Microwave Absorbing Properties of Ternary Linear Low-Density Polyethylene/Carbonyl Iron Powder/Carbon Black Composites

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ABSTRACT: Linear low-density polyethylene (LLDPE) was used as polymer matrix, carbonyl iron powder (CIP) and carbon black (CB) were used as fillers, and ternary composites with microwave absorbing properties were prepared by melt blending. Transmission electron microscopy was used to characterize the prepared samples. The absorbing ability (reflection loss) of the prepared composites was measured using the arch method, and the electromagnetic parameters of composites were determined by the transmission/reflection method. The filler contents of CIP and CB have effects on the absorbing peak positions and reflection loss, and there is the optimum filler content in composites to obtain the maximum microwave absorbing. The microwave absorption of LLDPE/CIP/CB composites comes from the combining contributions of the dielectric loss and the magnetic loss. The synergistic effects of CIP and CB effectively improve the microwave absorbing properties of polymer composites. CIP and CB are uniformly distributed in the polymer matrix. The theoretical calculation results of the absorbing ability are in agreement with the experimental results using the transmission line theory. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3434–3439, 2009

Key words: composites; polyolefins; carbon black; carbonyl iron powder; reflection loss

INTRODUCTION

Polymer matrix composites consisting of polymer and filler own excellent processability of the polymer and play very important roles in industry application, because the composites with the desired properties can be designed based on composite components.[1–3] For example, for the purpose of civil and military application, polymer matrix composites can be devised into microwave absorbing materials (MAMs) to attenuate the undesired electromagnetic waves using absorbent as filler. Recently, there is a growing and widespread interest in the investigation of polymer matrix MAMs since the applications of MAMs increase gradually. All kinds of polymer matrix MAMs have been designed out and prepared.[4–10] Composites based on polymethyl methacrylate, polypropylene, ethylene-propylene-diene-monomer, epoxy resin, nitrile rubber, polychloroprene, polyethylene, and polyurethane have been reported.[11–18] Generally, conductive metal powders, magnetic metal particles, ferrites, carbon products, and chiral materials are used as fillers/absorbents for MAMs.[6,19-21]

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Carbonyl iron powder (CIP) is composed of iron, carbon, nitrogen, and oxygen. With a high Curie temperature, specific saturation magnetization intensity, and value of microwave permeability and dielectric constant, CIP is extensively used as microwave absorbent.[4,20,22,23] Carbon black (CB) is widely used as conductive filler and has been intensively used as conductive filler for MAMs because of its low density, high modulus, high strength and wide availability, and electronic performances. Also, the composites filled with CB can be used as MAMs to attenuate microwave irradiation.[6,7,24,25] It is well known that the microwave absorbing mechanism of CIP-filled polymer composites is different from that of CB-filled composites. Filler CIP can result in the dielectric loss and magnetic loss of MAMs whereas filler CB can only lead to the dielectric loss of MAMs.[4,26,27] We expect that the synergistic effects of the absorbent CIP and CB can be used to improve the microwave absorbing properties of polymer composites. On the basis of the consideration, we choose CIP and CB as the absorbents.

Linear low-density polyethylene (LLDPE) is one of the most versatile polymers with its low density, good processability, and low cost. LLDPE composites filled with filler possess excellent properties and can be processed easily by melt blending. Therefore, we choose LLDPE as polymer matrix for MAMs. Thus, we prepared LLDPE/CIP/CB composites. Then, we determined the microwave absorbing properties and characterized the prepared composites.

This study aims at reporting LLDPE/CIP/CB composites with microwave absorbing properties. However, to the best of our knowledge, we find that there are few reports on LLDPE/CIP/CB composites as MAMs. Therefore, this should be a meaningful work.

EXPERIMENTAL

Materials

CIP (EW) was purchased from BASF Corporation. CB (HG-1F) was supplied from Shanghai Fuhua Industrial (Shanghai, China). LLDPE (7042, melt index 2.5 g/10 min) was provided by Guangzhou Petrochemial General Factory (Guangzhou, China). Stearic acid (1801) and titanate coupling agent (TM-A9) were used as additional agents. They were supplied from Guangzhou Qisheng Chemicals (Guangzhou, China) and Yangzhou Tianyang Auxiliaries (Yangzhou, China), respectively. All materials were of commercial grade and used without any further treatment.

