Microwave-Absorbing Properties of Linear Low-Density Polyethylene/Ethylene–Octene Copolymer/Carbonyl Iron Powder Composites

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ABSTRACT: Using linear low-density polyethylene (LLDPE)/ethylene–octene copolymer (POE) as a polymer matrix and carbonyl iron powders (CIPs) as filler, we prepared polymer matrix composites with microwave-absorbing properties by means of melt blending. Scanning electron microscopy and transmission electron microscopy were used to characterize the samples. The absorbing properties of the composites were measured with the arch method in the range of frequency 2.0–18.0 GHz. The results indicate that the absorbing peaks moved to low frequency as the CIP content in composites increased and that there was an appropriate CIP content in LLDPE/POE/CIP composites to achieve the best absorbing effectiveness. The electromagnetic parameters of the composites were determined with the transmission/reflection method in the range 2.6–17.8 GHz. The experimental results show that there were both dielectric loss and magnetic loss in the LLDPE/POE/CIP composites. Therefore, the microwave absorption of the LLDPE/POE/CIP composites was attributed to the combining contributions of the dielectric loss and magnetic loss. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 1911–1916, 2009

Key words: composites; matrix; polyolefins

INTRODUCTION

The use of electronic devices is experiencing exponential growth at an unprecedented rate in all fields of human life, and most of these devices work in the microwave range. On the one hand, they benefit human beings and bring about convenience. On the other hand, they can radiate unwanted electromagnetic signals at the same time, which not only interfere with electromagnetically controlled systems but also can harm the health of humans.[1–3] For the purpose of eliminating and decreasing electromagnetic interference, microwave-absorbing materials (MAMs) have been devised and used to prevent or minimize reflected electromagnetic energy incident on the surfaces of materials by the dissipation of the electromagnetic waves into heat. Particularly, MAMs, which can absorb radar radiation, have been widely used for civil purposes and in self-concealing technologies for military purposes. Therefore, investigations of MAMs have attracted great interest in recent years, and many MAMs have been designed or synthesized.[4–12]

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Microwave absorption is usually realized by dielectric loss and/or magnetic loss. Most MAMs are polymer matrix composites containing microwave absorbents. Polymer matrix MAMs with matrices of poly(methyl methacrylate),[1] paraffin wax,[2] epoxy resin,[4] ethylene–propylene–diene monomer,[6] nitrile rubber,[6] polyurethane,[13] polychloroprene,[14] poly (ethylene glycol terephthalate),[15] polypropylene,[15] and polyethylene[15] have been reported by some groups. Carbonyl iron powders (CIPs) are composed of iron, carbon, nitrogen, and oxygen. With a high Curie temperatures, specific saturation magnetization intensities, and values of microwave permeability and dielectric constants, CIPs are promising microwave absorbents[16–19] and have been widely investigated and extensively used as microwave absorbents.[3,14] Feng et al.[3] fabricated single-layer MAMs composed of CIPs or barium ferrite and double-layer MAMs composed of CIPs as the first layer and barium ferrite as the second layer using ethylene–propylene–diene monomer as the matrix material; they evaluated their microwave absorption properties and indicated that the absorption band of the double-layer MAMs was obviously wider than that of the single-layer MAMs. Pinho et al.[14] prepared MAMs using polychloroprene as the matrix material and CIPs as the absorbent, investigated the effect of aging on the reflectivity measurements in the frequency range 8–16 GHz, and

TABLE I
Properties of the Resins

Resin	Grade	Density (g/cm^3)	Melt index (g/10 min)	Source
LLDPE	7402	0.918	1.2	Beijing YanShan Petrochemical Co., Ltd.
POE	8999	0.875	5.12	Dupont

pointed out that the formation of a superficial layer of iron oxide on the composites was responsible for a reduction and change in the microwave absorption toward a higher frequency.

