Effect of Mixing Process on Electromagnetic Interference Shielding Effectiveness of Nickel/Acrylonitrile–Butadiene–Styrene Composites

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Received 15 April 2004; accepted 17 November 2004
DOI 10.1002/app.21740
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This article reports the effect of the mixing process on the electromagnetic interference (EMI) shielding effectiveness of nickel/acrylonitrile–butadiene–styrene (ABS) composites. Nickel in either powder or filament form was used as the filler material. It was mixed with ABS by two mixing processes: one was the Brabender-mixing method, in which nickel was mixed in the polymer melt by a strong shear at high temperatures, and the other was a simple dry mixing method performed in a centrifugal ball mill. Our results showed that the dry-mixing method could produce EMI shielding effectiveness of 36 dB at the 3 vol % nickel filaments level. In contrast, we need 20 vol % nickel powder to exhibit some shielding effectiveness for the Brabender method. After the nondestructive X-ray examination and four-point probe resistivity measurements, we concluded that better EMI shielding effectiveness could be achieved when the mixing method provided a state of uniformity on the macroscale, but not on the microscale. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 128–135, 2005

Key words: electromagnetic shielding; mixing; nickel; acrylonitrile–butadiene–styrene

INTRODUCTION

Because of the wide use of electronic products in recent years, electromagnetic interference (EMI) brings about many serious problems.[1] EMI not only causes the abnormal operation of electronic products but also is harmful to human health under certain circumstances. A metal shell or conductive case, which is mainly composed of conductive filler and polymer matrix, can be adopted to avoid EMI by its shielding effect. In general, the conductive filler can be made of metallic powder, metallic filaments (or fibers), or carbon fibers.[2] Filament fillers are especially preferred because of their high aspect ratio. Although carbon fibers also possess very high aspect ratios, their electrical conductivity is not as good as pure metal. For this reason, some researchers coated carbon fibers with a layer of nickel by ordinary or electroless plating in order to enhance their conductivity.[3–5] However, the weak adhesion between carbon fiber and nickel may cause problems during processing.[6] In addition, the enhancement in the EMI shielding effect may not be obvious if the coating layer of nickel is not thick enough.

Very little attention has been paid to the mixing effect in the research of EMI shielding. Yet, we believe that for composites the mixing process must play an important role in determining the distribution of fillers in the matrix and hence its final properties. A Brabender Plasticorder, which applies a strong shear force on the polymer melt by two rotating screws, is usually used for the uniform mixing of small amounts in the laboratory. Other mixing methods such as dry mixing in a ball mill may also be applied in some special cases. Here, the shear force would be much smaller than that of a Brabender Plasticorder. Few past efforts have been made to illustrate the relationship between the mixing processes, microstructure, and EMI shielding properties of the composites.

In this work, nickel filler including both filament and powder are mixed with ABS polymer by either Brabender Plasticorder or dry mixing in a centrifugal ball mill. In addition, we use the nondestructive X-ray examination and resistivity measurements to characterize the microstructure of Ni/ABS composites. These data are then compared and related to the EMI shielding performance of these composites obtained from both mixing methods.

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Contract grant sponsor: Chun-Shan Institute; contract grant number: BD92027P.

Journal of Applied Polymer Science, Vol. 97, 128–135 (2005)

EXPERIMENTAL

Synthesis of nickel filaments

Nickel filaments are synthesized by the chemical reduction method using nickel chloride (Showa) as the precursor and hydrazine (Union Chemical, Taiwan) as the reducing agent at 80°C in the presence of a magnetic field. Ammonia (Union Chemical), sodium hydroxide (Union Chemical), and dipotassium hydrogen phosphate (Showa) are also added to stabilize the nickel ions and adjust the pH of the solution. The starting composition is as follows: 0.10*M* $NiCl_2 \cdot 6H_2O$, 1.60*M* $N_2H_4 \cdot H_2O$, 0.30*M* NaOH, 0.23*M* K_2HPO_4, and 1.48*M* NH_4OH. The strength of the magnetic field is kept at 100 Oe. As the reaction goes on, the solution changes color from deep blue to dark, indicating the formation of nickel filaments. As the nickel filaments grow, the solution gradually becomes clear and eventually colorless at the end. Then, the filaments are separated, washed by deionized water, and dried in an oven at 50°C. More details about the synthesis of nickel filaments can be found in earlier work.[7]