Preparation of composites

LLDPE composites filled with CIP and/or CB were prepared using melt blending according to the recipe. The formulation of the composites is as follows.

LLDPE: 100.0, Stearic acid: 1.0, titanate coupling agent: 1.2, CIPs: x, CB: y. For convenience, the samples of composites are represented as S-CIP(x)-CB(y), where x and y are mass parts of CIP and CB per hundred parts of LLDPE, respectively.

CIP and/or CB, stearic acid, and titanate coupling agent were blended in a mixer for 8 min, followed by the addition of LLDPE and mixing for 8 min again in order to couple CIP and/or CB and LLDPE. Then, the obtained blends were further mixed for 20 min on a twin-roll mill at 438 K. Finally, the obtained mixtures were pressed into pieces of different dimensions ($180.0 \times 180.0 \times 4.0$, $34.04 \times 72.14 \times 4.0$, $22.14 \times 47.54 \times 2.5$, $15.80 \times 34.84 \times 2.0$, $10.16 \times 22.86 \times 2.0$, and $7.90 \times 15.80 \times 2.0$ mm^3) using molds at 458 K and 10 MPa for 10 min in order to determine the microwave absorbing properties and the electromagnetic parameters.

Characterization of composites

The piece ($180.0 \times 180.0 \times 4.0$ mm^3) was used to test the microwave absorbing properties by a scalar network analyzer (Model: HP 8757E) in the range of 2–18 GHz and the arch method. The different dimension pieces of $34.04 \times 72.14 \times 4.0$, $22.14 \times 47.54 \times 2.5$, $15.80 \times 34.84 \times 2.0$, $10.16 \times 22.86 \times 2.0$, and $7.90 \times 15.80 \times 2.0$ mm^3 were used to determine the electromagnetic parameters by a vector network analyzer (Model: HP8722 ES) and the transmission/reflection method in the ranges of 2.6–3.8, 4.0–5.8, 5.9–8.1, 8.2–12.4, and 12.6–17.8 GHz, respectively. TEM images were obtained on a Transmission Electron Microscope (Model: JEM-1230).

RESULTS AND DISCUSSION

Microwave absorption properties of LLDPE composites with different CIP and/or CB contents

Figures 1–7 show the effects of frequency on reflection loss (RL) of LLDPE composites filled with CIP and/or CB. According to Figure 1, the peak value achieves −16.79 dB at 5.2 GHz and the strong absorbing ranges (RL ≤ −10 dB) are in the ranges of 3.7–6.7 GHz for the sample S-CIP(500). The bandwidth corresponding to the strong absorbing ability is 3.0 GHz. As illustrated in Figure 2, LLDPE composites loading 7 wt % CB shows the absorbing peak of −16.39 dB at 13.4 GHz, and the strong absorbing ranges are in the ranges of 11.3–16.1 GHz and the strong absorbing bandwidth is 4.8 GHz. Comparing Figure 1 with Figure 2, one can conclude that LLDPE composites filled with CIP display the absorbing peak position and the strong absorbing ranges in lower frequency than LLDPE composites filled with CB. The absorbing curve displays two peaks for the sample S-CIP(500)-CB(6), and the peak values are −17.08 dB at 6.2 GHz and –12.24 dB at 12.4 GHz. We argue that the peaks at 6.2 and 12.4 GHz come possibly from the filler CIP and CB, respectively. The samples S-CIP(500)-CB(7) and S-

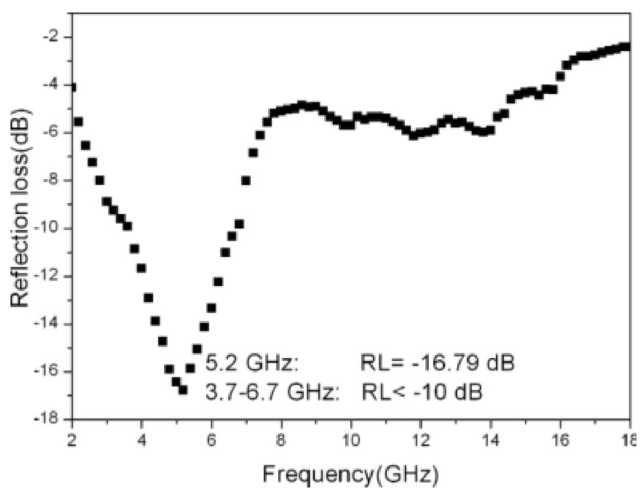

Figure 1 The effects of frequency on microwave absorbing properties of LLDPE composites filled with 500 wt % CIP.

