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Dispersion of fillers and the electrical conductivity of polymer blends filled with carbon black

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Abstract

Dispersion state of carbon black(CB) was studied in polymer blends which are incompatible with each other. It was found that CB distributes unevenly in each component of the polymer blend. There are two types of distribution. (1) One is almost predominantly distributed in one phase of the blend matrix, and in this phase fillers are relatively homogeneously distributed in the same manner as a single polymer composite. (2) In the second, the filler distribution concentrates at interface of two polymers. As long as the viscosities of two polymers are comparable, interfacial energy is the main factor determining uneven distribution of fillers in polymer blend matrices. This heterogeneous dispersion of conductive fillers has much effect on the electrical conductivity of CB filled polymer blends. The electrical conductivity of CB filled polymer blends is determined by two factors. One is concentration of CB in the filler rich phase and the other is phase continuity of this phase. These double percolations affect conductivity of conductive particle filled polymer blends.

Introduction

It has been known that the electrical conductivity of insulating polymers filled with conducting particles, such as carbon powder, discontinuously increases at a particular content ratio of filler to polymer.1)-10) This sharp break in the relationship between the filler content and the conductivity of composites implies some sudden change in the dispersal state of conducting particles,i.e., the coagulation of particles to form conducting networks which facilitate the electrical conduction through the composites. This phenomenon of percolation and critical volume fraction is called the percolation threshold.11)-12) In our studies about conductive polymer composites, the dispersion state of particles was found to be affected by such factors as surface energy 8) and viscosity of polymers,9) and the size of the filler particles.10) In the matrix of polymer blends which are incompatible with each other, added filler distributes unevenly to each component of the polymer blend. The aim of this study is to make clear the mechanism of this heterogeneous distribution of fillers and the effect of this distribution on the electrical properties of composites.

Experimental

1. Composite sample preparation

Three kinds of polymer,i.e., high density polyethylene(HDPE), polypropylene(PP) and poly(methyl methacrylate) (PMMA) were used as polymer samples. From these polymers, three kinds of polymer blends, i.e, HDPE/PP, PP/PMMA and HDPE/PMMA were used as blend matrices. Carbon black, Furnace black, Seast 300, 27 nm in diameter was used as a filler. Polymers were first blended and kneaded by a mixing roller and the filler was then added to the kneaded mixtures. Then, kneading was conducted for 15 minutes from the point of completion of the addition. Kneading temperature was 190°C. The kneaded sample was set in a predetermined mold. The sample was molten for 5 min at 190°C and then pressed in for 1 min. The samples were then cooled to obtain films about 0.5 mm thick. Polymer samples and preparation conditions of composites are listed in Table 1.

2. Electrical conduction measurements

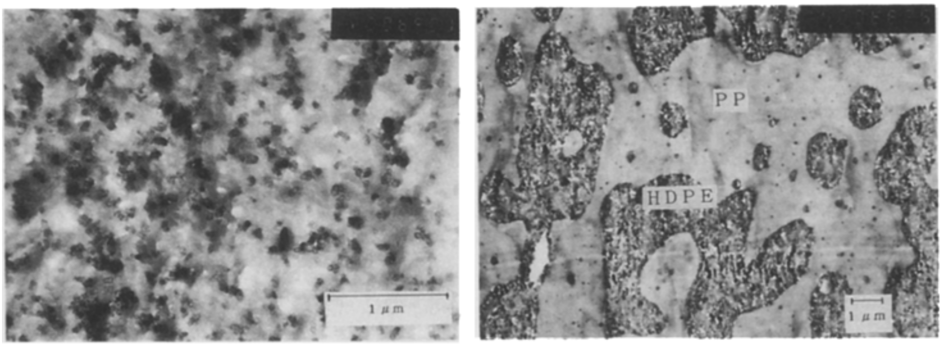
The electrical conductivity was measured through the vertical thickness of the composite films. Silver paste was used to ensure good contact of the sample surface with the electrodes of the conduction tester. The electrical conductivity of the samples varied over a wide range from $10^{-18}\ \Omega^{-1}\text{cm}^{-1} \sim 10^{-2}\Omega^{-1}\text{cm}^{-1}$. Low conductivity samples were measured under 2.5 KV/cm and 5.5 KV/cm using a Takeda Riken TR-84M vibrating reed electrometer, while high conductivity samples were measured by using TOA digital meter model DMM-120A under 10 V/cm and 15 V/cm.