Melt blending is one of the most conventional and practical ways of manufacturing polymer composites. Polyethylene composites filled with fillers can be processed by melt blending and can be extruded and further stretched uniaxially or biaxially to obtain polyethylene films.[20,21] Ethylene–octene copolymer (POE) is an excellent elastomer. We carried out an investigation of the performance of blends of linear low-density polyethylene (LLDPE) and POE and found that POE improved the processing properties of the LLDPE composites. In particular, we found that the functional films prepared with LLDPE/POE/filler could be conglutinated with polypropylene nonwoven fabric with the point hot-pressed composition method without adhesive, which was successfully realized in industrialization at Ningbo Shanquan Fiberglass Co., Ltd. (Ningho, China). We expected to prepare film-type composites with microwave-absorbing properties using melt blending.

To the best of our knowledge, few attempts have been made to investigate MAMs with LLDPE as a matrix. On the basis of this consideration, we carried out an investigation on the performance of blends of LLDPE and POE and succeeded in preparing MAMs that consisted of LLDPE/POE and CIPs. Therefore, this should be a meaningful work.

EXPERIMENTAL

Materials

CIPs were purchased from BASF Corp. (Ludwigshafen, Germany) The resins used in this study were LLDPE (7402) and POE (8999). The preliminary test indicated that the optimum formulation was at 88 : 12 (LLDPE/POE) for improving the processing properties of blends of polyethylene. The distinctive properties of the selected resins are summarized in Table I. Additional agents were used to improve the processing performance. The additional agents used in this study were stearic acid, aluminate–titanate coupling agent, oxidation polyethylene wax, and ethylene bisstearamide, and these were kindly provided by Ningbo Shanquan Fiberglass Co., Ltd. All chemicals were used without any further treatment.

For convenience, the sample composites was labeled S(x), where x corresponds to the mass fraction of CIPs. The formulations of the blends are listed in Table II.

Preparation

A mixer and a twin-roll mixing mill of plastics were used to manufacture the LLDPE/POE/CIP composites. CIPs were blended with stearic acid, aluminate–titanate coupling agent, oxidation polyethylene wax, and ethylene bisstearamide in mixer for 5 min. Subsequently, LLDPE and POE were fed into the mixer and commingled for 5 min. Last, the obtained blends were mixed for a further 30 min in the twin-roll mixing mill of plastics at 140°C.

To determine the microwave-absorbing performance, the complex permittivity and permeability of the prepared composites in pieces with different sizes (180.0 × 180.0 × 4.0, 34.04 × 72.14 × 4.0, 22.14 × 47.54 × 2.5, 15.80 × 34.84 × 2.0,10.16 × 22.86 × 2.0, and 7.90 × 15.80 × 2.0 mm^3) were then press-cured at 180°C under a pressure of 150 kg/cm^2.

Characterization

Scanning electron microscopy (SEM) photographs were obtained with an S-4700 scanning electron

TABLE II
Formulations of the Blends (wt %)

Ingredient	S(0)	S(200)	S(400)	S(600)
Resin[a]	100	100	100	100
CIP	0	200	400	600
Stearic acid	0.5	0.5	0.5	0.5
Aluminate–titanate coupling agent	1.1	1.1	1.1	1.1
Oxidation polyethylene wax	1.2	1.2	1.2	1.2
Ethylene bisstearamide	5.0	5.0	5.0	5.0

[a] LLDPE/POE = 88 : 12.

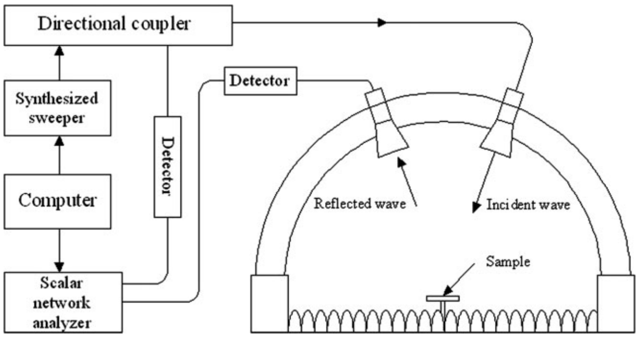

Figure 1 Schematic measurement setup for the reflection loss of LLDPE/POE/CIP composites.

microscope (Hitachi, Japan). Transmission electron microscopy (TEM) was carried out with a JEM-1230 transmission electron microscope (JEOL, Japan).

