

Morphology and Electrical Properties of Carbon Black Filled LLDPE/EMA Composites

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ABSTRACT: The morphology and electrical properties of linear low density polyethylene (LLDPE)/poly (ethylene-methyl arylate) (EMA) blends filled with carbon black (CB) are investigated in this work. Comparing to LLDPE/CB composite, the higher percolation threshold of EMA/CB composite is attributed to the good interaction between EMA and CB. However, carbon black is found to locate preferentially in the LLDPE phase of LLDPE/EMA immiscible blends from the characterization of SEM and electrical properties, which greatly decreases the percolation

threshold of the composites. The viscosity of the two polymers is the key factor to determine the distribution of CB instead of interfacial energy in this system. This suggests a method to control the distribution of CB in the immiscible blends by choosing the viscosity ratio of polymer blend. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 487–492, 2007

Key words: carbon black; immiscible blend; LLDPE; PTC effect; conductivity; ethylene-methyl arylate

INTRODUCTION

Conductive polymer composites have been widely used in many fields, such as electrostatic dissipation, self-heating materials, and overcurrent protectors. Most important of which is the composites with positive temperature coefficient of resistance (PTC, defined as the ratio of maximum resistivity to the resistivity at room temperature) used for overcurrent protector in electric circuit.^{1,2} Typically, the most popular conductive particles are chosen to be carbon fiber, metallic powder, and carbon black (CB). CB is more popular due to its low price and good electric properties. However, it is often required a rather high CB concentration to achieve reasonable electrical conductivity, giving a result of increasing melt viscosity and decreasing processability properties of composites. One of the tendencies to solve this problem is developing multicomponent polymer blends as composite matrix.^{3,4} The conductivities of these composites are influenced by the distribution of CB in the composites and the phase morphology of the composites.⁵ There are two types of distribution of CB in the composites. First, CB is distributed predominantly in one phase of the blend.^{6,7} Especially, when CB preferentially

located in the continuous phase of two polymers, CB-filled phase became conductive after the CB concentration reached the percolation level in that phase, which is referred as "double-percolation" effect.⁸ Second, the conductive particles mainly locate at the interface of the two-phase polymer blends,^{9,10} however no electric properties have been evaluated for these composites with interfacial distribution of CB. There are many factors that influence the distribution of CB in the blend, such as the affinity of CB to different polymers, the interfacial tension between polymers, mixing kinetics, and viscosity ratio of the polymer components. According to the study of Sumita et al.¹¹ on the HDPE/PP, HDPE/PMMA, and PP/PMMA systems, a simple model from the interactions energy is suggested to predict the distribution of CB, and CB is found to readily locate in the more affinity phase. But, in this model, the viscosity factor is ignored by using the polymers with comparable viscosities. Chan and coworkers¹² studied CB-filled non-polar PP/PMMA system, and found that with the different melt viscosity ratio of two polymers, CB would preferentially distributed in the comparatively low viscosity phase. Above all, the interaction between CB and polymer and the viscosity of polymers are considered independently on the distribution of CB. There is no clear idea as to which factor is the dominant one. Therefore, the nonpolar LLDPE and polar EMA are chosen to be matrix polymers to check the effect of the CB/polymer interaction and polymer viscosities.

Meanwhile, LLDPE is suitable for manufacturing the conductive polymer composites due to its excel-

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lent processability, mechanical property, and stability. EMA with polar function group MA (methyl acrylate), is immiscible with LLDPE phase.¹³ CB would locate heterogeneously in this incompatible blend, which could tremendously decrease the filling amount of CB with reasonable electrical properties and other acquiring abilities. The objective of this study is to focus on the selective distribution of CB in the immiscible blends of LLDPE/EMA, and the correlation between the volume resistivity and phase morphology of the composites.

EXPERIMENTAL

Materials

The materials used in this study are all commercial products. LLDPE (Dowlex 2047AC) is obtained from the Dow Chemical (Michigan). Its density is 0.917 g/cm³ and MFI (melting flow index) is 2.3 g/10 min (190°C, 2.16 kg). EMA (Optema TC115, density = 0.937 g/cm³, MFI = 0.7 g/10 min (190°C, 2.16 kg), and MA content = 16.5%) is supplied by Exxon Mobil (Texas). Carbon black (CB) (Vulcan XC200), a conductive grade by Cabot Corp., is used in this work.

