JOURNAL OF MATERIALS SCIENCE 39 (2004) 6209–6214

Electromagnetic shielding capacity of carbon matrix composites made from nickel-loaded black rice husk

QINGLEI LIU, TONGXIANG FAN*, DI ZHANG
State Key Lab of Metal Matrix Composites, Shanghai Jiaotong University, 200030, Shanghai, People's Republic of China
E-mail: txfan@mail.sjtu.edu.cn

Non- and nickel-loaded carbon matrix composites were made from rice husk to measure their electromagnetic shielding (EMS) capacities in the range of 30–1500 MHz. The results showed that the EMS capacity was dependent on carbonization temperature, content of nickel loading, molding pressure and pore size diameter. The combination of carbonization at 1200°C, molding at 20 MPa and loading of 6 wt% nickel can provide 80–60 dB EMS capacity over the measuring frequency range.

1. Introduction

The use of electronic equipments has recently increased over the last decades, which in turn leads to the increase of the amount of electromagnetic radiation. Such electromagnetic radiation causes unwanted electromagnetic interference (EMI), which seriously interferes the equipments and does harm to the health of people.

To alleviate the EMI, many electromagnetic shielding (EMS) materials have been manufactured, most of which are metallic composite materials or coatings. Due to the reflective loss associated with the high electrical conductivity, metallic composite materials have an effective shielding effectiveness, while result in appreciable weight penalties. The alternate approaches to EMI shielding include metal power filled polymers, metallic meshes, metal whisker filled polymers, and metal-coated carbon fiber reinforced plastics. These alternate approaches can yield lower weight materials, but they cannot provide as high an electrical conductivity as metallic composite materials [1–6].

In this report, we develop a process making a new sort of effective electromagnetic shielding material. With a natural and special porous microstructure probably contributing to absorbing of electromagnetic waves, rice husk was chosen as the raw material and then loaded nickel in a sol-gel process. The shielding effectiveness of the fabricated composites was measured by the coaxial cable method and the effects of different processing parameters were discussed.

2. Experimental

2.1. Material preparation

Fig. 1 shows the procedure of nickel-loaded composites preparation. Rice husk were elementarily carbonized at 800°C. Hereinafter, the product was called black rice husk, the primary components of which were amorphous SiO_2 and carbon [7]. In a sol-gel process, black rice husk was impregnated in nickel nitrate solutions of different concentration chosen as the precursor of nickel for 24 h. This procedure was carried out for the purpose of obtaining higher dispersion of nickel nitrate in black rice husk. Non- and nickel-loaded black rice husk was milled to powders, and then mixed well with 15 wt% phenolic resin powder chosen as a curing agent in a stainless steel vessel. Finally the mixture was molded into disk specimens with 115 and 6 mm in diameter and thickness, respectively. In these molding processes, various pressures (12,16 and 20 MPa) were applied on the mixture for initial 20 min, and then solidification of the mixture was continued free from compression for 12 h. Secondary carbonization was carried out at the temperatures of 800, 1200 and 1400°C to yield nickel-loaded carbon matrix composites.

2.2. Characterization

The phase identification was characterized by X-ray diffraction (XRD) using Rigaku Dmax-rC, with Ni-filtered Cu radiation at 20 KV and 20 mA employed to obtain a chart recording in the 2θ range from 10° to 90° with a scanning step of 0.2°/s.

The morphologies of the non-carbonized and carbonized rice husk were observed by scanning electron microscopy (SEM) using HVTACHI S-520, which was operated at 20 KV and 20 mA.

Pore size distributions of the composites were measured by method of "mercury porosimetry" using AutoPore IV 9500, which was manufactured by Micromeritics INC. In the experiment, contact angle was 130°, Hg surface tension was 485.00 dynes/cm, and Hg density

*Author to whom all correspondence should be addressed.