The microwave absorption properties were measured on a network analyzer system consisting of an HP83751B synthesized sweeper and an 8757E scalar network analyzer at 2–18 GHz with the arch method (Aligent, America).[22] The schematic measurement setup for the reflection loss of the LLDPE/POE/CIP composites is shown in Figure 1. The electromagnetic parameters of the composites were determined with the transmission/reflection method at 2.6–17.8 GHz with an HP8722 ES vector network analyzer (Aligent, America).[23] These tests were carried out at Beijing Institute of Aeronautical Materials.

RESULTS AND DISCUSSION

The morphology and the degree of dispersion of the CIPs in the matrix LLDPE/POE were observed by a combination of SEM and TEM. SEM images were used to observe the morphology of the CIPs and composites. Figure 2 shows the SEM images of the CIPs and the fractured cross sections of samples S(200), S(400), and S(600). From Figure 2, the average size of the CIPs could be calculated according to statistics, and the mean particle diameter was about 3.0 um. In addition, the CIPs in the composites were clearly identified, and the CIPs were well dispersed in the polymer matrix at the same time. TEM images

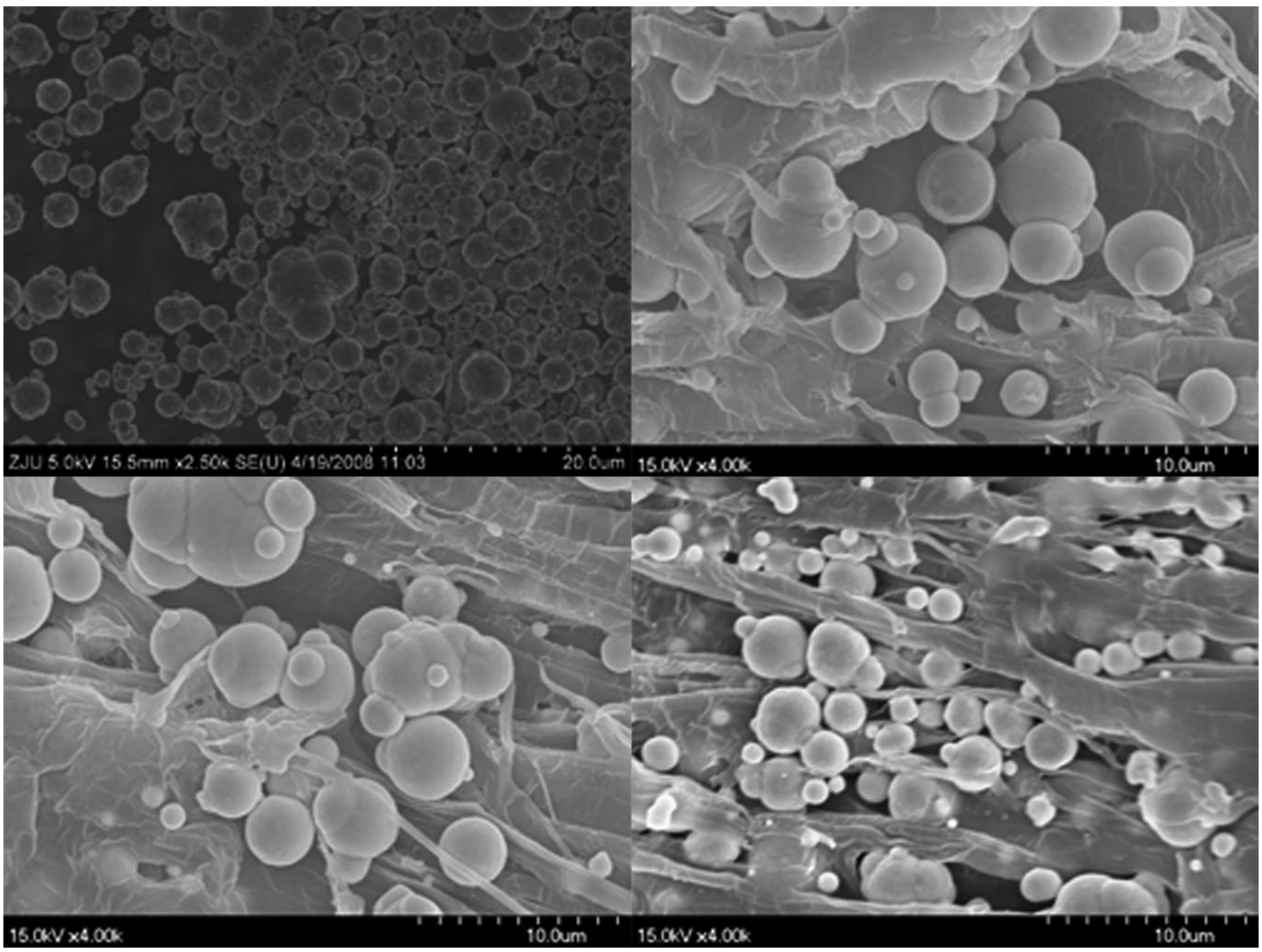

Figure 2 SEM images of the samples: CIPs (first row, left), S(200) (first row, right), S(400) (second row, left), and S(600) (second row, right).

