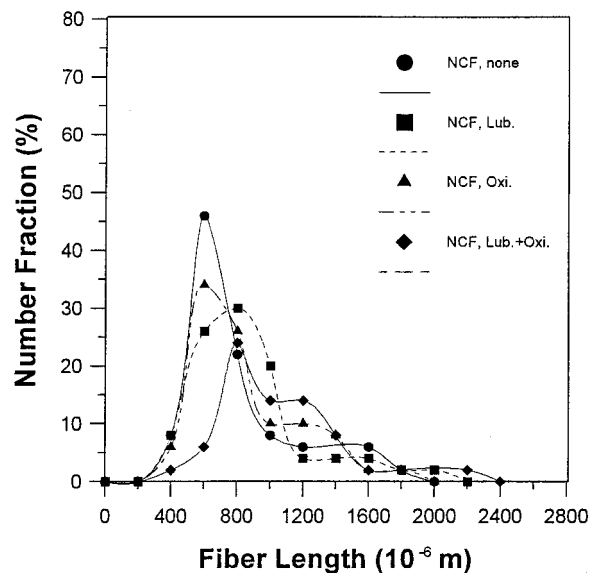


Figure 2 The fiber length distributions of NCF (30 phr)/ABS composites blending at 220°C with and without additives.

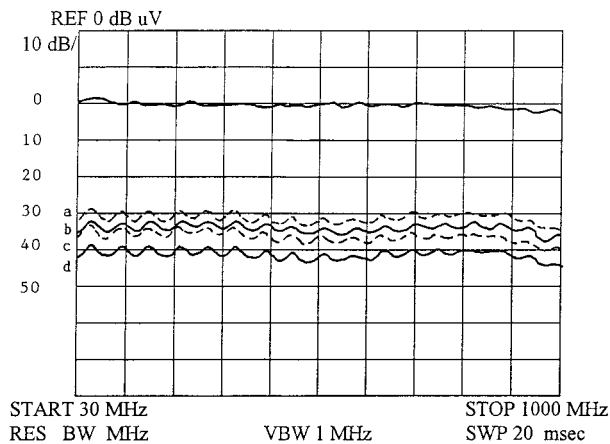
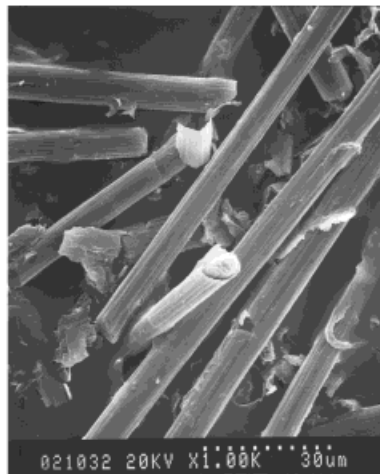


Figure 3 The effect of processing temperature on SE of ENCF (30 phr)/ABS composites: (a) ENCF(T300C)/ABS blending at 220°C, (b) ENCF(T700SC)/ABS blending at 200°C, (c) ENCF(T700SC)/ABS blending at 220°C, (d) ENCF(T300C)/ABS blending at 200°C.

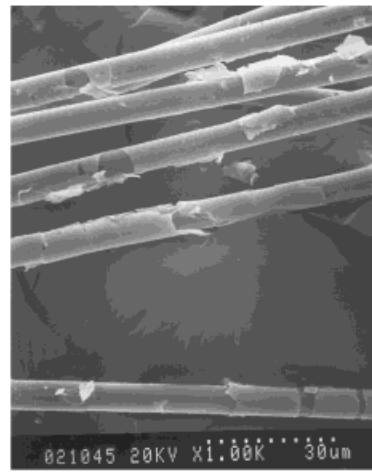
at lower temperature when other processing parameters have been maintained at a constant state. Thus, blending at high temperature could reduce the shear stress and prevent fibers from being broken. This permits the conductive network to form and results in increasing the SE of composites.