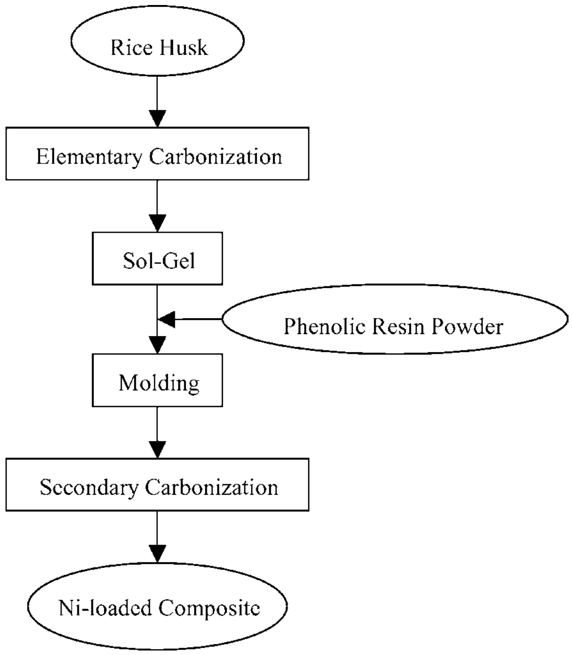

Figure 1 Procedure of nickel-loaded composites preparation.

was 13.5335 g/mL. Data was acquired in scanning fashion and corrected in type of blank correction [8].

2.3. Measurement of EMS capacity

Fig. 2 shows the apparatus for measuring electromagnetic shielding capacity, which is named "Shielding Effectiveness Test Device for Coaxial Cables". In the figure, an electromagnetic wave with a fixed frequency generating from Vector Network Analyzer was transmitted through a coaxial cable, and then the declined wave after passing through a specimen was received by Vector Network Analyzer. The intensity of the wave signal generated and received by Vector Network Analyzer was E_0 and E_S, respectively. In this system, EMS capacity was given as the total of surface reflection, absorption and multi-path reflection. It can be calculated by the following equation and expressed as shielding effectiveness (SE) in decibel (dB).

$$SE = -20\log(E_0/E_S)(\text{dB}) \quad (1)$$

where E_0 is field strength (V/m) for incidence (without a specimen), and E_S is field strength for transmission (with a specimen).

On the other hand, shielding effectiveness (SE) of the conductive materials can be expected by the following expression [9].

$$SE(\text{dB}) = R + A \quad (2)$$

where R is the reflected energy, and A is the absorbed energy.

3. Results

3.1. Morphologies of the rice husks

Fig. 3 displays morphologies of the non-carbonized and carbonized rice husks. It shows that the carbonized rice husks were characterized by high porous structure, where the rice husk's original structure still remained.

3.2. Influence of carbonization temperature

Fig. 4 shows electromagnetic shielding effectiveness against frequency for non- and 6 wt% nickel-loaded composites carbonized at different temperatures. All the composites were molded at 20 MPa. From the figure, we can conclude that the SMS capacity of composites, whether nickel was loaded or not, decreased slightly with increasing frequency. As shown in Fig. 4a, for composites without nickel, the SE values of the composites carbonized at 800, 1200 and 1400°C decreased from 58 to 48 dB, 65 to 50 dB and 60 to 43 dB, respectively, in the range of 30–1500 MHz. The results show that carbonization temperature played an indistinctive effect on EMS capacity of non-nickel-loaded composites.

Comparatively, in Fig. 4b, the SE values of 6 wt% nickel-loaded composites carbonized at 800, 1200 and 1400°C decreased from 60 to 45 dB, 80 to 57 dB and 70 to 45 dB over the same range of frequency, respectively. Obviously, carbonization temperature had a remarkable influence on SE capacity of nickel-loaded composites.