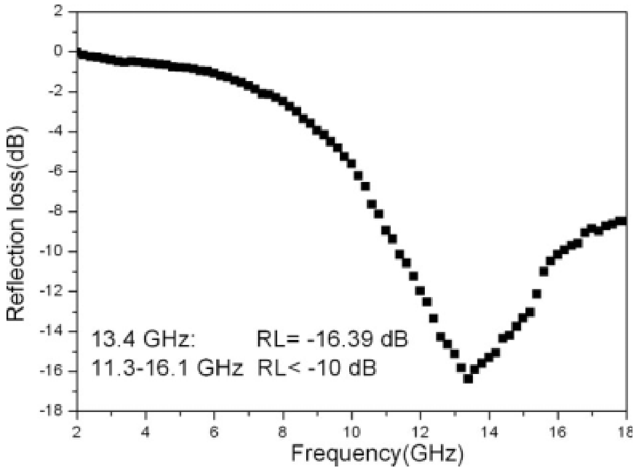

Figure 2 The effects of frequency on microwave absorbing properties of LLDPE composites filled with 7% CB.

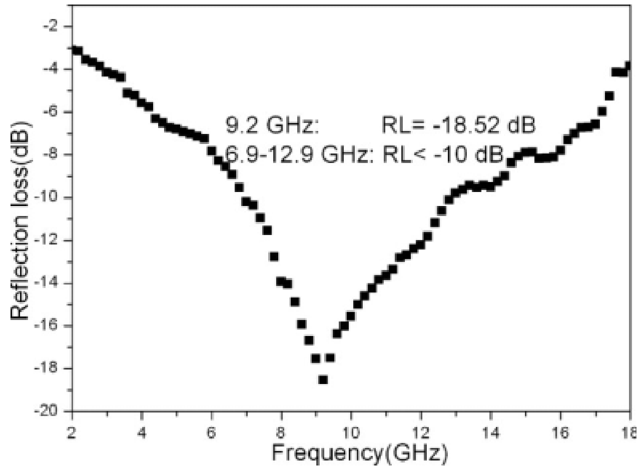

Figure 4 The effects of frequency on microwave absorbing properties of LLDPE composites filled with 500 wt % CIP and 7 wt % CB.

CIP(500)-CB(8) display the absorbing peaks of –18.52 dB at 9.2 GHz and –15.48 dB at 9.6 GHz, respectively. One can conclude that the absorbing peak positions of LLDPE/CIP/CB composites shift to high frequency ranges as CB contents in composites increase when the loading of CIP is fixed at 500 wt %. The bandwidths (RL $\leq$ –10 dB) are 4.2, 6.0, and 3.8 GHz for the samples S-CIP(500)-CB(6), S-CIP(500)-CB(7), and S-CIP(500)-CB(8). It can be seen that there are not much differences in absorbing peak values for these samples. As for the strong absorbing ranges, LLDPE composites containing 7 wt % CB is best when the loading of CIP is fixed at 500 wt %. As the sample S-CIP(500)-CB(6) displays, the samples S-CIP(400)-CB(7) shows two peaks. The peak values are –14.16 dB at 5.6 GHz and –16.11 dB at 11.6 GHz, and they are possibly from the filler CIP and CB, respectively. Comparing Figures 4, 6, and 7, one can observe that the absorbing peak positions of LLDPE/CIP/CB composites shift to low frequency ranges as CIP contents in composites increase when the loading of CB is fixed at 7 wt %. The bandwidths (RL $\leq$ –10 dB) are 5.6, 6.0, and 4.6 GHz for the samples S-CIP(400)-CB(7), S-CIP(500)-CB(7), and S-CIP(600)-CB(7). As for the strong absorbing ranges, LLDPE composites containing 500 wt % CIP is best when the loading of CB is fixed at 7 wt %. Based on the above results, the optimum formulation is at 100 : 500 : 7 (LLDPE : CIP : CB) in composites as for the bandwidths (RL $\leq$ –10 dB). In fact, on the one hand, the absorbent CIP and CB can absorb microwave. On the other hand, they can reflect microwave at the same time. The more contents of CIP and CB in the composites increase the probability of reflection of microwave. Therefore,