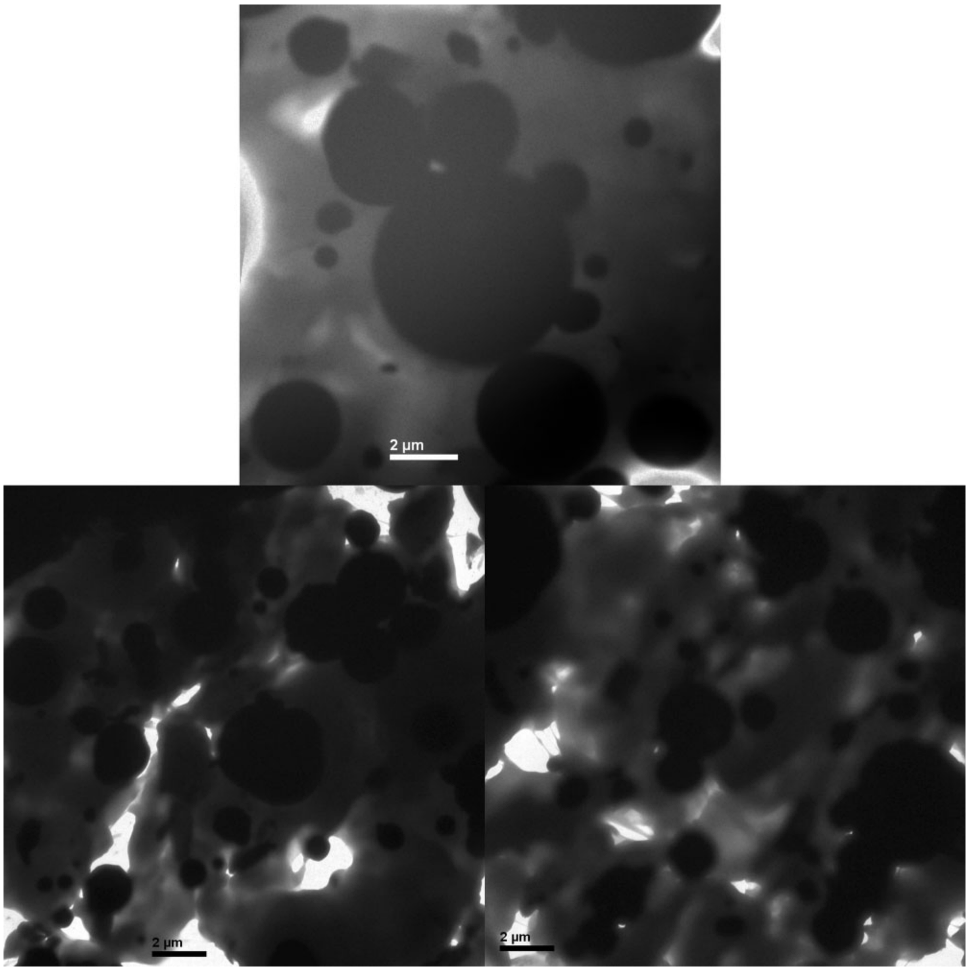

Figure 3 TEM images of the LLDPE/POE/CIP composites: S(200) (first row), S(400) (second row, left), and S(600) (second row, right).

were used to observe the degree of dispersion of the CIPs in the LLDPE/POE matrix. Figure 3 shows the TEM photographs of the fractured cross sections of samples S(200), S(400), and S(600). As illustrated in Figure 3, the dispersion of the CIPs in the LLDPE/POE polymer matrix was good, and few agglomerates presented in these samples. The results from the SEM and TEM images demonstrate that the LLDPE/POE/CIP composites were fabricated by melt blending.

Figure 4 shows the microwave-absorbing properties of the LLDPE/POE/CIP composites containing different contents of CIPs. Sample S(0) exhibited hardly any