Sample preparation

All the raw materials are vacuum-dried at 85°C for 8 h to remove the water. After that, LLDPE and EMA are mixed simultaneously in HAAKE Rheocord 90 Mixer. When the torque of mixer reached an equilibrium value, certain amount of CB is added to mix with the melting polymer blends for 15 min. Weight ratio is used in all the samples. In all the processes, the speed and temperature for HAAKE Rheocord 90 mixer are set in 30 rpm/min and at 160°C. The blends are then compressed into 1 mm thick sheet by a hot compression at 160°C under the pressure of 10 MPa for 10 min. The samples are coated immediately with two copper electrodes to decrease interfacial resistance, and then cooled under the same pressure of hot compression in the air to room temperature, cutting the sample about 10 × 10 × 1 mm³ in size. The sheet sample is maintained in oven at 85°C for 8 h to release residual thermal stress before the subsequent measurements.

The composites are crosslinked by irradiation with electron beam in air at room temperature to eliminate the NTC effect (negative temperature coefficient), and the radiation dose is 150 KGy. To avoid the postradiation effects, the irradiated sample should be held for overnight before measurement.

The measurement of sample

The viscosity of pure LLDPE and EMA is measured by the rotational rheometer (Bohlin Gemini 200 HR),

using a small amplitude oscillatory shear flow in the linear viscoelastisty regime at the strain of 5%. Measurements are made in the range 0.01–100 rad/s.

Electrical resistance of these composite samples is measured by a four-point probe apparatus, and the relationship between the temperature and resistance is measured progressively by elevated temperature with the heating rate of 2°C/min. The resistance can be converted to resistivity or conductivity according to the equation

$$\sigma = \frac{1}{\rho} = \frac{L}{R \times S}$$

where R is the resistance, ρ is the resistivity, σ is the conductivity, S is the area of cross section, and L is the thickness of samples.

The microstructures are analyzed by scanning electron microscopy (SEM). A SEM by Hitachi (model S-2150) and a field emission scanning electron microscope (FESEM by JEOL, model JSM-7401F) are used to characterize the morphology. All the specimens are fractured in liquid nitrogen and gold-sputtered before observation.

RESULTS AND DISCUSSION

The distribution of CB and morphology of the blends

Figure 1 shows the phase morphology of LLDPE/EMA blends without CB. LLDPE/EMA blends without CB exhibit an expected two-phase morphology that has also been found in other immiscible blends.¹⁴

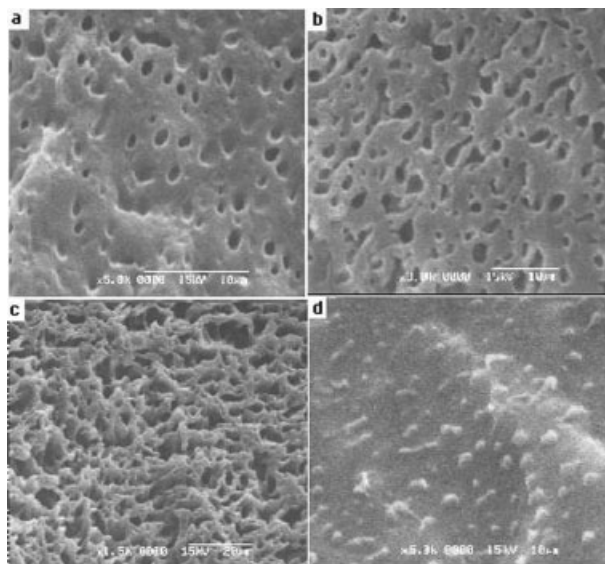


Figure 1 The morphology of LLDPE/EMA blends without CB: (a) LLDPE/EMA (80/20, EMA etched); (b) LLDPE/EMA (60/40, EMA etched); (c) LLDPE/EMA (40/60, EMA etched); (d) LLDPE/EMA (30/70).