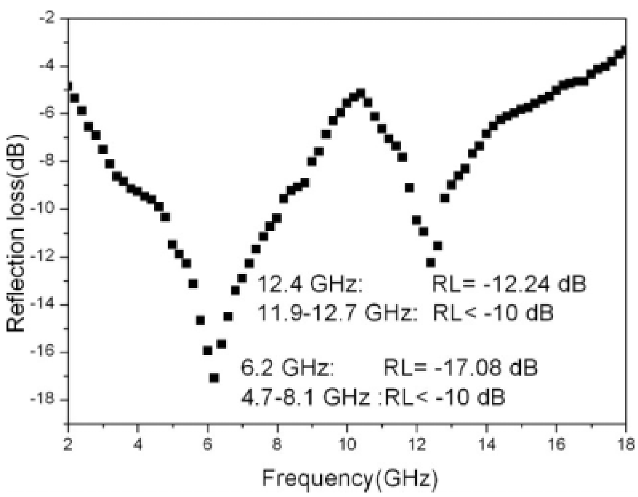

Figure 3 The effects of frequency on microwave absorbing properties of LLDPE composites filled with 500 wt % CIP and 6 wt % CB.

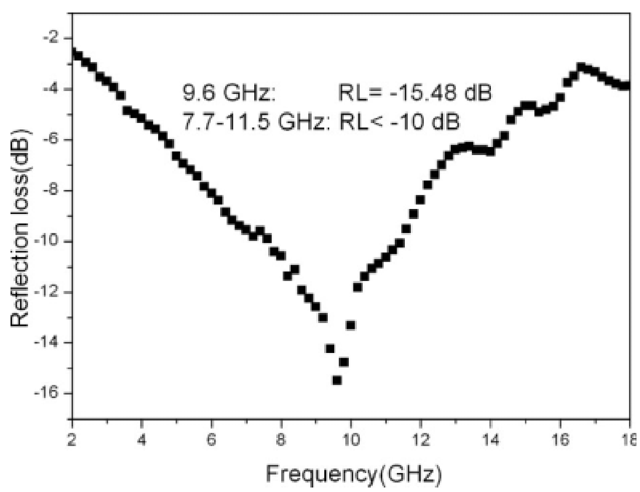

Figure 5 The effects of frequency on microwave absorbing properties of LLDPE composites filled with 500 wt % CIP and 8 wt % CB.

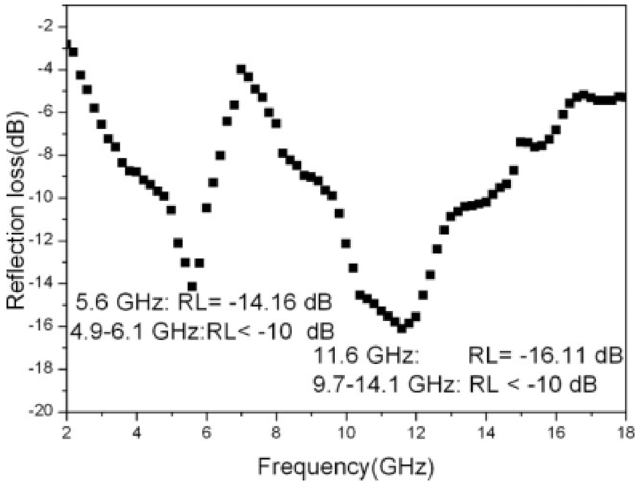

Figure 6 The effects of frequency on microwave absorbing properties of LLDPE composites filled with 400 wt % CIP and 7 wt % CB.

there is the optimum formulation in composites as for the bandwidths (RL ≤ –10 dB). It is obvious that LLDPE/CIP/CB composites can attenuate more than 90% microwave in a very wide frequency ranges. One can conclude that the strong absorption ranges can be regulated easily by changing CIP and/or CB contents in LLDPE. Comparing Figures 3–7 with Figures 1 and 2, one can conclude that the synergistic effects of CIP and CB effectively improve the microwave absorbing properties of polymer composites.