Results and Discussion

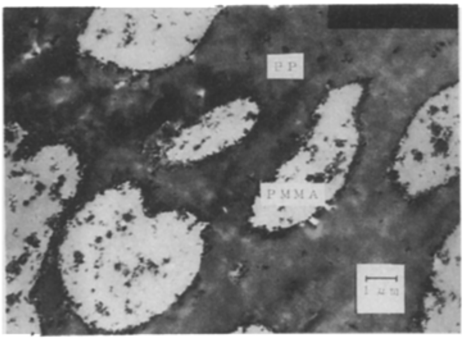
Fig.1 shows transmission electron microscope(TEM) photograph of carbon black(CB) filled polymer and polymer blends. Fig.1(a) is for HDPE and Fig.1(b),(c) are for HDPE/PP, PMMA/PP matrices. From the observation of TEM, in HDPE/PP blend, the majority of CB particles were distributed in the HDPE phase, and within this phase CB particles are relatively

Table 1. Polymer samples and preparation conditions of composites

Polymer	Grade	Mixing Temp.(time)	Molding Temp.(time)
HDPE	Sholex F5012M (Showa Denko Co.)	190°C (15min)	190°C (1min)
PP	Shoaromer MA210(Showa Denko Co.)	190°C (15min)	190°C (1min)
PMMA	MF (Mitubishi Rayon Co.)	190°C (15min)	190°C (1min)



(a)HDPE (b)HDPE/PP



(c)PP/PMMA

Fig.1 TEM photograph of CB filled polymer and polymer blend

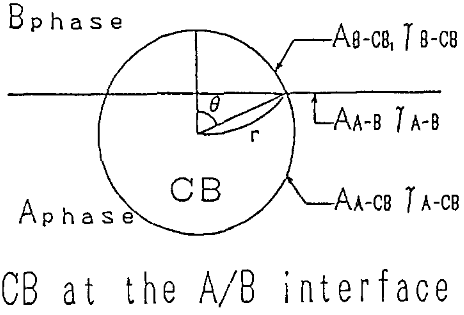


Fig.2 Schematic interpretation of carbon black at the A/B interface.

homogeneously dispersed like the HDPE one phase matrix in Fig.1(a). However, for the PMMA/PP blend, the majority of CB particles distributed in the PMMA phase and especially at the interface of the two polymers. Namely, an envelope formation of CB particles is seen around each PMMA domain. Similar distribution was observed in the HDPE/PMMA blend matrix. In this case, CB filler is located in the HDPE phase and is especially concentrated at the interface of the two polymers like an envelope formation. So, it is found that CB particles distribute unevenly in polymer blend matrices. There are two types of distribution. (1) One is almost predominantly distributed in one phase of the blend matrix and in this phase fillers are relatively homogeneously distributed in the same manner as a single polymer composite. (2) In the second, the filler distribution concentrates at interface of two polymers. Heterogeneous distribution of CB in blend rubber was first found by Walters and Keyte,the mechanism for this, has not been examined quantitatively.13) Why is the dispersion state different with the type of polymer blends? We consider this mechanism based on a simple model. Fig.2 is used to explain the wetting behavior of powder at the interface of two liquid phases. If the interfacial free energy at the interface is at minimum, the next equilibrium equation is valid:

$$\begin{aligned}\delta G &= \gamma_{CB\text{-}A}\cdot\delta A_{CB\text{-}A} + \gamma_{CB\text{-}B}\cdot\delta A_{CB\text{-}B} + \gamma_{A\text{-}B}\cdot\delta A_{A\text{-}B}\\ &= \gamma_{CB\text{-}A}(2\pi r\sin\theta\, r\,\delta\theta) - \gamma_{CB\text{-}B}(2\pi r\sin\theta\, r\,\delta\theta)\\ &\quad + \gamma_{A\text{-}B}(2\pi r\sin\theta\, r\,\delta\theta)\cos\theta\\ &= 0 \qquad (1)\end{aligned}$$

where r is a radius of powder and A_{ij}, γ_{ij} are area and surface tension of i/j interface.

