STUDY OF THERMAL AND DIELECTRIC BEHAVIOR OF LOW-DENSITY POLYETHYLENE COMPOSITES REINFORCED WITH ZINC OXIDE WHISKER

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Abstract

Different scanning calorimetry and dynamic mechanical analysis are used to study the thermal behavior of composites by melt-mixing low-density polyethylene (LDPE) matrix and zinc oxide whisker (ZnO_W) fillers. Micrographs of the composites illustrate that needle or wedge shaped ZnO_W are distributed uniformly in the LDPE matrix. Dielectric properties of the composites are measured in a frequency range of 1–10 MHz. The results show that the addition of ZnO_W does not affect the melting behavior of LDPE, but has an important effect on the heat of fusion, dynamic mechanical behavior, and dielectric behavior of the composites.

Introduction

The increasing need for polymeric materials with good mechanical properties, appropriate service temperature and lower dielectric constant has led to active research in the development of new performance polymeric materials. At present, blending some functional organic or inorganic fillers could modify a lot of polymers. The process can bring out some new characteristics of polymers. Therefore, blending is a particularly interesting method to new engineering composites. Furthermore, blending gives rise to a range of properties in the final product by changing the blend compositions [1, 2].

Polyethylene with low dielectric constant can be employed in the integrating circuit field. But some static charges (namely space charges) can form in the sites of charge traps in polyethylene when it is used as electric and electronic devices [3–5]. The devices could be damaged when charges are releasing. The LDPE matrix composites reinforced with zinc oxide (ZnO), a compound semiconductor with a wide di-

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rect-band gap of 3.3 eV [6], may be a good potential candidate for such an application field. It could be expected that such composites can inhibit a great deal of accumulation of static charges.

In this paper, ZnO_w with a length of 50–100 μm is used as functional inorganic fillers. The composites with different proportions of ZnO_w filler are obtained by melt-mixing process. Many properties of the composites, such as melting behavior, heat of fusion, dynamic mechanical behavior, and dielectric behavior are studied.

Experimental

Materials

Thermoplastic matrix used in this study is low-density polyethylene with a melt index of 0.2 g min^{-1}. ZnO_w is prepared by means of a gas expanding method [7]. The mass fraction $w(ZnO_w)$ in the matrix is varied from 5 to 60%.

Preparation of composites

Filled LDPE materials are obtained by mixing LDPE grain with a certain amount of ZnO_w filler by Hakke mixer at 120°C for 10 min. Following this process, the mixture is compressed molding into plaques for 15 min at 120°C under 10 MPa (pre-pressing for 5 min at the same temperature, following by cooling to 40°C under the same pressure, with an average cooling rate of 15°C min^{-1}). Then the plaques are tailored into films in order to carry on different measurements.

Characterization

Differential scanning calorimetry

A DSC 2910 differential scanning calorimetry (TA instruments) is used to determine the melting peaking temperature (T_m) and the heat of fusion (ΔH_f) of pure LDPE and the composites. A heating rate of 10°C min^{-1} is used. All the measurements are preformed to 140°C. The whole analysis is carried out in air atmosphere.

## *Dynamic mechanical measurements*

Dynamic mechanical measurements are carried out on a DMA 2980 dynamic mechanical analyzer (TA instruments). A frequency of 10 Hz and a heating rate of 10°C min^{-1} is used. Dimensions of samples are 60×15×1 mm and analysis is carried out from –60 to 80°C.

Scanning electron microscopy

The surface morphology of the samples is observed by a scanning electron micros-
copy (SEM, Hitachi model S-450). The samples are coated with a thin layer of gold
prior to SEM observations.