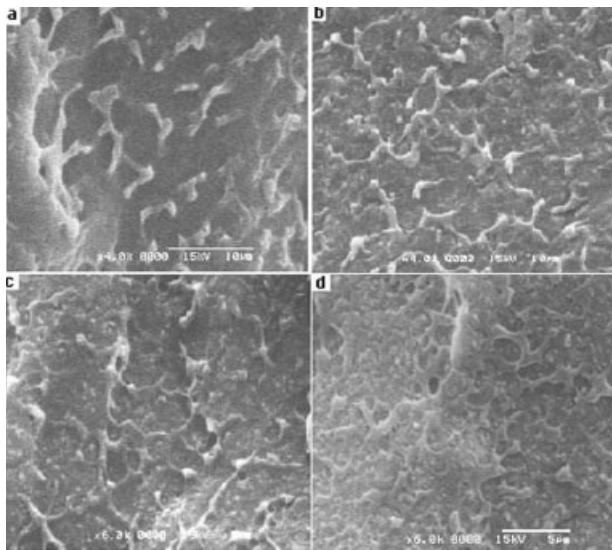


Figure 2 The SEM of LLDPE/EMA (60/40) with no CB-filled and different CB content: (a) No CB; (b) CB 2.91 wt %; (c) CB 7.40 wt %; (d) CB 13.04 wt %.

Four compositions are shown in Figure 1, and EMA is etched by chloroform at the temperature of 50°C in 80/20, 60/40, and 40/60 blends. It is clear that the morphology of the LLDPE/EMA varies with the weight ratio of two polymers. For 80/20 blend, LLDPE form as the continuous phase and EMA separates as droplets. Increasing the weight fraction of EMA results in a coarser morphology. Further increase in the amount of EMA produces a cocontinuous structure (40/60 blend). After this, the phase inversion happens and EMA serves as the continuous phase, as shown in Figure 1(d).

The morphologies of the CB-filled composites are shown in Figures 2 and 3. The morphology of LLDPE/EMA (60/40), which described in Figure 2, did not change greatly with the addition of CB. When the CB content is gradually close to the percolation value, the CB aggregates are clearly presented in the matrix by SEM micrograph and an apparent “conductive network” is illustrated in Figure 2(d), as confirmed by the experimental percolation threshold in

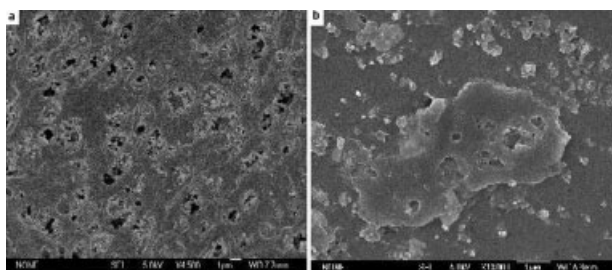


Figure 3 The SEM of LLDPE/EMA (80/20) with different CB content: (a) CB 4.71 wt % (EMA etched by chloroform); (b) CB 9.09 wt %.

Figure 4. However, it is hard to judge whether there are any CB in the droplet phase from Figure 2. A FESEM is used to see the distribution of CB in two phases under a smaller scale. The microstructures of LLDPE/EMA (80/20) blends containing 4.71 and 9.09 wt % CB are shown in Figure 3. Obviously, the particle size of EMA phase is about 1–2 μm. It is clear that CB is mainly dispersed in the matrix and only a little bit of CB can be found in the droplet. As the CB content increases, CB particles fuse into primary aggregates, and van der Waals forces cause these aggregates to join in more loosely assembled agglomerates,¹⁵ as could be seen from Figures 2(c,d) and 3(b). Size of single CB particle is less than 100 nm, and the CB agglomerates is ~500 nm or above. From the observations for the LLDPE/EMA blends, it is found that the preferential location of CB is not in the polymer of higher percolation threshold as commonly reported.¹⁶ The affinity or interaction of CB to EMA, which is also a key factor to determine the distribution of CB in immiscible blends, is just available when the melt viscosities of the two polymers are comparable.¹⁷ In our system, the melting viscosities of LLDPE and EMA differ greatly from each other, as shown by the complex viscosity in Figure 4. LLDPE exhibits smaller viscosity than EMA over a wide range of shear rate.