microwave absorption. The reflection loss achieved −7.13 dB at 5.4 GHz for sample S(200). When the CIP mass fraction was 400%, the minimum value was −15.75 dB at 4.4 GHz, the reflection loss of the composites was below −10 dB (90% absorption) in the range 3.5–5.4 GHz, and the bandwidth corresponding to the reflection loss below −10 dB was about 1.9 GHz. Also, the reflection loss of the composites was below −5 dB (70% absorption) in the range 2.5–18.0 GHz for sample S(400). Obviously, sample S(400) absorbed more than 70% of the microwaves in a very wide range of frequency between 2.5 and 18.0 GHz. As illustrated in Figure 4, sample S(600) showed an absorbing peak at

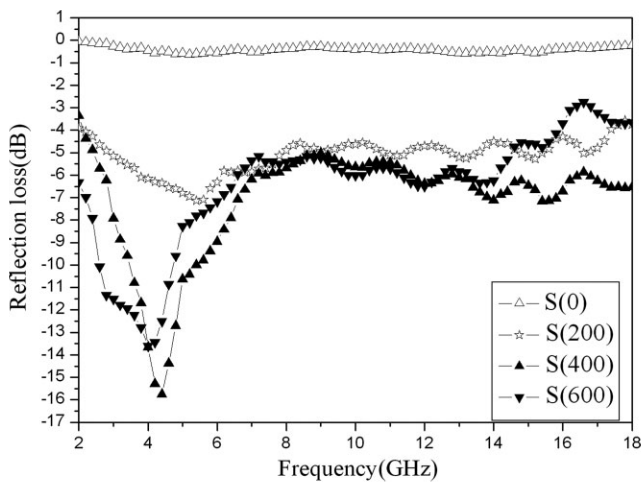

Figure 4 Microwave-absorbing properties of the LLDPE/POE/CIP composites.