Mixing processes for ni/acrylonitrile–butadiene–styrene (ABS) composites

Both synthesized nickel filaments and commercial Ni powder (Inco) are mixed with ABS polymer by two types of mixing processes and then hot compressed to produce EMI test samples. The first mixing process (Brabender-mixing process) is carried out in a Brabender Plasticorder (Brabender PLE 300). Here, the ABS pellets (Taida Chemical, Taiwan) are first melted at 200°C, and then the nickel filaments (or powder) are loaded in gradually. The rotating speed of the screws is kept at 50 rpm and the mixing process is continued for about 10 min until the torque becomes constant, indicating the steady-state mixing condition. After cooling, the Ni/ABS composite can be obtained. The second mixing process (dry-mixing process) is performed in a centrifugal ball mill (Pulveristte 6, Fritsch) in which ABS powder (Aldrich) is simply mixed with either nickel filaments or powder at 400 rpm for 5 min (without any balls). The product is Ni/ABS mixed powder after dry mixing.

Preparing EMI test samples and characterization

After either mixing process, a fixed volume of sample (about 50 cm^3) is put into a circular mold, heated to 200°C, and pressed at this temperature under 1000 psi for 3 min. Then, the mold is removed immediately to another press and it is kept there at room temperature under 1000 psi for cooling. The final sample is 133 mm in diameter and 3 mm in thickness.

The EMI shielding effectiveness is measured by a coaxial transmission line test according to the ASTM ES-7-83 standard. The test frequency is tuned from 200 to 1800 MHz. In order to understand the microstructure of the Ni/ABS composite, both nondestructive X-ray examination (according to ASTM E94-00) and four-point probe electrical resistivity (1-mm spacing, osmium probe head, 125-μm head radii, C4S-54/5S, Cascade Microtech) are performed on these composites. For four-point probe measurements, the sample was divided into 32 regions and one measurement was made for each region, which is a total of 32 measurements for each sample. In addition, the morphology of the nickel powder and filaments are examined by scanning electron microscopy (JSM 5600, JEOL) after adhering these samples to a conductive carbon tape, and the specific surface area was determined by the Brunauer–Emmett–Teller (BET) method (ASAP 2000, Micromeritics).

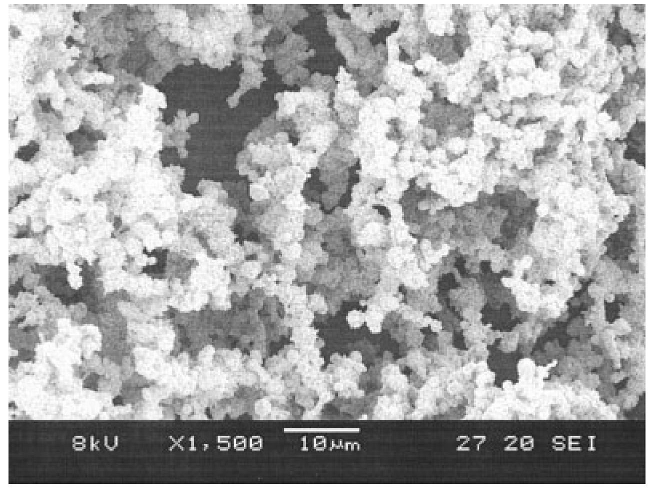

Figure 1 Nickel powder (Inco type 255) with a BET surface area of 0.7 m^2/g and an average particle size of 2.2–2.8 μm (provided by vendor).