$$\omega a = \frac{\gamma_{CB\text{-}B} - \gamma_{CB\text{-}A}}{\gamma_{A\text{-}B}} \qquad (2)$$

This is called Young's equation. ωa is called the wetting coefficient. The next phenomenon is predicted:

when	$\omega a > 1$	CB particles distribute within the A phase
	$-1 < \omega a < 1$	CB particles distribute at the interface
	$\omega a < -1$	CB particles distribute within the B phase

For this calculation, components of surface tension in each polymer matrix at molding temperature 190°C are listed in Table 2. By using these values, interfacial tension can be calculated and are listed in Table 3.

Table 2. Surface tension (190°C)

	γ	γ^d (dyne/cm)	γ^p
HDPE	25.9	25.9	0
PP	20.2	19.8	0.4
PMMA	28.1	20.2	7.9
CB	55	51~49	4~6

$\gamma = \gamma^d + \gamma^p$

γ^d : Dispersion component

γ^p : Polar component

Source:S.Wu;"Polymer Interface and Adhesion",Marcel Dekker Inc. New York(1982).

Table 3. Interfacial tensions

1	2	γ_{12}(dyne/cm)
HDPE	CB	13.1~12.2
PP	CB	17.1~16.7
PMMA	CB	12.2~14.6 (γ_{CB}:4~6)
HDPE	PP	1.2
HDPE	PMMA	8.6
PMMA	PP	6.8

Table 4. Wetting coefficient (ω_A)

Aphase	Bphase	ω_A	TEM
PMMA	PP	0.75～0.31	interface
HDPE	PMMA	-0.10～0.28	interface
HDPE	PP	3.50～3.75	PEphase

In this calculation, Wu's harmonic mean average equation was used.14)

$$\gamma_{12}=\gamma_1+\gamma_2-4\left[\frac{\gamma_1^d\gamma_2^d}{\gamma_1^d+\gamma_2^d}+\frac{\gamma_1^p\gamma_2^p}{\gamma_1^p+\gamma_2^p}\right] \tag{3}$$

Further, calculated wetting coefficient are listed in Table 4. From these calculations, in PMMA/PP and HDPE/PMMA matrices, CB is predicted at the interface of each polymer, and for HDPE/PP, CB is predicted to be dispersed in HDPE phase. These predictions are coincident with the observation of TEM photograph. So, interfacial energy is found to be one of the most important factors affecting the distribution of CB particles in polymer blends. This phenomenon must be considered from not only an equilibrium view point, but in light of rate of process. For example, the effects of viscosity of each matrix must be checked. Viscosity of a matrix polymer is responsible for the aggregation of fillers.9) If the viscosities of two polymers are comparable, interfacial energy is the main factor determining uneven distribution of fillers in polymer blend matrices. Next, we consider how this heterogeneous distribution of fillers affects the electrical properties of the composites. Fig.3 shows the relation between electrical conductivity and HDPE content of 10 phr CB filled HDPE/PP blend. This figure shows that at some content of HDPE, the samples have excellent conductivity. Fig.4 is the case for PMMA/PP blend. Similar results are obtained. From the solvent extraction and its TEM photograph, we determine at which fraction the filler rich-polymer phase begins to form a continuous structure in the blend matrix.16) In Fig.3-4, the point at which conductivity begins to rise corresponds to this fraction. The product of these two factors,i.e., the concentration effect of fillers in the filler rich phase and the structural continuity of that phase affect the conductivity of composites. In other words, the filler rich phase becomes conductive at the percolation threshold and the polymer blend sample becomes conductive at a phase ratio threshold where structural continuity is achieved. The conductivity of the polymer blend sample therefore,is determined by these two factors or percolations. As for the difference of two types of heterogeneous distribution between HDPE/PP and PP/PMMA samples, Fig.5 (a) shows the results of CB filled HDPE and HDPE/PP blend. For the polymer blend sample, volume fraction of CB is calculated within HDPE phase. Two curves are almost coincident. This is due to the dispersion state of CB being the same in the HDPE phases. Fig.5(b) shows the relation between electrical conductivity and

CB volume fraction of CB filled PMMA and PP/PMMA blend. Also in this figure, volume fraction of CB is calculated in PMMA phase. Fig.5(b) shows that the percolation threshold occurred at a smaller filler content in PP/PMMA sample compared to PMMA single matrix sample. This is due to envelope formation of CB particle around PP domain which makes the conduction path more effective than the PMMA single matrix and HDPE/PP blend matrix.