Dielectric properties measurement

The dielectric constant and loss are measured by employing an HP 4192A LF
impedance meter in the frequency range of 1–10 MHz at an average voltage of 1 V
under room temperature. The sample is clamped between two metallic electrodes di-
rectly applied on it.
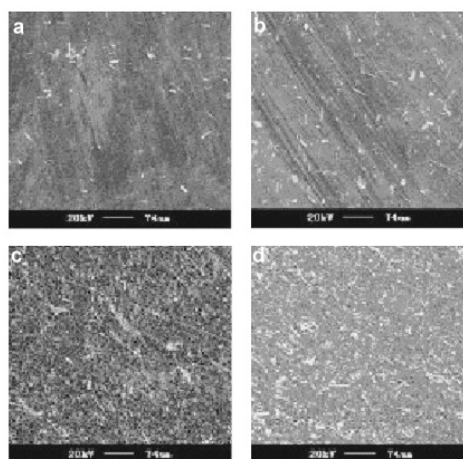
Fig. 1 SEM surface morphology of LDPE with different mass fraction of ZnO filler;
a – w(ZnO)/%: 10; b – w(ZnO)/%: 20; c – w(ZnO)/%: 50; d – w(ZnO)/%: 60
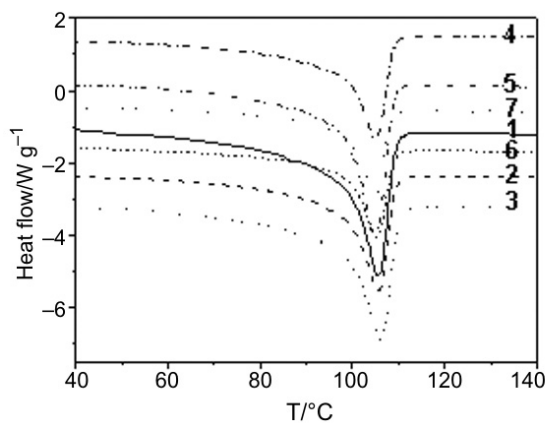
Fig. 2 DSC heating curves of ZnO/LDPE samples

Results and discussion

Figure 1a–d shows the surface morphology of the composites. From microstructural examination of the bulk samples, it is found that the distribution of ZnO_W is uniform in the LDPE matrix although they do not arrange in same direction.

Figure 2 shows the DSC curves of second heating for the pure LDPE and ZnO_w/LDPE composites, 1-pure LDPE; $w(ZnO)$/% of 2, 3, 4, 5, 6, 7 are 5, 10, 20, 30, 50, 60 respectively to determine the melting behavior of these samples, such as the onset melting temperature (T_e), the melting peaking temperature (T_m) and the heat of fusion (ΔH_f). The data obtained from DSC are shown in Table 1.

Table 1 Data obtained from the DSC curves

$w(ZnO)$/%	T_m/°C	T_e/°C	ΔH_f/J g^{-1}
0	105.7	99.0	69.5
5	105.6	98.0	68.2
10	106.2	98.4	61.2
20	105.0	98.1	58.4
30	105.0	98.3	49.5
50	105.4	98.9	33.5
60	104.8	98.6	29.4

No crystallization exotherm peak is observed in the DSC curves because of the inherent crystalline nature of the samples, though LDPE is half-crystalline state material. Figure 2 and Table 1 show negligible dependence of T_e and T_m on $w(ZnO)$. T_m is around 105°C and this temperature is just the melting point of the LDPE matrix. The small variation in the melting point can be attributed to morphological effect as reported by some researches [2, 8–9]. But there is a large difference in the heat of fusion (Table 1). ΔH_f decrease with increasing $w(ZnO)$ in the composites. The data illustrate that ΔH_f is just the endotherm of LDPE component as a matrix. The whisker dispersion in the melt and consequently the blend morphology could affect the apparent heat of fusion.

Figure 3a shows the storage modulus (E') of the composites with different proportion of ZnO_w fillers as a function of temperature. In all cases E' decrease basically with increasing temperatures. Also at any given temperature, the storage moduli increase with increasing ZnO_w filler due to enhancing of the stiffness of the matrix.

Figures 3b and 3c show the loss modulus (E'') and the loss tangent (tanδ) for the composites, respectively. Both of them increase with increasing temperature up to a peak maximum followed by a reversion with further temperature rise. The peak maximum of both E'' and tanδ show slight shift towards higher temperature which is due to compatibility and enhancement of ZnO_w fillers. Incidentally, with increasing ZnO_w fillers loading, the peak maximum of tanδ decreases and that of E'' increases. This is