Fig. 5 shows the XRD profiles of non- and 6 wt% nickel-loaded composites carbonized at various temperatures. In Fig. 5a, the broad peak at $2\theta = 21$–$24°$ illustrated that most carbon existed in the state

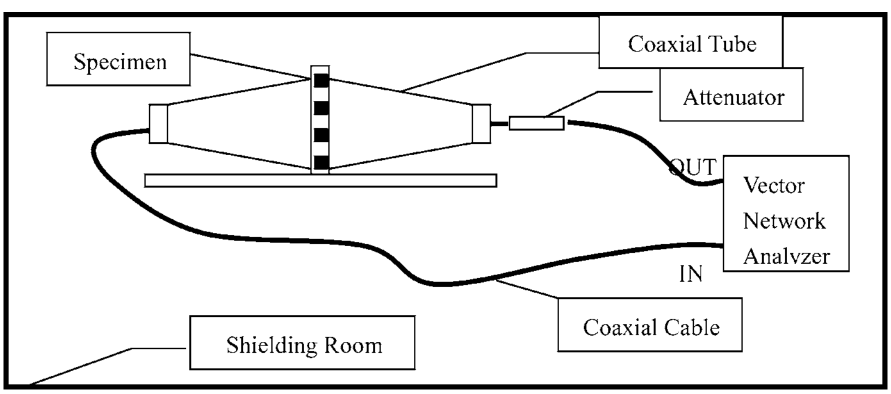

Figure 2 Shielding Effectiveness Test Device for Coaxial Cables (30 MHz–1.5 GHz).

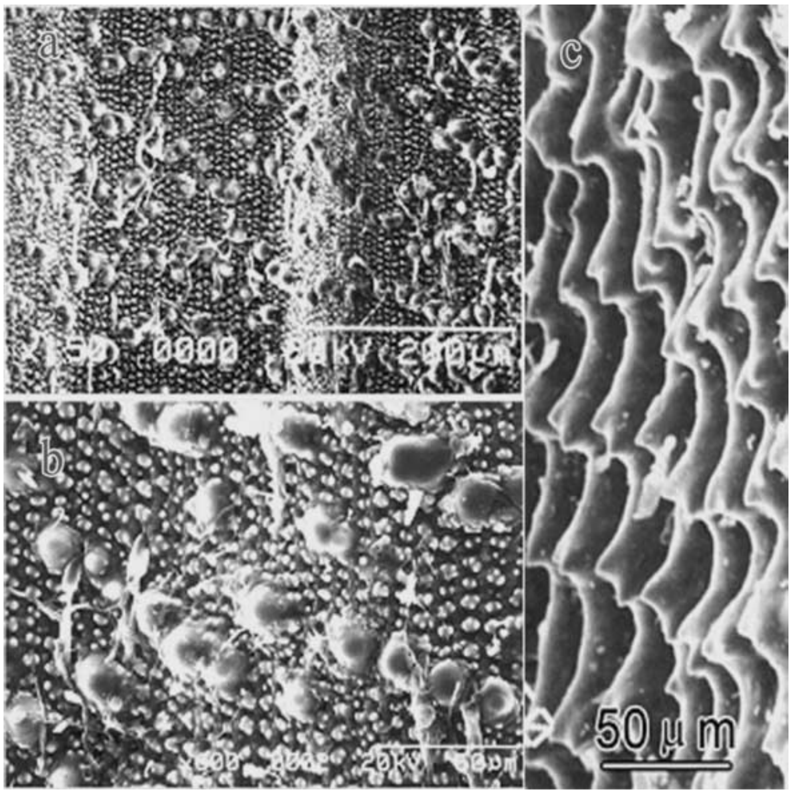

Figure 3 Morphologies of the non-carbonized and carbonized rice husks: (a) Surface of non-carbonized rice husks, (b) Surface of carbonized rice husks and (c) Cross section of rice husks.