In this study, there is another element to be considered simultaneously besides the effect of processing temperature on SE of composites. This element is the type of fiber. In our previous investigation, the adhesion of EN coating on T300C

fibers is better than that on T700SC fibers.⁷ The SE of composites, which incorporated 30 phr ENCF blending at 220°C (with torque 8 ~ 12 Nm/Kpm) and 200°C (with torque 14 ~ 15 Nm/Kpm), is shown in Figure 3. From the results, the SE of ENCF(T700SC)/ABS composites blending at 220°C is higher than that from blending at 200°C. However, the SE of ENCF (T300C)/ABS composites blending at 200°C is higher than that from blending at 220°C. This unusual phenomenon was attributed to the good adhesion between EN deposits and T300C fibers and the good dispersion of fibers at 200°C processing temperature. The good adhesion of EN coating on T300C fibers eliminated stripping of EN coating from fibers [Fig. 4(a)] and avoided reduction in the number of conduction paths. Due to high torque at low processing temperatures, the dispersion of ENCF within ABS is better. Therefore, the ENCF (T300C)/ABS composite blending at 200°C has a very good SE even though the fiber might be broken by higher shear stress. While the adhesion between EN coating and T700SC fiber is poor [Fig. 4(b)], the SE of ENCF(T700SC)/ABS composites blending at 220°C would be better than that blending at 200°C due to higher fiber length (Fig. 5) and less delamination of EN deposit by lower shear stress. Therefore, high processing temperature is preferred for ENCF (T700SC) blending with ABS, but low processing temperature is preferred for ENCF (T300C).



(a)



(b)

Figure 4 The surface morphology of ENCF of ENCF/ABS composites after blending at 200°C: (a) ENCF(T300C), (b) ENCF(T700SC).

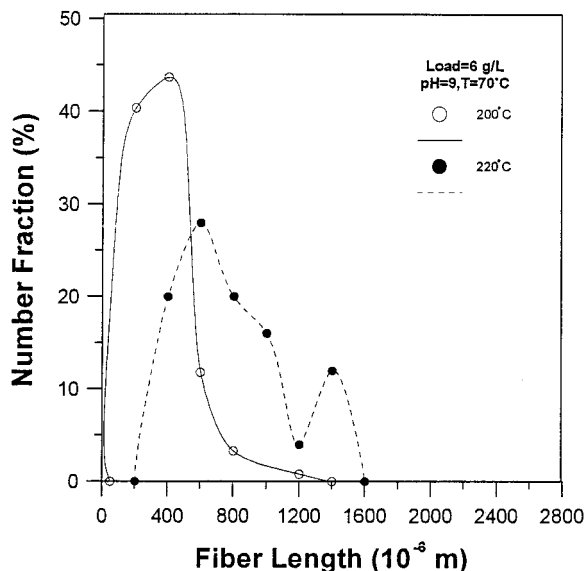


Figure 5 The fiber length distributions of ENCF (30 phr)/ABS composites blending at 200 and 220°C.

Effects of Fiber Loading Amounts

The SE of composites that contain 20 phr (parts per hundred of resin) and 30 phr ENCF (T700SC) are shown in Figure 6. It was found that the SE of composite with a loading of 30 phr ENCF is only slightly better than that of a loading of 20 phr ENCF at low workload (2 g/L) during plating and that there is a greater difference in the SE of composites between 30 and 20 phr ENCF loading

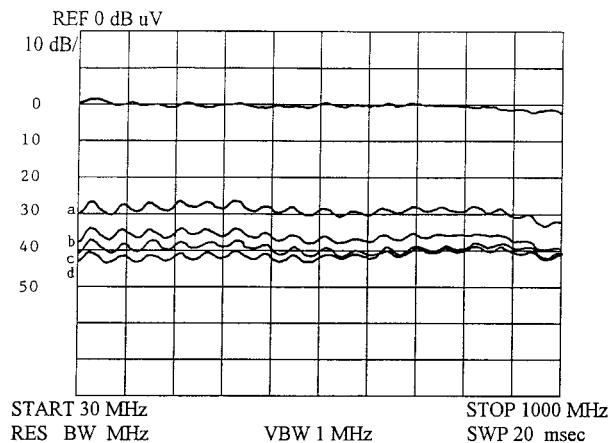


Figure 6 The effect of different loadings on SE of ENCF/ABS composites blending at 220°C: (a) ENCF (6 g/L, 20 phr)/ABS, (b) ENCF (6 g/L, 30 phr)/ABS, (c) ENCF (2 g/L, 20 phr)/ABS, (d) ENCF (2 g/L, 30 phr)/ABS.