Especially, at the fixed rotator speed of 30 rpm/min that used in the melt mixing process, the corresponding mean shear rate at this rotator speed can be estimated by the following equation:¹⁸

$$\dot{\gamma} = 2\pi N / \ln(\beta) \text{ and } \beta = R_e / R_i$$

where $\dot{\gamma}$ is the shear rate, N is the rotator speed (30 rpm/min), R_e is the radius of mixer wall, R_i is the radius of rotator, and in here, β is about 2 for the rotator used here. The shear rate is about 4.5 s⁻¹. The viscosity ratio between LLDPE and EMA is about 1.72 under

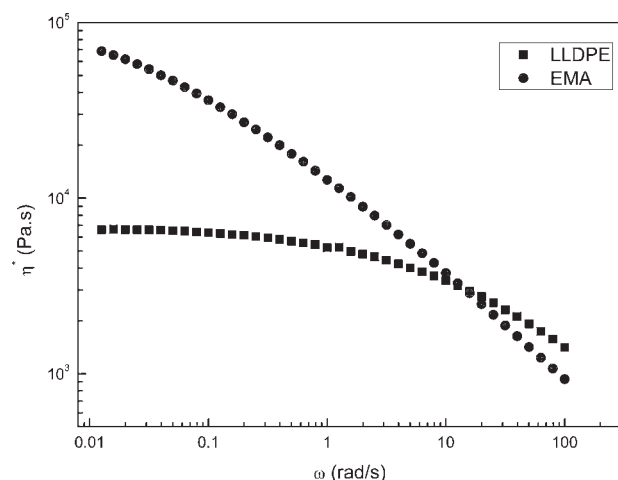


Figure 4 The complex viscosity of pure LLDPE and EMA at the temperature 160°C.

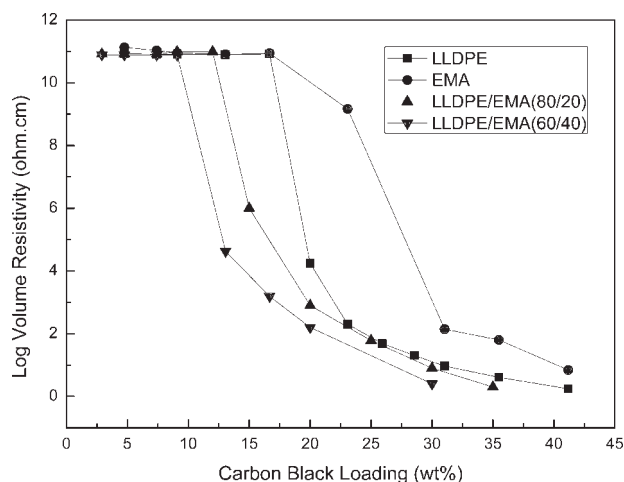


Figure 5 The curves of volume resistivity versus CB content for different LLDPE/EMA weight variation.

such shear rate. The melt viscosity difference between two polymers make CB more easily locate in the less viscous LLDPE phase, instead of more viscous EMA phase. This is consistent when compared with the results of Narkis and coworkers.¹⁹ Therefore, it is possible to control the distribution of CB in a specific phase of blend by changing the viscosities of polymers. The affinity between CB and polymers could be important when the viscosities of two polymers are comparable.

The electrical properties of the composites

The dependence of the volume resistivity of CB/polymers on CB concentration is clearly elucidated in Figure 5. The electrical resistivity of the entire samples decreases dramatically when the CB content reaches percolation threshold. The percolation threshold of CB/LLDPE is ~ 20 wt % CB content, while the EMA exhibit percolation value at higher CB content about 32 wt % CB loading. The percolation thresholds of CB-filled LLDPE/EMA systems are much lower than that of both LLDPE and EMA, and the thresholds decrease with the increase of EMA concentration. The blends LLDPE/EMA (60/40) just with 13.04 wt % CB could form conductive network and the blends LLDPE/EMA (80/20) composition needs about 16.66 wt % CB to percolate. It is not difficult to understand that the CB/EMA composite have higher percolation threshold than CB/LLDPE system. The strong absorption between MA functional group of EMA and CB could partly prevent the flocculation of CB aggregates, which propelled CB uniform distribution and also difficult to aggregate the conductive network at low CB loading. For CB/EMA composites, the well interaction or affinity between EMA and CB made CB more evenly dispersed in the matrix and higher concentra-