TEM morphology

Figure 8 displays the TEM images of CIP, CB, and the cross-section of the typical sample S-CIP(500)-CB(7). On the one hand, one can clearly observe CIP and the uniform distribution of CIP in composites. On the other hand, one cannot see big CB

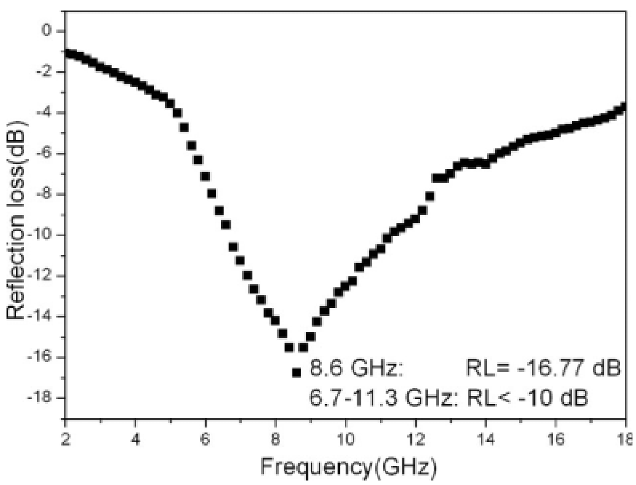

Figure 7 The effects of frequency on microwave absorbing properties of LLDPE composites filled with 600 wt % CIP and 7 wt % CB.

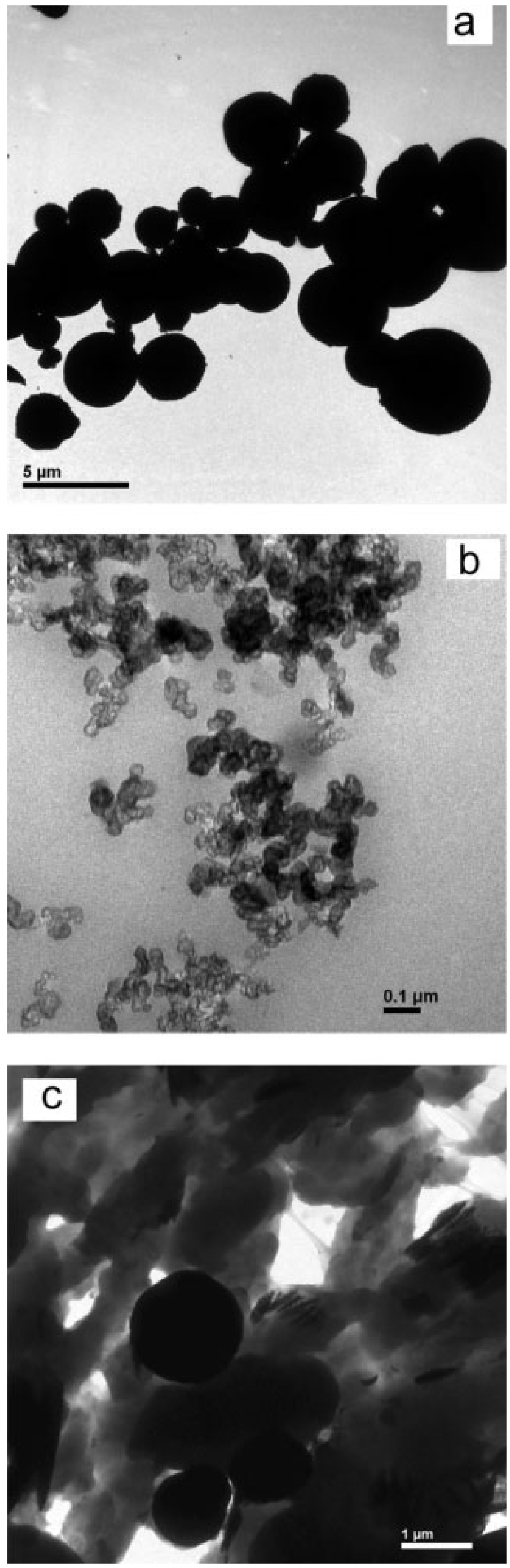

Figure 8 TEM images of CIP, CB, and the cross-section of the typical sample S-CIP(500)-CB(7): (a) CIP, (b) CB, and (c) S-CIP(500)-CB(7).