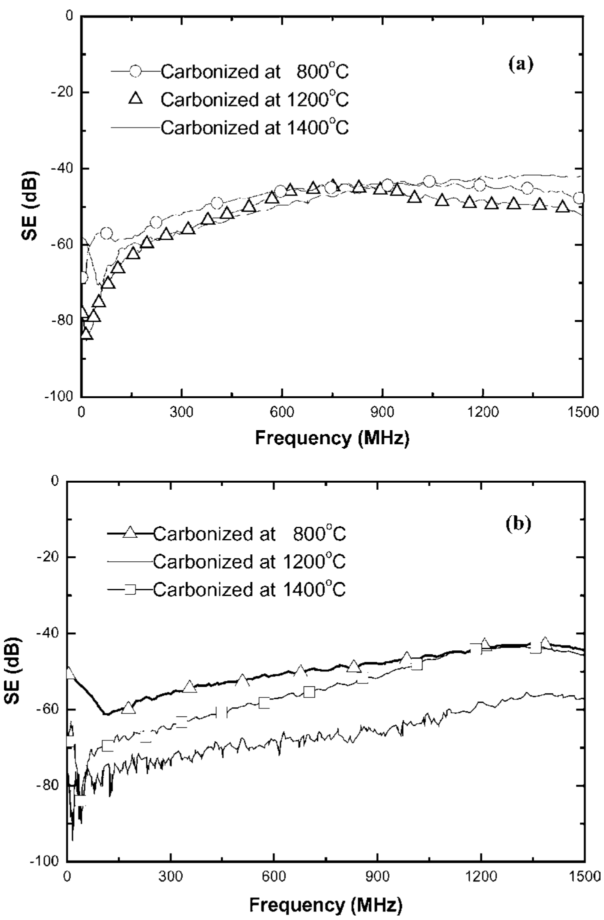

Figure 4 Influence of carbonization temperature on EMS capacities of non- and 6 wt% nickel-loaded specimens: (a) SE of non-nickel-loaded specimens and (b) SE of 6 wt% nickel-loaded specimens.

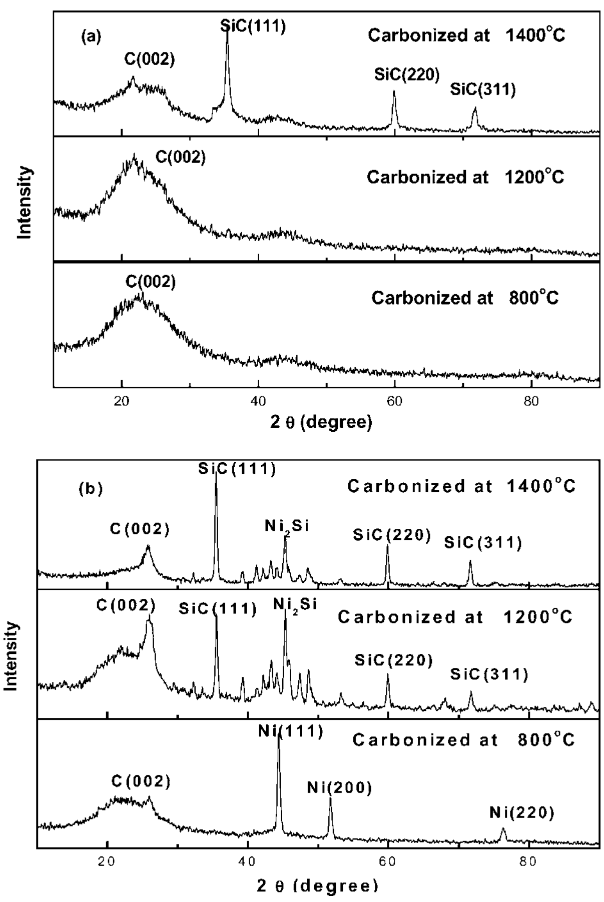

Figure 5 X-ray diffraction profiles for non- and 6 wt% nickel-loaded specimens carbonized at 800, 1200 and 1400°C: (a) XRD profiles for non-nickel-loaded specimens, and (b) XRD profiles for 6 wt% nickel-loaded specimens.

of amorphous carbon in non-nickel-loaded composites carbonized at 800, 1200 and 1400°C. As shown in Fig. 5a, there was no obvious difference between XRD profiles of non- nickel-loaded composites carbonized at 800 and 1200°C. Although the yield of SiC, which contributed to EMS capacity, the intensity of amorphous carbon decreased in composites carbonized at 1400°C. The results above illustrated that EMS capacity of non-nickel-loaded composites varied little with carbonization temperature.