RESULTS AND DISCUSSION

Morphology of nickel fillers

The morphology of the commercial nickel powder and synthesized filaments are shown in Figures 1 and 2. The size of the powder is about 2.2–2.8 μm, whereas that of the filament is around 1–2 μm in diameter. The BET surface areas are 0.7 and 1.6 m^2/g, respectively. The specific surface area of the filament is slightly larger than the calculated value for filament-shape samples, that is, $S = 4/(\rho d)$, where d is the diameter of the filament and ρ is the density of nickel (8.9 g/cm^3). It therefore suggests that the surface is not smooth and may contain some features of small sizes.

EMI shielding effectiveness of Ni/ABS composites

Brabender-mixing method

The average EMI shielding effectiveness of Ni/ABS composites by the Brabender-mixing method are only

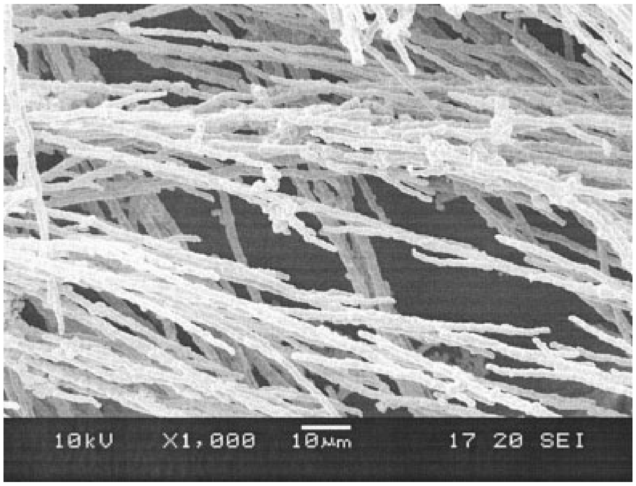

Figure 2 Nickel filaments synthesized by the chemical reduction method; BET specific surface area = 1.6 m^2/g.

1.3 and 1.1 dB for 7 vol % Ni filaments and 7 vol % Ni powder, respectively. This indicates that at this level of Ni content, the composites from the Brabender-mixing method show no EMI shielding effect at all. A higher level is needed for EMI shielding, as indicated in Figure 3. We can notice here that the Ni/ABS composite starts to exhibit EMI shielding effects when the Ni powder content is over 20 vol %. No similar experiments were done for Ni filaments because of insufficient quantities of synthesized Ni filaments.

In the literature, Shui and Chung[8] reported good EMI shielding effects for 7 vol % Ni-coated carbon fibers. However, they prepared their samples by hand mixing only. At first, we would suspect that the high shear might break our Ni filaments. We therefore used chloroform to dissolve the ABS from the composite and to recover Ni filaments, which is shown in Figure 4. As can be seen, the Ni filament is strong enough to withstand the shear and roughly retains its original fibrous morphology. Therefore, the poor EMI shielding performance might be derived from the mixing process itself and the way in which the Ni filaments are distributed in the composites (i.e., its microstructure) after the Brabender mixing.

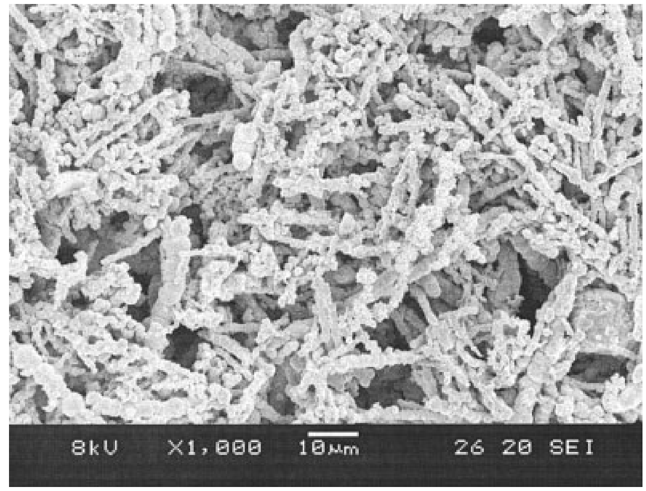

Figure 4 Nickel filaments after separation from the Ni/ABS composite made by the Brabender-mixing method (3 vol % nickel filaments).