4.0 GHz, and the peak value of the reflection loss was −13.61 dB. The reflection loss of the composites was below −10 dB in the range 2.5–4.7 GHz, and the bandwidth corresponding to the reflection loss below −10 dB was about 2.2 GHz. The absorbing peak value for sample S(600) (−13.61 dB) was more than that for sample S(400) (−15.75 dB). Possible reasons are that the absorbent CIPs could absorb microwaves and may have reflected microwaves at the same time, and the higher content of CIPs in the composites increased the probability of the reflection of microwaves. Therefore, the optimum concentration should be achieved to gain the best absorbing effectiveness. The absorbing peaks were at 5.4, 4.4, and 4.0 GHz for samples S(200), S(400), and S(600), respectively. Therefore, we concluded that the absorbing peaks moved to low frequency as the CIP content in the composites increased and that the LLDPE/POE composites containing 400% CIPs were excellent MAMs, which could absorb more than 90% of microwaves in the frequency range 3.5–5.4 GHz.

The electromagnetic parameters of the composites were characterized with the complex relative permittivity ($\varepsilon' - i\varepsilon''$) and the complex relative permeability ($\mu' - i\mu''$), where ε' and ε'' are the real and imaginary parts of the complex relative permittivity, respectively, and μ' and μ'' are the real and imaginary parts of the complex relative permeability, respectively. Microwave absorption may result from dielectric loss and magnetic loss.[11] To investigate the possible mechanism of microwave absorption, the complex relative permittivity and permeability were determined. Figure 5 displays the frequency dependence of the complex relative permittivity of sample S(400). As shown in Figure 5, the real part of the complex relative permittivity for sample S(400) was about 18 at 2.60 GHz and decreased gradually as the frequency increased. The value decreased to 10.92 when the frequency increased to 12.0 GHz and fluctuated between 10.84 and 10.20 from 12.2 to 17.8 GHz. As illustrated in Figure 5, ε'' for sample S(400) decreased slowly from 12.36 to 10.14 in the frequency range 2.6–5.0 GHz, decreased rapidly from 10.14 to 2.05 in the frequency range 5.0–8.4 GHz, and fluctuated between 2.05 and 1.12 from 8.4 to 17.8 GHz.

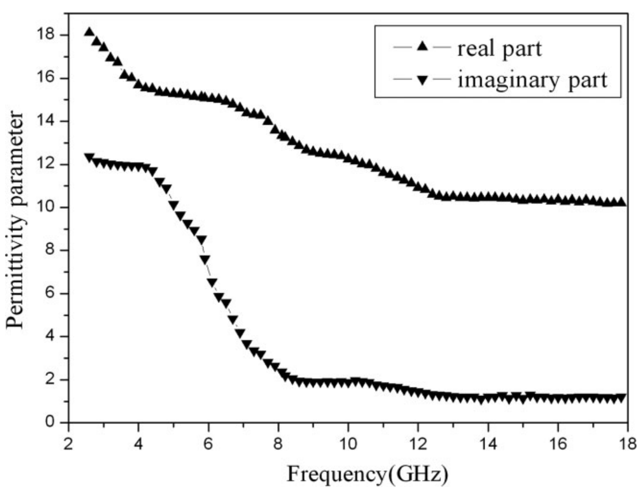

Figure 5 Frequency dependence of the complex relative permittivity of sample S(400).

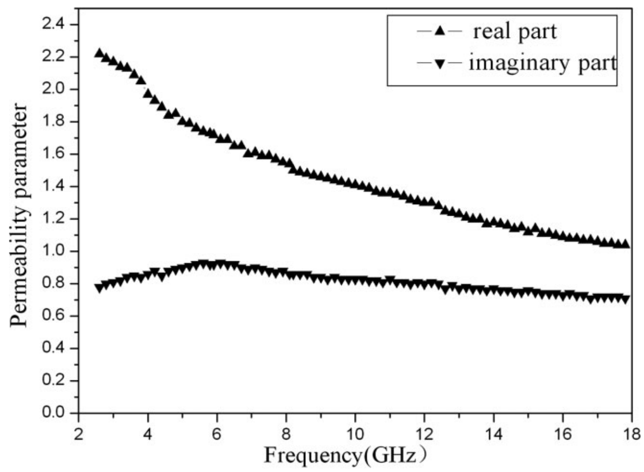

Figure 6 Frequency dependence of the complex relative permeability of sample S(400).