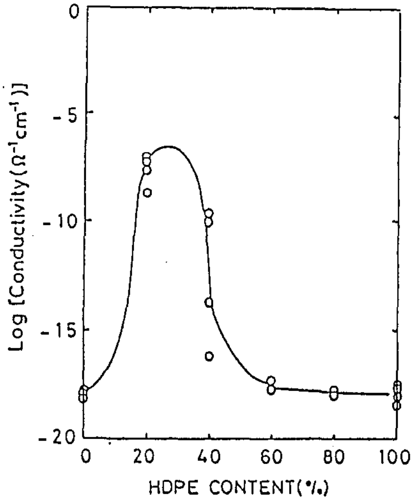


Fig.3 Electrical conductivity of 10phr CB filled HDPE/PP as a function of HDPE fraction.

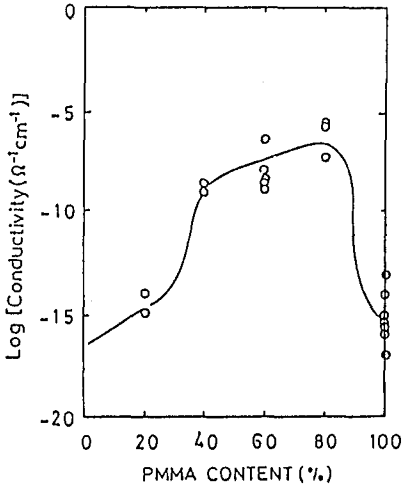


Fig.4 Electrical conductivity of 10phr CB filled PMMA/PP blend as a function of PMMA fraction.

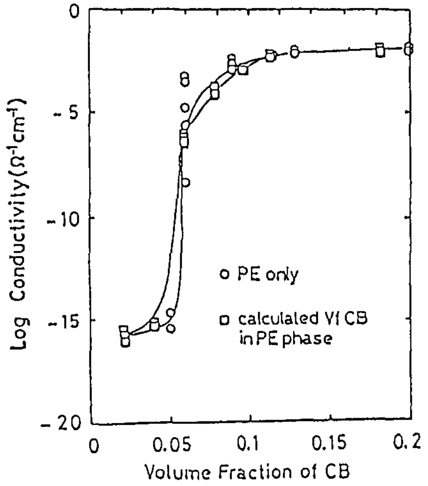


Fig.5 (a)Electrical conductivity of CB filled HDPE and HDPE/PP blend as a function of CB volume fraction.

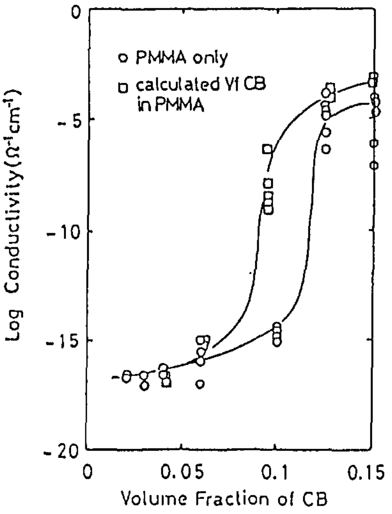


Fig.5 (b)Electrical conductivity of CB filled PMMA and PP/PMMA blend as a function of CB volume fraction.

Conclusions

(1) The uneven distribution of fillers in a polymer blend matrix is mainly due to the difference in affinity of CB particles to each component of polymer blend.
(2) There are two type of heterogeneous distributions of CB particles in filled polymer blends. One is almost predominantly distributed in one phase of a blend matrix and the other is distributed concentratedly at the interface of two polymers.
(3) The electrical conductivity of CB filled polymer blends is determined by two factors. One is the concentration of CB in the filler rich phase and the other is structural continuity of this phase. These double percolations affect conductivity of conductive particle filled polymer blends. Using this method, we can produce an effective conductive polymer blend using significantly less filler material which is both stable and simple to produce.

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