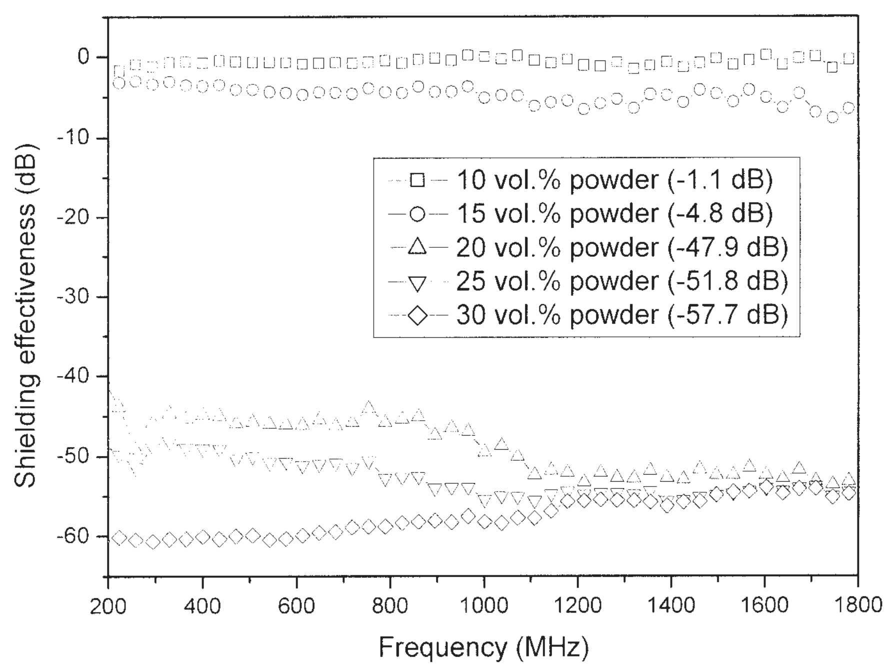

Figure 3 EMI shielding effectiveness of Ni powder/ABS composite obtained by the Brabender-mixing method.

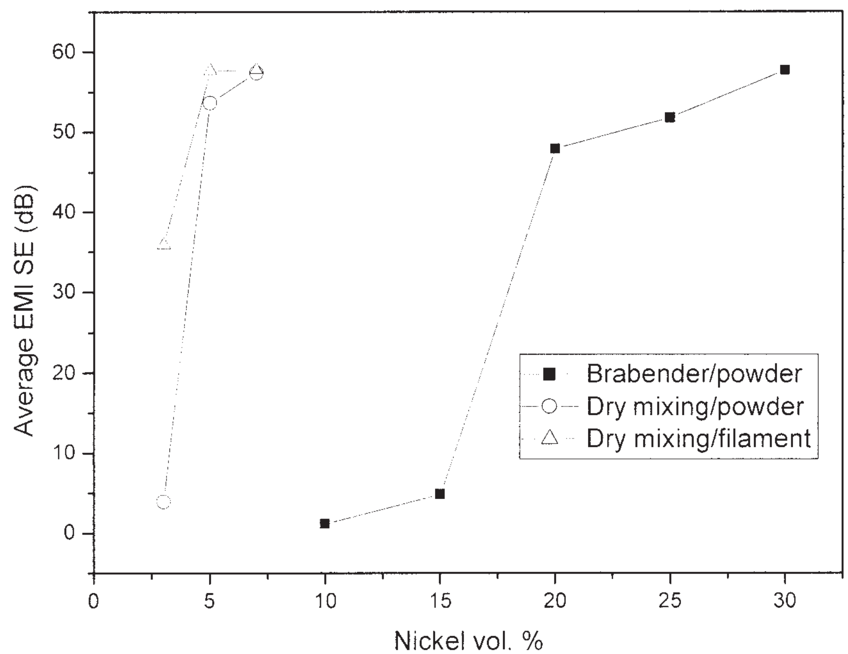

Figure 5 The average EMI shielding effectiveness (SE) of Ni/ABS composites by the Brabender-mixing and dry-mixing methods.