tion of CB are needed for the conducting network formation, when compared with the CB/LLDPE systems. This is similar to the experiments by Tchoudakov et al.²⁰ on the systems of PP/PC and a copolyamide 6/6-9, where the good interaction between CB and nylon 6 reduced the contact between CB particles to form conductive network until a higher concentration is reached.

The immiscible LLDPE/EMA blends percolate at lower CB concentration than pure LLDPE and EMA, which means that the conductive network of CB can form at lower concentration. It is known from the morphological observation that CB is mainly distributed in LLDPE. Before the phase inversion, the more EMA entering in the systems, the less CB is needed to form conductive network. This is also called the "double-percolation phenomena." In fact, a simple method to verify the distribution of CB is to plot the resistivity versus the effective concentration in the conductive phase. According to a study of Sumita et al.,²¹ the resistivity versus volume fraction of CB/HDPE are found to be similar when compared with the plot of CB/HDPE/PP blends by using effective CB concentration in the HDPE phase. Since CB is known to locate in LLDPE, we define the effect CB concentration as

$$CB_{eff}\% = \frac{\text{Weight}(CB)}{\text{Weight}(LLDPE)}$$

Figure 6 shows that the curves of LLDPE/EMA blends using effective CB concentration in the LLDPE phase are very close to that of CB/LLDPE system, which implies that the majority of CB locates in the LLDPE phase. This comparison is consistent with scanning electron micrographs (SEM) too, which illustrated that CB is distributed within the LLDPE phase.

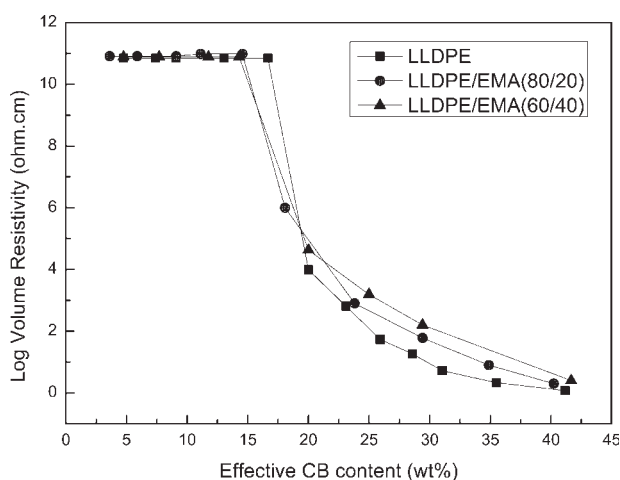


Figure 6 The plot of the effective resistivity on the effective CB concentration in LLDPE and LLDPE/EMA systems.

The curves of LLDPE/EMA (80/20) and (60/40) deviate a little from the CB filled pure LLDPE, especially after the percolation value. This could be attributed to the incomplete distribution of CB in LLDPE phase in the composite since a very small part of CB can still be found in the EMA phase.

Figure 7 shows the PTC behaviors of CB-filled composites. The PTC intensities of LLDPE, LLDPE/EMA (80/20), and LLDPE/EMA (60/40) are not influenced by the mixing of EMA phase, because most CB are comprised in LLDPE. The physical properties of LLDPE would determine PTC curves of the composites. For LLDPE/EMA (20/80), the PTC point turns to the EMA melt point, as a result of the most CB distributed in the EMA, because EMA transformed to continuous phase and the dispersed phase LLDPE had not enough capacity to adopt the over CB as energy barrel at the 30 wt % CB concentration. No double PTC effect is observed for all the samples, which imply that the CB distribute mainly in one phase while not the two phase.²²

The conductivity of CB filled LLDPE/EMA blends are determined by the continuity of the CB-rich phase, as seen in Figure 8. The value of resistivity begins first to descend with EMA content, reaching a minimum value at the EMA addition of about 40 wt %, and then the resistivity ascends with further increase in the content of EMA. As discussed earlier, CB first disperses in the LLDPE phase with low fraction of EMA. When the EMA content increases, the effective CB in LLDPE will be higher; this will be beneficial to the conductivity of the immiscible systems. But, further addition of EMA phase would induce the phase inversion, meaning that the continuity of LLDPE disrupted and EMA became continuous phase. The conductivity of the conductive immiscible blends is mostly influenced by the two factors: the distribution of CB and the continuity of the CB-rich phase.