Table II A Contrast of Weight Percent With Volume Percent at Different Workloads

	30 phr	20 phr
2 g/L	10.0 vol %	7.0 vol %
4 g/L	11.4 vol %	8.0 vol %
6 g/L	12.1 vol %	8.4 vol %

at high workload (6 g/L) as plating. Table II lists a contrast of weight percent (phr) with volume percent (vol %) of ENCF content of composites from different workloads. The EN coated fibers at high workload increased 3.7 vol %, but that at low workload increased 3 vol % with increasing 10 phr fiber content, respectively. Thus, the increased SE of composite contributes by loading additional 10 phr ENCF (6 g/L) more than that contributed by loading 10 phr ENCF (2 g/L) when the fiber loading amounts of composites increased.

The fiber length of loading 20 phr ENCF at low workload (2 g/L) is very long (Fig. 7). This would be very helpful to the SE of composites and reduce the difference in SE of composites between loading 30 and 20 phr ENCF. In addition, the EMI shielding effectiveness of composites usually increases by increasing the fiber loading amount, but it has a limit of SE which will not increase by increasing the fiber loading amount. It suggests

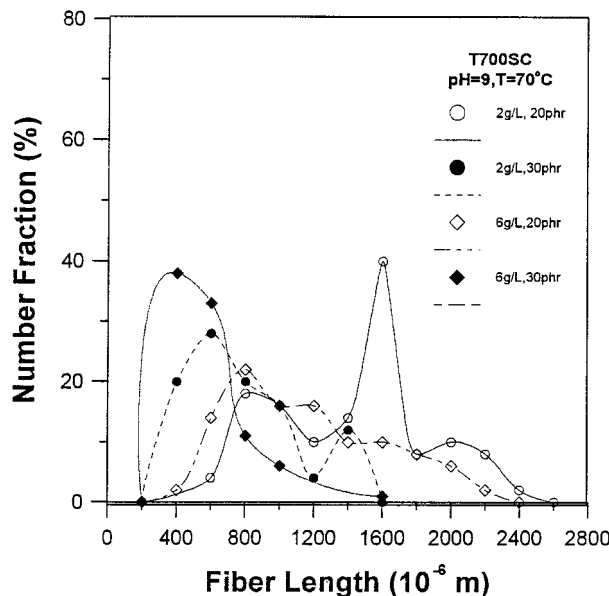


Figure 7 The fiber lengths distributions of ENCF (20 phr)/ABS and ENCF (30 phr)/ABS composites blending at 220°C.

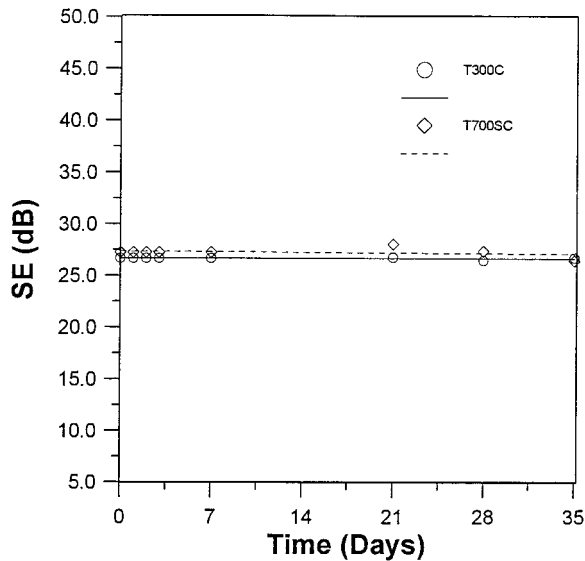


Figure 8 SE of CF (30 phr)/ABS composites degrading with heating time at 30 MHz.

that loading 20 phr ENCF (2 g/L) is enough for EMI shielding since higher loading (above 20 phr) could only enhance shielding effectiveness slightly.