Dry-mixing method

The EMI shielding effectiveness of the Ni/ABS composite (including both powder and filament) by the dry-mixing method is shown in Figure 5. The corresponding results for the Ni powder/ABS composite by the Brabender-mixing method are also included for comparison. It is very apparent that the dry-mixing method produces composites that show higher EMI shielding effectiveness than the Brabender-mixing method for both nickel filaments and powder at a low nickel level (5 vol %). Moreover, the Ni filaments/ABS composite exhibits a 36-dB value at only the 3 vol % nickel level, suggesting the better performance of fillers with a high aspect ratio. Nevertheless, the difference becomes small when the nickel content becomes high.

Microstructure characterization of Ni/ABS composites

Here we used a nondestructive X-ray examination to observe the distribution of Ni in the whole sample and a four-point probe electrical measurement as another method to characterize the Ni distribution and connection in the sample. Figure 6 presents pictures of the X-ray examination of two samples from the Brabender-mixing process. Both samples appeared extremely uniform, showing no Ni aggregation on the microscale, which would be noticeable as a bright region in these X-ray photographs. Figures 7 and 8 show similar pictures for samples obtained from the dry-mixing method using Ni powder and Ni filaments, respectively. Here, the bright regions are clearly observed in all pictures, suggesting that the Ni fillers (filament or powder) are still aggregated on the microscale in the sample. However, viewing the sample as a whole, these bright regions can be considered as uniformly distributed on the macroscale. In these pictures, the dark region corresponds to the polymer material. Judging from the better shielding performance of dry-mixed samples, we can conclude that the aggregation of nickel filler on the microscale is beneficial to EMI shielding because it helped to form the conducting path.

Next, we used a four-point probe to characterize the Ni distribution on a much smaller scale than the X-ray examination. The resistivity and its scatter offer additional evidence about the distribution of Ni filler inside the composite sample. In theory, a very uniform composite sample would produce uniform resistivities with little or no scatter. Consequently, the scatter of the resistivity data of a real sample simply reflects the distributional variation of the conductive filler within the sample. Shown in Figure 9 are the data of samples from Brabender mixing. When the nickel powder is below 20 vol %, the resistivities are very high and out of the scale of the instrument ($>10^6$ Ω cm). The samples are nearly insulated and lack any EMI shielding capacity. Only when the nickel level is over 20 vol % does the resistivity becomes measurable and the composite starts to show EMI shielding effect. With increasing nickel content, both the average resis-