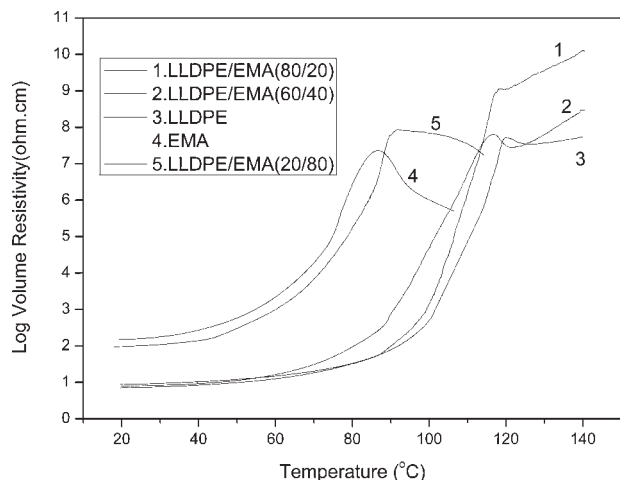


Figure 7 The function of log volume resistivity and temperature (the CB weight fraction is 30 wt %).

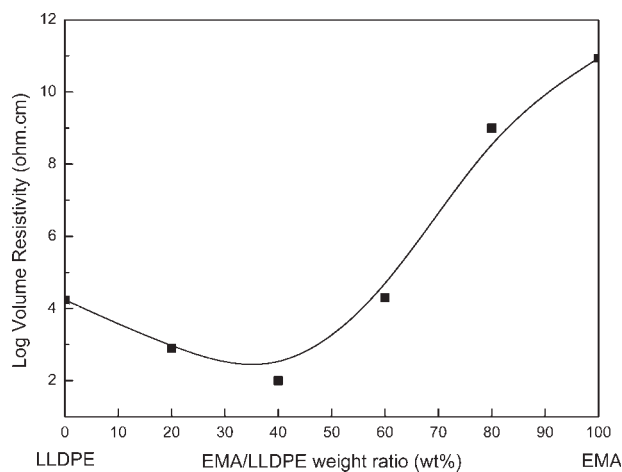


Figure 8 The relationship between the volume resistivity and EMA/LLDPE weight ratio when containing 30 wt % CB.

CONCLUSIONS

In the work, the polar polymer EMA and the nonpolar polymer LLDPE are employed to compose the immiscible blends. CB is found to be selectively distributed in the LLDPE/EMA blend. Both the characterization of SEM micrographs and the electrical properties confirm that CB mainly locates in the LLDPE phase. The selective distribution of CB in the nonpolar LLDPE phase is due to the lower viscosity of LLDPE when compared with EMA, although the interaction or interfacial energy between CB and EMA is stronger than that between CB and LLDPE. Therefore, among all the factors affecting the distribution of CB, the melt viscosity of the components will contribute greatly to CB's location and CB prefers to stay in the low viscosity phase. The interfacial energy of particles/polymer would be of considerable importance just when the viscosities of the two polymers are comparable.

The percolation threshold of CB-filled LLDPE/EMA systems is much lower than the CB-filled pure LLDPE or EMA due to the comparatively high effective CB concentration in LLDPE phase. Room resistivity changes with the concentration of EMA in LLDPE/EMA. The PTC intensity of the LLDPE/EMA/CB composites does not decrease with the addition of EMA, and no double PTC effect is found in all the composites. Therefore, it is possible to control the CB dispersion by changing the viscosity ratio of polymer blend. The selective CB distribution is believed to decrease the percolation value without loss of the conductivity of the composites.

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