also due to rising of the stiffness of the matrix and the effect of interface between the LDPE matrix and ZnO_w fillers.
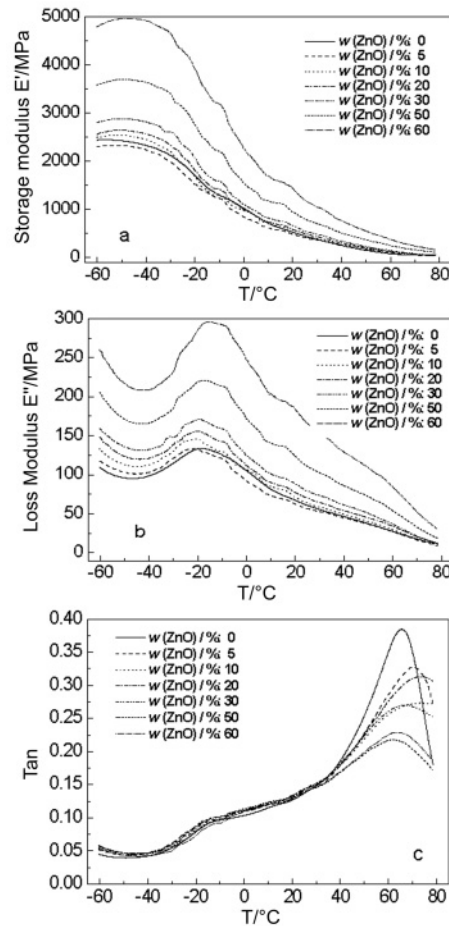
Fig. 3 Temperature dependence of storage modulus E' a – loss modulus E'' b – and tanδ c – for ZnO/LDPE samples

The dielectric constants and losses of all samples are shown in Figs 4a, b. The dielectric constants measured at 1 MHz are 2.82, 2.85, 2.89, 3.38, 4.18 and 4.58 for w(ZnO) 5, 10, 20, 30, 50 and 60% composites, respectively. The dielectric losses are 0.002, 0.0025, 0.0038, 0.006, 0.0112 and 0.0133 for these films. For the LDPE matrix, dielectric constant remains about 2.5 and dielectric loss is 0.0032 at 25°C. Then the dielectric constants and losses of the composites almost keep stable when the measured frequency is up to about 3 MHz. However, both of them increase with the frequency. The reason is that ZnO is a polar molecular. When a high frequency alternative current (AC) field is applied, ZnO molecular is in polarization. The polariza-

tion is quick and consumes a great deal of energy. The composites in this study can be employed in an integrated circuit field, which needs some lower dielectric constant materials [10].
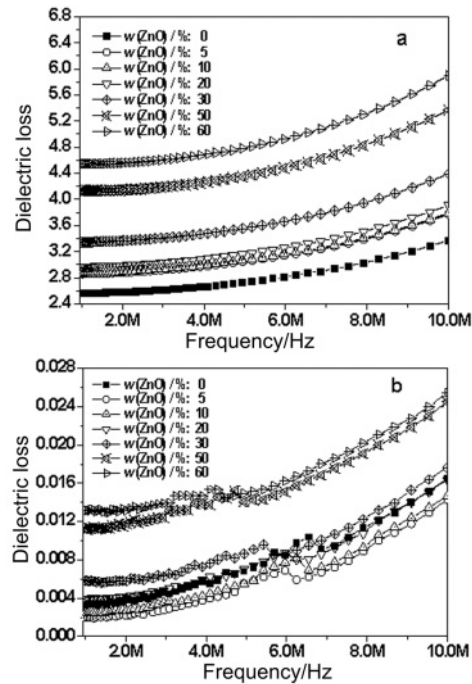

Fig. 4 Frequency dependence of dielectric constants a – and losses b –for ZnO/LDPE samples

Conclusions

The addition of ZnOw filler does not affect the melting behavior of LDPE when blended with it. But it plays an important effect on the heat of fusion of the composites. The heat of fusion decreases with an increasing of ZnOw fillers.

ZnO_w affects the storage modulus, loss modulus and tanδ of all samples. With an increase of ZnO_w fillers, the storage modulus and the peak maximum of E'' increase, then the peak maximum of tanδ decrease. This is also due to the rise of the stiffness of the matrix and the effect of interface between LDPE matrix and ZnO_w fillers.

The dielectric constants and losses increase with an increasing ZnO_w contents. Though the composites have the higher dielectric constant, the constants are still lower in an integrated circuit field.

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