In Fig. 5b, the presence of nickel led to the appearance of sharp peak at about 26° in XRD profile of composites carbonized at 800°C, which illustrated that amorphous carbon progressed to graphite structure. In XRD profile of composites carbonized at 1200°C, the intensity of the sharp peak became higher and peaks of SiC appeared. Comparatively, the intensity of peak at 26° decreased and the intensities of SiC peaks increased in XRD profile of composites carbonized at 1400°C. The results above showed that carbonization temperature influenced structure and content of carbon and SiC in nickel-loaded composites. Moreover, the fact that EMS capacity of composites carbonized at 1200°C was higher than that of composites carbonized at 1400°C, showed that the crystal structure of carbon was more important than formation of SiC in determining the EMS capacity of composites.

It need to point out that composites carbonized at 800°C, whether nickel was loaded or not, provided over 45 dB over the entire range of frequency, which greatly exceeded the practical standard, 30 dB.

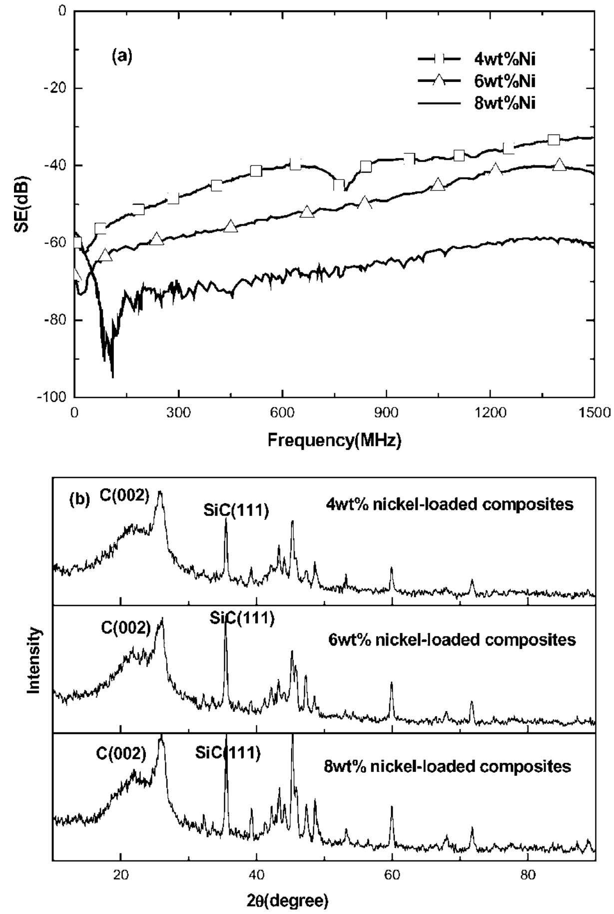

Figure 6 Influence of content of nickel on EMS capacity of nickel-loaded composites carbonized at 1200°C: (a) EMS capacities of composites containing different ratios nickel and (b) XRD of these composites.

3.3. Influence of the content of nickel

Fig. 6a displays the shielding capacities of composites loaded different ratios nickel. These composites were all carbonized at 1200°C and molded at 16 MPa. As the figure shows, with increasing content of nickel, the composites showed better EMS capacity in the whole range of measuring frequency. The EMS capacity of composites with 4, 6 and 8 wt% nickel slightly decreased from 60 to 32 dB, 70 to 42 dB and 80 to 60 dB, in the range of 30–1500 MHz, respectively.

Fig. 6b shows the XRD profiles of these composites. As the figure shows, both the intensity of sharp peak at about 26° and the intensities of peaks of SiC increased with increasing content of nickel, which illustrated that the more content of nickel composites contained, the more remarkable the nickel played catalytic effects on crystallization of carbon and yield of SiC. Needless to say, a larger amount of graphite and nickel would improve electrical conductivity, which favoured the capacity of EMS of composites.