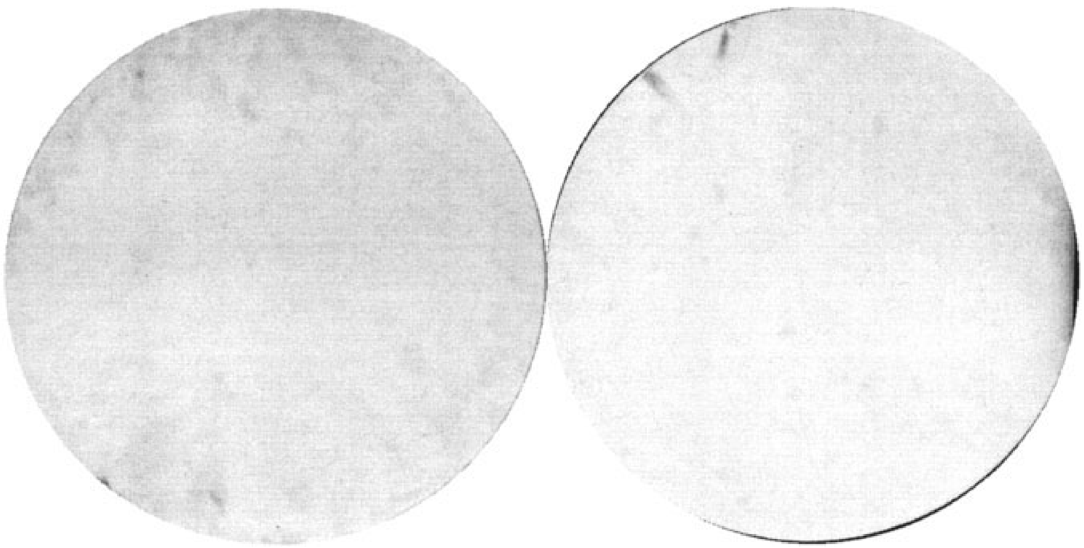

Figure 6 Nondestructive X-ray examination of Ni powder/ABS composites by the Brabender-mixing method: (left) 15 vol % and (right) 20 vol %.

tivity and its degree of scatter decrease as clearly indicated by the data in Figure 9. At 20 vol %, 12 of 32 measurements are out of range and the measured resistivity data scatter between 10^6 and 10^{-3} Ω cm. However, at 30 vol %, every measurement is within the range and they scatter in a narrow range from 10^{-3} to 10^{-2} Ω cm. The composites from the dry-mixing process show the same tendency but the resistivity starts to be measurable at low nickel content, for example, 3 vol % for filaments. The resistivity data for the Ni filament/ABS composite from the dry-mixing process are exhibited in Figure 10 for comparison.

To summarize the information from the resistivity data, we define a parameter called the percent measurable, which is the ratio between the numbers of measurements within the scale to the total number of resistivity measurements (i.e., 32). These ratios are presented in Figure 11 for samples obtained from both mixing processes. These data exhibit a clear resemblance to those presented in Figure 5 for the EMI results. Because it is necessary for the fillers, either as powder or filament, to become connected to conduct electricity, a measurable resistivity therefore refers to a state where there is sufficient filler material to form the conducting path. In contrast, a nonmeasurable case refers to the situation where either there is not enough filler material to form the conducting path or the fillers are very

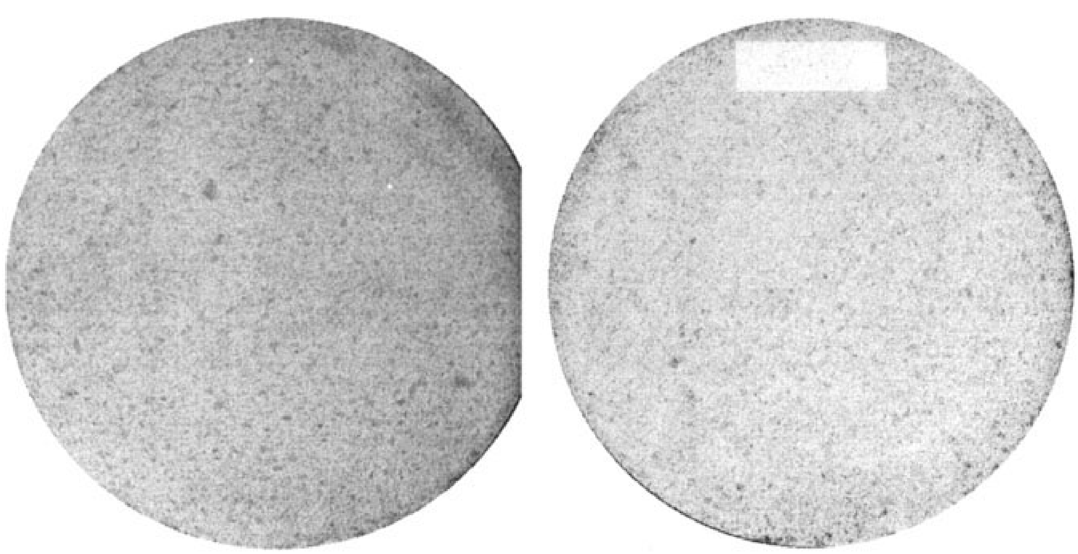

Figure 7 Nondestructive X-ray examination of Ni powder/ABS composites by the dry-mixing method: (left) 3 vol % and (right) 7 vol %.