Figure 6 shows the frequency dependence of the complex relative permeability of sample S(400). As shown in Figure 6, the real part of the complex relative permeability for sample S(400) decreased gradually from 2.22 to 1.04 in the frequency range 2.6–17.8 GHz, and μ'' for sample S(400) hardly changed in the frequency range from 2.6 to 17.8 GHz.

The *dissipation factor* (loss tangent) is defined as the ratio of the imaginary part to the real part (the dielectric dissipation factor $\tan \delta_E = \varepsilon''/\varepsilon'$, and the magnetic dissipation factor $\tan \delta_M = \mu''/\mu'$). Figure 7 shows the frequency dependence of the dissipation factor of sample S(400). As displayed in Figure 7, $\tan \delta_E$ for sample S(400) changed between 0.11 and 0.76 from 2.6 to 17.8 GHz and showed a peak value of 0.76 at 4.2 GHz. The magnetic dissipation factor for sample S(400) increased as the frequency augmented from 2.6 to 17.8 GHz. Therefore, there were both dielectric loss and magnetic loss in the LLDPE/POE/CIP composites, which indicated that the microwave absorption of the composites was due to the combining contributions of the dielectric loss and magnetic loss. In addition, we defined the total dissipation factor as $\tan \delta_Z = \tan \delta_E + \tan \delta_M$. Tan δ_Z exhibited a peak of 1.22 at 4.2 GHz according to Figure 7, which agreed well with the results from Figure 4, in which sample S(400) showed an absorbing peak of −15.75 dB at 4.4 GHz.

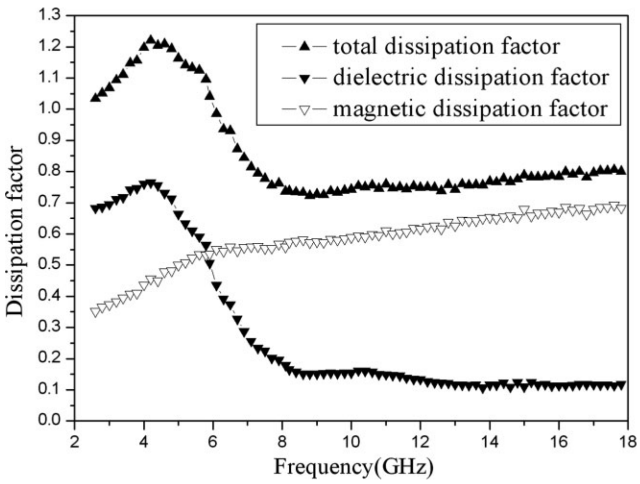

Figure 7 Frequency dependence of the dissipation factor of sample S(400).

CONCLUSIONS

LLDPE/POE matrix MAMs with CIPs as microwave absorbents were prepared, and CIPs were well dispersed in the polymer matrix. The absorbing peaks of the LLDPE/POE/CIP composites moved to low frequency as the CIP content in the composites increased. The LLDPE/POE composites containing 400% CIPs absorbed more than 70% of microwaves (−5 dB) in a very wide range of frequency between 2.5 and 18.0 GHz, achieved an absorbing peak of −15.75 dB at 4.4 GHz, and attenuated more than 90% of the microwaves (−10 dB) in the range 3.5–5.4 GHz. The bandwidth corresponding to the reflection loss below −10 dB was about 1.9 GHz. The LLDPE/POE/CIP composites were excellent MAMs, in which the dielectric loss and magnetic loss were responsible for the attenuation of microwaves. LLDPE/POE/CIP composites can be manufactured by melt blending, which is one of the most conventional and practical ways of fabricating polymer composites. Therefore, LLDPE/POE/CIP MAMs are quite promising and feasible for industrial application to MAMs.

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