3.4. Influence of molding pressure

Fig. 7 exemplifies the influence of molding pressure on EMS capacities of 6 wt% nickel-loaded composites carbonized at 1200°C. As showed in Fig. 7, the EMS capacity of composites molded at 12-, 16- and 20 MPa slightly decreased from 64–40 dB, 70–50 dB and 80–60 dB, respectively. It is obvious that EMS capacity of the composites increased with increasing molding pressure. As seen from the figure, an increment of SE values in the pressure from 16 to 20 MPa was more beneficial than that from 12 to 16 MPa. Needless to say, a higher molding pressure resulted in a higher density, which increased the contact area among conducting particles of graphite and metallic nickel in composites to enhance the electrical conductivity. The density of the composites moulded at 12, 16 and 20 MPa was 0.65, 0.72 and 0.81 g/cm^3, respectively. Accordingly, we can draw the

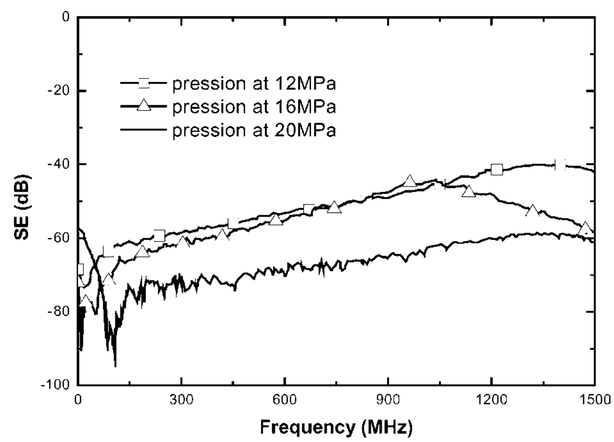

Figure 7 Influence of molding pressure on EMS capacities of 6 wt% nickel-loaded composites carbonized at 1200°C.

conclusion that in many cases, heightening densities of composites by increasing molding pressure is an effective method to improve EMS capacity of materials.

4. Discussion

4.1. Influence of nickel loading

The foregoing results demonstrated the important influence of nickel loading on improving EMS capacity of composites. The primary way for the influence was the catalytic activity of the metallic nickel upon crystallization of carbon and yield of SiC. As foregoing results demonstrated, for composites without nickel, the increase of carbonization temperature over 800°C had no obvious influence on EMS capacity. The reason for this was that most carbon existed in state of amorphous carbon in composites. However, for composites containing nickel, carbonization temperature had a remarkable influence on EMS capacity of composites. As the XRD profiles of these composites showed, the presence of nickel decreased the graphitization temperature of amorphous carbon and the yield temperature of SiC so that partial amorphous carbon transformed to graphite over 800°C and some SiC was observed at 1200°C. Moreover, the content of graphite and SiC increased with increasing of the content of metallic nickel. Accordingly, decreasing the graphitization temperature of amorphous carbon with the aid of nickel catalyst was a practical method in application of preparation of EMS composites and deserved much attention.

Moreover, another way for metallic nickel for improving the EMS capacity of composites was that metallic nickel particles enhance the electrical conductivity of composites by acting as conducting fillers, which was adopted as the usual way for improving EMS capacity. As mentioned above, the primary reason for the influence of molding pressure on EMS capacity was that increasing density of composites by increasing molding pressure enlarged the contact area among conducting particles. Undoubtedly, increasing the content of nickel and densification by compression were two ways for enlarging the electrical conductivity.

4.2. Influence of pore size

It has been proposed that porous structure greatly contributes to EMS capacity of material [10]. To illustrate the proposition, Kiyotaka Shibata *et al.* established a Pore Model and a corresponding equivalent circuit [10]. In the model, at the electric equivalent circuit at each point, A, B, C and D were thought to be a parallel of RL series component capacitance in a microwave circuit. Electromagnetic waves passing through the material with porous structure would yield polarized electrical current. Circuiting the pores to flow, the polarized electrical current got consumed, which led to the consumption of energy of electromagnetic waves.