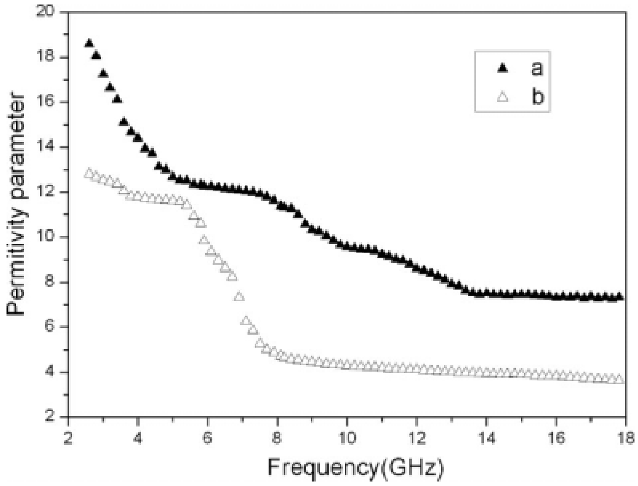

Figure 9 The effects of frequency on the complex relative permittivity of the sample S-CIP(500)-CB(7): (a) the real part and (b) the imaginary part.

agglomerates in composites. These indicate that CIP and CB were well dispersed in the polymer matrix.

Mechanism analysis

The dielectric loss and magnetic loss are responsible for the microwave absorption. To analyze the possible mechanism of microwave absorption, we tested the electromagnetic parameters of the composites S-CIP(500)-CB(7) (the complex relative permittivity $\varepsilon = \varepsilon' - j\varepsilon''$, ε' and ε'' are the real part and the imaginary part of the complex relative permittivity; the complex relative permeability $\mu = \mu' - j\mu''$, μ' and μ'' are the real part and the imaginary part of the complex relative permeability). Figure 9 depicts the effects of frequency on the complex relative permittivity of the sample S-CIP(500)-CB(7). From Figure 9, the real part of the complex relative permittivity for the sample S-CIP(500)-CB(7) changes between 18.58 and 7.26 in the range from 2.6 to 17.8 GHz. The imaginary part of the complex relative permittivity for the sample S-CIP(500)-CB(7) decreases gradually from 12.81 to 3.65 in the range from 2.6 to 17.8 GHz.

Figure 10 depicts the effects of frequency on the complex relative permeability of the sample S-CIP(500)-CB(7). As illustrated in Figure 10, the real part of the complex relative permeability for the sample S-CIP(500)-CB(7) decreases gradually from 2.51 to 1.07 in the range from 2.6 to 17.8 GHz with increasing frequency. The imaginary part of the complex relative permeability for the sample S-CIP(500)-CB(7) is between 0.68 and 0.80 in the range from 2.6 to 17.8 GHz. Therefore, one can conclude that microwave absorption of LLDPE/CIP/CB composites comes from the combined contribution of the dielectric loss and magnetic loss, which is in good agreement with the fact that CIP is magnetic metal particles and can lead to the dielectric loss and magnetic loss of polymer composites, and CB can result in the dielectric loss of polymer composites.[4,26,27]