Figure 8 Nondestructive X-ray examination of Ni filaments/ABS composites by the dry-mixing method: (left) 3 vol % and (right) 7 vol %.

uniformly distributed and separated from each other, thus preventing the formation of conducting paths for electricity. Because the four-point probe measures the resistivity of a small area (~4 mm^2), these data therefore indicate the nickel aggregation on the microscale. Comparing the two mixing processes at the same nickel content, the dry-mixing process shows the higher percent measurable, suggesting a more aggregative Ni distribution on the microscale. This observation is also consistent with the nondestructive X-ray examination mentioned earlier. Furthermore, the same comment can be applied to the comparison between Ni filaments and Ni powder samples from dry mixing. In general, a nickel filament may be considered as Ni particles distributed in a specific manner (or nonuniformly), which is beneficial to conducting electricity.

CONCLUSION

In this work, two different mixing processes are tested for their effects on the EMI shielding perfor-

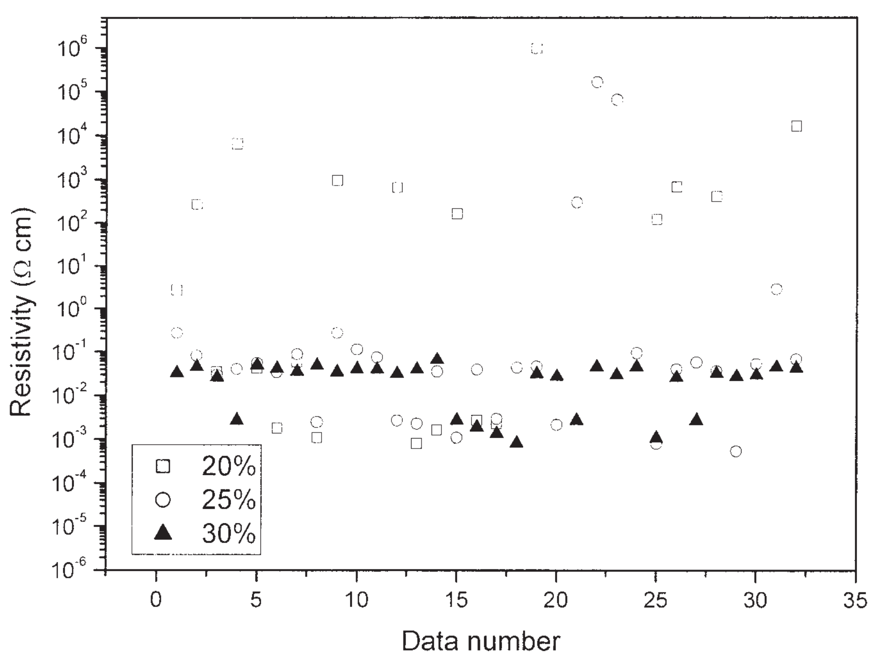

Figure 9 The resistivity of Ni powder/ABS composites by the Brabender-mixing method.