Thermal Stability of EMI SE of ENCF/ABS Composites

According to the reports of Bigg,^{10,11} it was found that thermal conditions, particularly temperature cycling, have an adverse affect on metal-filled composites in a low temperature polymer such as ABS. Our investigation tallies with those results. Figure 8 shows the SE of CF (uncoated)/ABS composites after heat treatment. It shows that the SE of composites are not affected by heat treatment because CF/ABS composites are not metal-filled composites. Figure 9 is the SE of ENCF/ABS or NCF/ABS composites with varying heating time. There is a trend that the SE of composites decreased slowly with increasing heating time. The causes of this decrease may be due to different expansion of the fiber and polymer, or chemical reaction. It has been reported that the electrical conductivity of conductive filler-filled polymers is caused by the presence of a continuous network of the conductive filler within the polymer matrix. Any increase in the distance between adjacent fibers has a significant effect on the overall conductivity of the composites because the ability of electrons to hop or tunnel across a physical gap decreases exponentially with in-

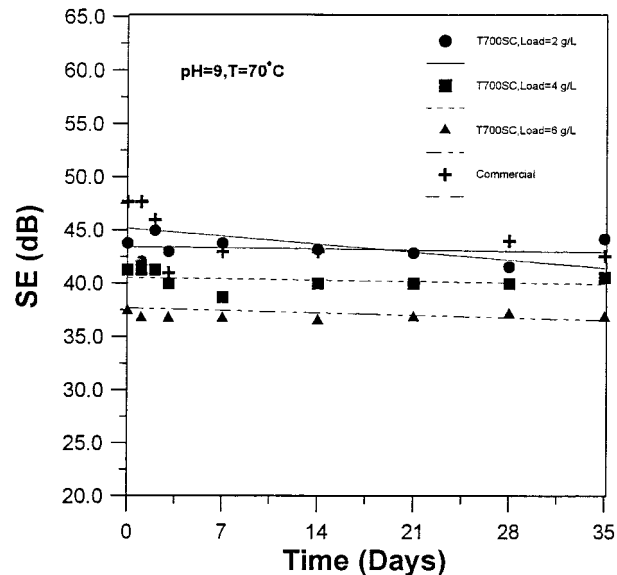


Figure 9 SE of ENCF (T700SC, 30 phr)/ABS composites degrading with heating time at 30 MHz for different workloads of plating bath.

creasing distance between adjacent conductive fibers. During heat treatment, different expansion between fiber and polymer would reduce EMI SE due to a decrease of the conductivity of composites. Chemicals can also affect the interparticle spacing in a filler-filled composite. When bonded, the fiber reinforced composite underwent heat treatment, low viscosity liquids readily wicked along the fiber-polymer interface. The wicking

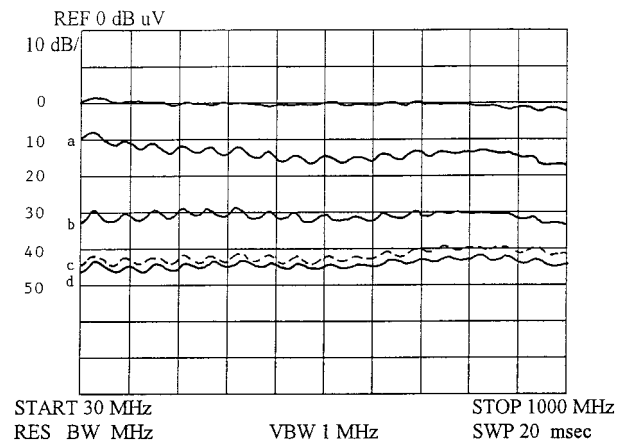
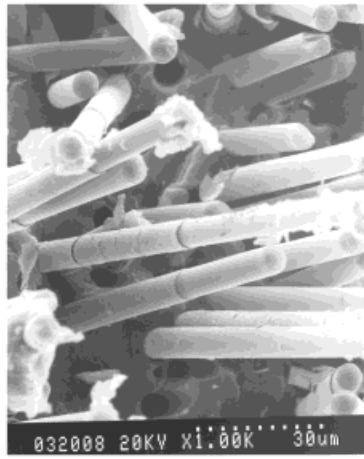
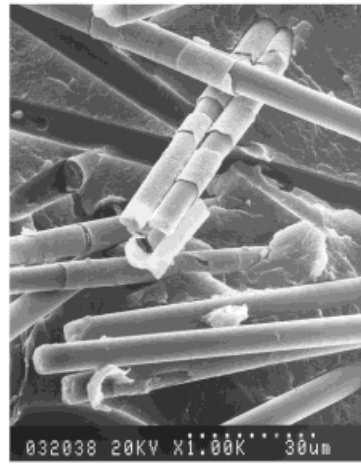