Theoretical simulation of microwave absorbing ability

According to the transmission line theory, when a normal incident electromagnetic wave gets to a meta1-backed single-layer absorber, the electromagnetic wave will reflect and transmit on the surface of the MAMs. The reflection loss (R) of the incident electromagnetic wave is decided by the difference between the input impedance and can be calculated by,

$$R = 20\log|(Z_{in} - Z_0)/(Z_{in} + Z_0)| \quad (1)$$

where Z_0 is the characteristic impedance of free space and Z_{in} is the input impedance at the interface of free space and material. Z_0 and Z_{in} are calculated by,

$$Z_0 = \sqrt{\frac{\mu_0}{\varepsilon_0}} \quad (2)$$

$$Z_{in} = \sqrt{\frac{\mu_0\mu}{\varepsilon_0\varepsilon}}\tanh(j2\pi fd\sqrt{\mu_0\varepsilon_0\mu\varepsilon}) \quad (3)$$

where ε_0 and μ_0 are constants ($\varepsilon_0 = 8.854 \times 10^{-12}$ F/m and $\mu_0 = 4\pi \times 10^{-7}$ H/m), ε is the complex relative permittivity ($\varepsilon = \varepsilon' - j\varepsilon''$), μ is the complex relative permeability ($\mu = \mu' - j\mu''$), f is the microwave frequency, and d is the thickness of MAMs.[7,18,26,27]

With the electromagnetic parameters of the sample S-CIP(500)-CB(7) from Figures 9 and 10, we calculated the reflection loss using eqs. (1)–(3). The calculation results are shown in Figure 11. As illustrated in Figure 11, one can observe that the simulation curve displays the peak of –15.41 dB at 8.8 GHz, the reflection loss is below –10 dB in the range 7.0–13.9

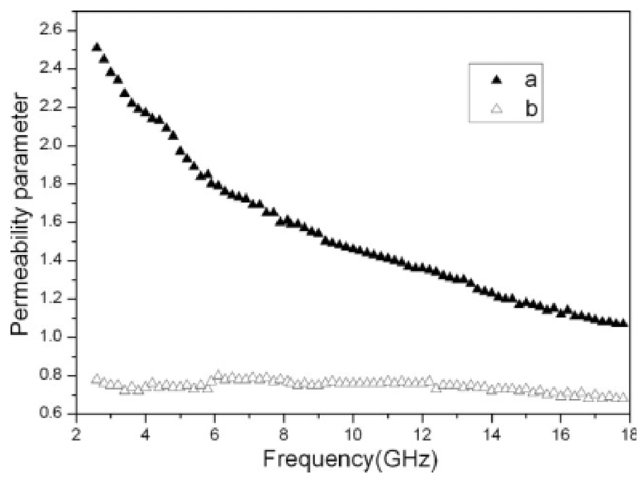

Figure 10 The effects of frequency on the complex relative permeability of the sample S-CIP(500)-CB(7): (a) the real part and (b) the imaginary part.

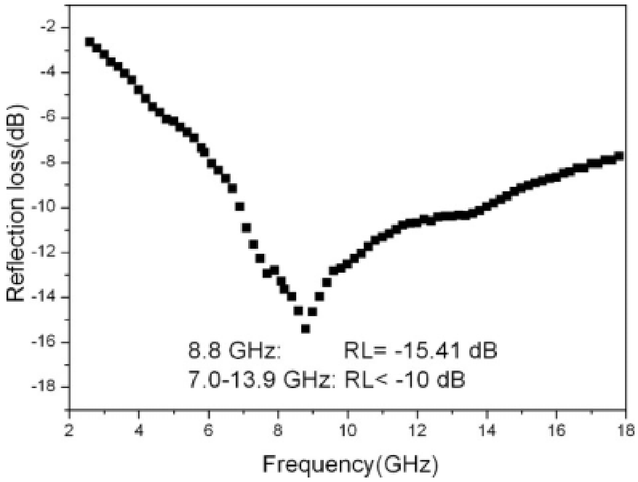

Figure 11 The theoretical calculation results of absorbing ability of the sample S-CIP(500)-CB(7).

GHz, and the bandwidth (RL $\leq$ –10 dB) is 6.9 GHz. Also, one can observe that the curve pattern is similar with Figure 4. These indicate that the theoretical calculation results of absorbing ability are in agreement with the experimental results.

CONCLUSIONS

Ternary LLDPE/CIP/CB composites were prepared by melt blending. CIP and CB are uniformly distributed in LLDPE. The CIP and CB contents have effects on absorbing properties of composites. The prepared composites exhibit excellent microwave absorbing properties. LLDPE/CIP/CB composites can absorb microwave in a very wide ranges of frequency and one can regulate the strong microwave absorbing ranges by changing CIP and/or CB contents in LLDPE. The dielectric loss and magnetic loss are responsible for the microwave absorption ability of LLDPE/CIP/CB composites. The synergistic effects of CIP and CB effectively improve the microwave absorbing properties of polymer composites.