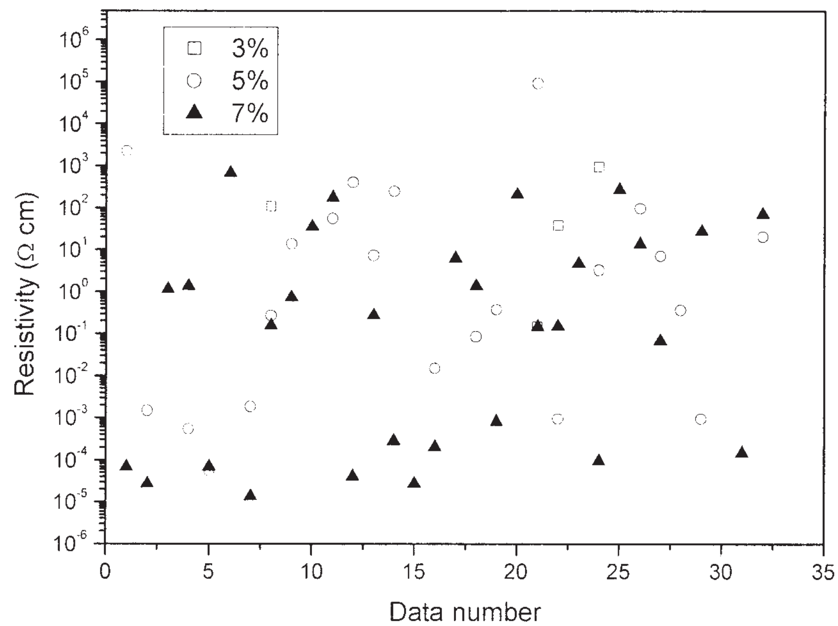

Figure 10 The resistivity of Ni filament/ABS composites by the dry-mixing process.

mance of Ni/ABS composites. Our results show that the mixing process affects the distribution of nickel in the product and hence affects the EMI shielding effectiveness values. The Brabender-mixing process provides a strong mixing torque so that the nickel fillers are well dispersed in the polymer matrix on both the macro- and microscale. In other words, the fillers are completely surrounded by the polymer and thus separated from each other after mixing. As a result, high nickel content is needed to ensure proper connection among the fillers. Such a state of uniformity is therefore a disadvantage to EMI performance.

In contrast, the dry-mixing method offers uniformity on the macroscale, as evidenced by X-ray examination, but not on the microscale, as indicated by four-point probe resistivity measurements. In addition, it produces samples with better EMI

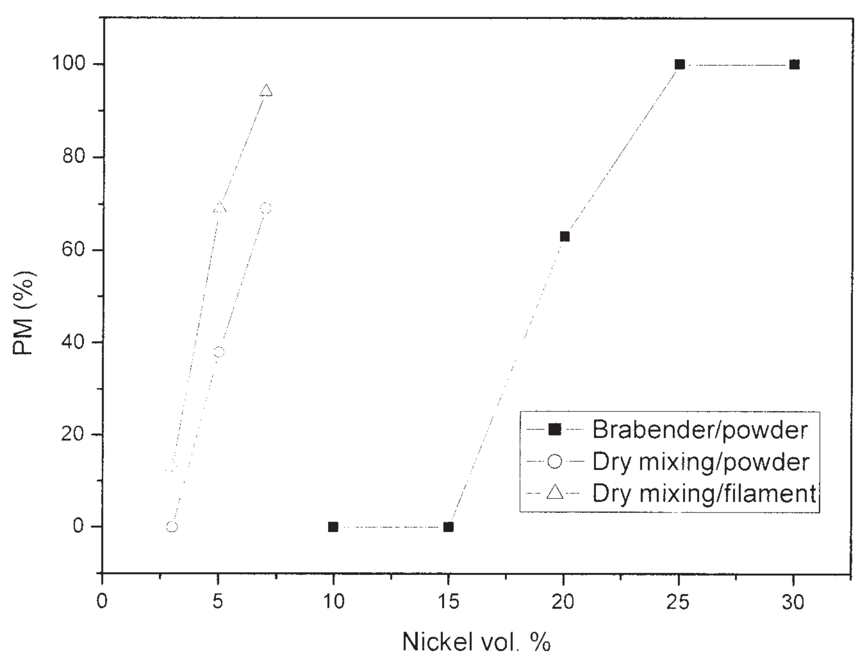

Figure 11 The percent measurable (PM) of Ni/ABS composites by the Brabender-mixing and dry-mixing methods.

shielding performance. Via local aggregation, it seems easier for nickel fillers to form conductive networks in the composite products. Moreover, Ni filaments, because of their high aspect ratio, start to exhibit effective shielding at as low as 3 vol %.

The authors thank to Dr. C. Y. Huang of Tatung University for his help on the measurements of the EMI shielding effectiveness. The financial support from Chun-Shan Institute is also acknowledged.

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