Fig. 8 presents pore size distribution of 6 wt% nickel-loaded composites carbonized at 1200°C. In the figure, multimodal distributions were observed, which illustrated comparatively broad pore size distributions. In detail, the ranges of the pore sizes mainly covered

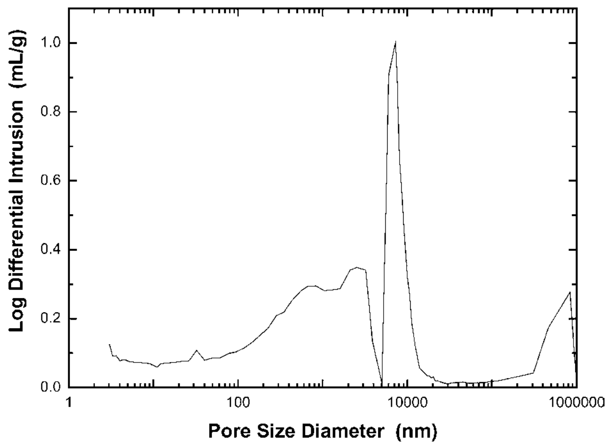

Figure 8 Pore size distributions of 6 wt% nickel-loaded composites carbonized at 1200°C.

microns unit level and millimetres unit level and the amount of pores with 10 μm reached a maximum.

As shown in above figures, the composites, whether nickel was loaded or not, displayed a comparatively constant EMS value in the measuring range of frequency. It was different from a lot of conventional metallic EMS materials, whose SE values decrease greatly with increasing of frequency. In general, with increasing of frequency of electromagnetic waves, absorbed loss contributed more to the electromagnetic shielding. As far as these carbonized composites were concerned, various diameter pores played various roles in a range of frequency. In detail, as illustrated in the pore model, various diameter pores were thought to be various RL series component capacitances. Each RL series possessed respectively corresponding resonant frequency, at which the consumption of electromagnetic energy reached the maximum. Owning to the different amounts of pores, the consumption of energy attributed to these RL series varied with frequency. Nevertheless, the role that the various diameters pores played in microwave- absorbing required further study.

5. Conclusions

In the present work, electromagnetic shielding composite materials were fabricated from black rice husk and the effects of processing parameters upon the EMS capacity was investigated. The results were summarized as follows:

(1) The capacity is mainly dependent on carbonization temperature, molding pressure, nickel loading and the porous structure.

(2) The combination of carbonization at 1200°C, molding at 20 MPa and 6 wt% loading nickel can provide 80–60 dB EMS capacity over the measuring frequency range.

Acknowledgements

The authors wish to express thanks to the financial support of National Natural Science Foundation of China (No. 5027104 and No. 50371055), "863" Program (No. 2002AA334030), Excellent Young Teacher

Program of MOE, P. R. China, Shanghai Fundamental Research Program (No. 03JC14044) and For Ying Tung Foundation (No. 94010).

References

1. J. WANG, V. V. VARADAN and V. K. VARADAN, *SAMPE Journal* **32**(6) (1996) 18.
2. CH.-Y. HUANG and J.-F. PAI, *J. Appl. Polym. Sci.* **63**(1) (1997) 115.
3. J. WANG, V. V. VARADAN and V. K. VARADAN, *SAMPE J.* **32**(6) (1996) 18.
4. D. W. RADFORD, *J. ADV Mater.* **26**(1) (1994) 45.
5. L. LI, P. YIH and D. D. L. CHUNG, *J. Electr. Mater.* **21**(11) (1992) 1065.
6. L. LI and D. D. L. CHUNG, *Composites* **22**(3) (1991) 211.
7. HUA WANG and YONGNIAN DAI, "The Research for Making Si_3N_4 Ultra-Micro Powder From Rice Husk" (Yunnan Science and Technology Press, Kunming, 1997, In Chinese) p. 91.
8. CARLOS A. LEÓN Y LEÓN, *Adv. Coll. Interf. Sci.* **76–77** (1998) 341.
9. SHUNICHI SHINAGAWA, YAOMI KUMAGAI and KEI URABE, *J. Porous Mater.* **6** (1999) 185.
10. KIYOTAKA SHIBATA, TOSHIHIRO OKABE *et al.*, *ibid.* **4** (1997) 269.

Received 10 September 2003
and accepted 28 May 2004