References

1. Wang, S.; Liang, R.; Wang, B.; Zhang, C. Carbon 2009, 47, 53.
2. Chatterjee, T.; Mitchell, C. A.; Hadjiev, V. G.; Krishnamoorti, R. Adv Mater 2007, 19, 3850.
3. Sugawara, A.; Oichi, A.; Suzuki, H.; Shigesato, Y.; Kogure, T.; Kato, T. J Polym Sci Part A: Polym Chem 2006, 44, 5153.
4. Ling, Q. C.; Sun, J. Z.; Zhao, Q.; Zhou, Q. Y. J Appl Polym Sci 2009, 111, 1911.
5. Ohlan, A.; Singh, K.; Chandra, A.; Dhawan, S. K. J Appl Polym Sci 2008, 108, 2218.
6. Kim, J.-B.; Lee, S.-K.; Kim, C.-G. Compos Sci Technol 2008, 68, 2909.
7. Wu, K. H.; Ting, T. H.; Wang, G. P.; Ho, W. D.; Shih, C. C. Polym Degrad Stab 2008, 93, 483.
8. Lakshmi, K.; John, H.; Mathew, K. T.; Joseph, R.; George, K. E. Acta Mater 2009, 57, 371.
9. Håkansson, E.; Amiet, A.; Nahavandi, S.; Kaynak, A. Eur Polym J 2007, 43, 205.
10. Zou, T.; Shi, C.; Zhao, N.; Li, J.; Yang, K. Mater Sci Eng B 2007, 142, 51.
11. Motojima, S.; Hoshiya, S.; Hishikawa, Y. Carbon 2003, 41, 2658.
12. Tang, J.; Radosz, M.; Shen, Y. Macromolecules 2008, 41, 493.
13. Annadural, P.; Mallick, A. K.; Tripathy, D. K. J Appl Polym Sci 2002, 83, 145.
14. Peng, C. H.; Hwang, C. C.; Wan, J.; Tsai, J. S.; Chen, S. Y. Mater Sci Eng B 2005, 117, 27.
15. Roselena, F.; Aline, D. R.; Mauro, A. S. O.; Mirabel, C. R.; Marco, A. D. P. Polym Bull 2005, 55, 299.
16. Pinho, M. S.; Gregori, M.; Nunes, R. C. R.; Soares, B. G. Polym Degrad Stab 2001, 73, 1.
17. Dishovsky, N.; Grigorova, M. Polym Bull 2000, 35, 403.
18. Liu, Z.; Bai, G.; Huang, Y.; Li, F.; Ma, Y.; Guo, T.; He, X.; Lin, X.; Gao, H.; Chen, Y. J Phys Chem C 2007, 111, 13696.
19. Tanrattanakul, V.; Bunchuay, A. J Appl Polym Sci 2007, 105, 2036.
20. Kimura, S.; Kato, T.; Hyodo, T.; Shimizu, Y.; Egashira, M. J Magn Magn Mater 2007, 312, 181.
21. Zhao, D.-L.; Shen, Z.-M. Mater Lett 2008, 62, 3704.
22. Wang, Y.; Afsar, M. N. Microwave Opt Technol Lett 2004, 42, 458.
23. Feng, Y. B.; Qiu, T.; Shen, C. Y. J Magn Magn Mater 2007, 318, 8.
24. Wang, G.; Chen, X.; Duan, Y.; Liu, S. J Alloys Compd 2008, 454, 340.
25. Oh, J.-H.; Oh, K.-S.; Kim, C.-G.; Hong, C.-S. Compos Part B 2004, 35, 49.
26. Kwon, S. K.; Ahn, J. M.; Kim, G. H.; Chun, C. H.; Hwang, J. S.; Lee, J. H. Polym Eng Sci 2002, 42, 2165.
27. Barba, A. A.; Lamberti, G.; Amore, M.; Acierno, D. Polym Bull 2006, 57, 587.