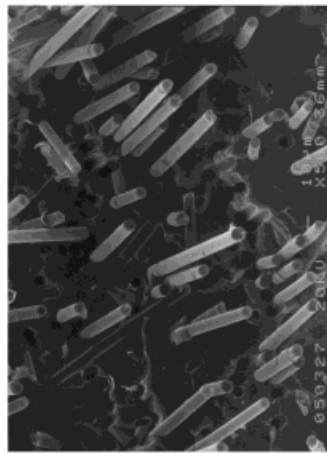
Figure 10 The effect of heat treatment of ENCF (30 phr)/ABS composites blending at 220°C: (a) ENCF (350°C, 2 h, air)/ABS; (b) ENCF (400°C, 1 hr, N₂)/ABS, (c) ENCF/ABS, (d) ENCF (600°C, 1 hr, N₂)/ABS.



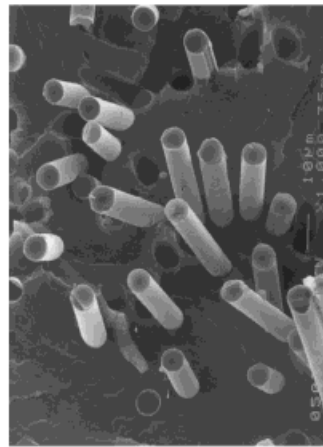
(a)



(b)



(c)



(d)

Figure 11 The fracture surface morphology of ENCF (30 phr)/ABS composites blending at 220°C vary with heat treatment of ENCF: (a) no heat treatment, (b) 350°C, 2 h, air, (c) 400°C, 1 hr, N₂, (d) 600°C, 1 hr, N₂.

chemical can physically separate the polymer from the fiber to provide more room for the fibers to move in response to thermal stress, or it may react with either the fiber. If it reacts with the fibers, it may render the surface of deposits non-conductive. This insulates neighboring particles in the network, reducing the conductivity of the composites. Thus, the interface adhesion between the two components is a very important factor

effect on SE. The larger adhesive force provides for the more thermally stable shielding effectiveness.

Figure 9 shows that the SE value of ENCF/ABS composite degrades rapidly over time. The SE values of ENCF/ABS composites remain constant, though the SE values of ENCF/ABS composites are not as high as those of NCF/ABS composites. This illustrates that the resistance to

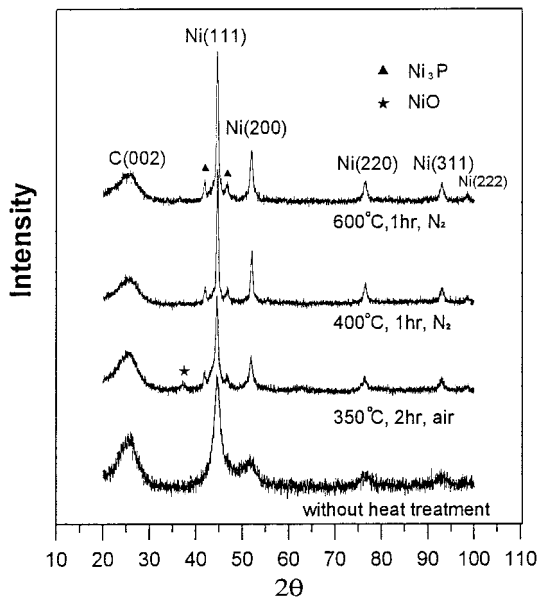


Figure 12 XRD patterns of ENCF vary with heat treatments.

reaction of ENCF is better than that of NCF. The ENCF/ABS composites will be suitable for the application of EMI shielding over a long time.

It has been reported that the properties of EN coating would be changed by heat treatment. The electrical conductivity and magnetic property, which are beneficial to EMI shielding, can be elevated by optimum heat treatment.^{5,12,13} The ENCF as plated were heat treated at different conditions. The effect of heat treatment of ENCF on SE of ENCF/ABS composites is shown in Figure 10. ENCF heating at 600°C for 1 h under nitrogen gives the best SE of all composites. ENCF heating at 350°C for 2 h in air has the lowest SE. Figure 11 shows the fracture surface of composites incorporating ENCF with and without heat treatment. Figure 11(a) shows that the unheated ENCF exhibits delamination of deposits at the end of fibers. Figure 11(b) shows that the ENCF heated at 350°C for 2 h in air is stripped. This is contributed to low SE of composites (Fig. 10). However, inferior SE might also be induced by oxidation of deposits, which could be proven by XRD in Figure 12. Figure 11(c) shows that the ENCF heated at 400°C for 1 h under nitrogen has a similar diffraction pattern as composites heated under nitrogen at higher temperature for longer times. However, the SE is not as good as that of unheated ENCF. It was proposed by Spencer¹⁴

that magnetic properties of EN coatings could be increased by heat treatment at about 350°C and vary with *P* content. Osaka et al.¹⁵ also reported that EN deposits heated at 400°C have both good conductivity and magnetic properties. However, these two reports did not provide the heating time. Park and Lee¹⁶ reported that after heating for a long time, the initial Ni₃P crystals would be recrystallized. This might be the reason that the sample of Figure 11(c) has a lower SE than ENCF without heat treatment. ENCF heated at 600°C for 1 h under nitrogen [Fig. 11(d)] shows excellent adhesion between deposit and fiber. This is the major reason that it possessed the best SE. According to Perry et al.,¹⁷ nickel could be readily recrystallized by heat treatment for 1 to 2 h at 600°C, and there is a slight interaction between nickel and carbon fiber. It could be suggested that the adhesion of EN deposited on fibers could be improved by heat treatment at 600°C due to the interaction between nickel and fiber.

The SE thermal stability of ENCF/ABS composites, in which ENCF has been heat treated, is shown in Figure 13. The SE values of these composites remain constant. An optimum heat treatment of ENCF can indeed improve the SE of composites and does not destroy the SE thermal stability of composites.

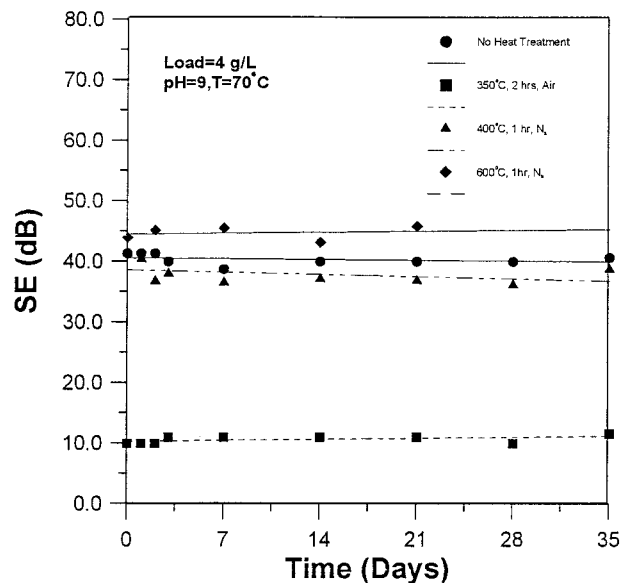


Figure 13 SE of ENCF/ABS composites degrading with heating time at 30 MHz for different heat treatments of ENCF.

CONCLUSIONS

Ideal EMI shielding effectiveness of ENCF/ABS composites could be achieved by adding additives and adopting suitable temperature and loading fiber during the blending process. Addition of both lubricant and antioxidant is essential during producing ENCF/ABS composites to obtain the best EMI SE of composites. Because of the difference in adhesion of EN coating on carbon fibers, high processing temperature is beneficial to ENCF (T700SC)/ABS composites, but low processing temperature is beneficial to ENCF (T300C)/ABS composites. By selecting optimum depositing conditions for ENCF, the SE of composites with 20 phr ENCF is almost as good as that with 30 phr ENCF. ENCF/ABS composites display lower EMI SE than NCF/ABS composites but present excellent thermal stability of shielding performance. The EMI SE of composites is improved further by heating the ENCF at 600°C before blending with ABS. Therefore, the ENCF/ABS composite is the ideal choice for EMI shielding application.

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