Effect of Interfacial Free Energy on the Heterogeneous Distribution of Oxidized Carbon Black in Polymer Blends

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ABSTRACT: The effect of oxidation of carbon black (CB) on the heterogeneous distribution in polymer blends was examined. In three kinds of polymer blends, *i.e.*, high density polyethylene (HDPE)/isotactic polypropylene (PP), PP/atactic poly(methyl methacrylate) (PMMA), and HDPE/PMMA, the heterogeneous distribution of CB and oxidized CB were observed. The heterogeneous distribution of fillers in a polymer blend matrix was mainly due to the difference in affinity of CB particles to each component of the polymer blend. In HDPE/PP blend, the dispersion state of oxidized CB was different from that of unoxidized CB. The dispersion states of the fillers in these samples were predicted qualitatively from the values of the wetting coefficient which were calculated from the interfacial free energies, and they were coincident with the observations by scanning (SEM) and transmission (TEM) electron microscopies.
    KEY WORDS   Carbon Black / Polymer Blends / Dispersion / Heterogeneoues Distribution / Interfacial Free Energy / Oxidation / Wetting Coefficient /

    The properties of filled polymers greatly depend on not only the volume fraction of the filler but also the dispersion of the filler. In our previous studies, the dispersion state of particules in the matrix of a single polymer was found to be affected by such factors as surface free energy[1] and melt viscosity of polymers,[2] and the size of the filler particles.[3] In the matrix of polymer blends which are incompatible with each other, added filler distributes unevenly to each component of the polymer blend. The heterogeneous disgribution of carbon black (CB) in blend rubber was first found by Walters and Keyte.[4] The mechanism for this distribution, however, has not been examined quantitatively. In our previous paper,[5] we made the mechanism of uneven distribution of CB in polymer blend matrices clear. If the melt viscosities of two polymers are comparable, the uneven distribution of fillers in a polymer blend matrix is mainly due to the difference in affini-ty of CB particles to each component of the polymer blend. In this paper, the difference in affinity of CB particles to the polymer matrix has been changed by oxidation of CB, and discuss the effect of the oxidation of CB on the heterogeneous distribution of the particles.

EXPERIMENTAL

Composite Sample Preparation

    Three kinds of polymers, *i.e.*, high density polyethylene (HDPE) (Sholex F5012M; Showa Denko Co.), isotactic polypropylene (PP) (Shoaromer MA210; Showa Denko Co.), and atactic poly(methyl methacrylate) (PMMA) (MF; Mitsubishi Rayon Co.) 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 balck (CB) (Seast 300, low structure, 27 nm in diameter from Tokai

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Carbon Co.) was used as a filler. In order to vary the surface free energy of the filler, Seast 300 was oxidized for 3 h in 25% and 50% boiling nitric acid. Polymers were first blended and kneaded by a mixing roller for 5 min, and the filler was added to the kneaded mixtures and kneaded for 10 min. The volume fractions of each component were 0.475 (polymer 1), 0.475 (polymer 2), and 0.05 (CB), and the kneading temperature was 190°C. Prior to mixing, the polymers were dried at 50°C for 12 h under vacuum and the CB was dried at 105°C for 1 h. Films of 0.5 mm thickness were compression-molded from the polymer blend–CB mixtures at the temperature of 190°C for 30 min under a pressure of 10 kg cm^{-2}, followed by quenching into ice water.

Electron Microscopy

The fracture surfaces of the samples, which have broken in liquid nitrogen, were observed by scanning electron microscopy (SEM). The thin films of the samples, which have dyed by a heavy metal of tetroxide ruthenium (RuO$_4$), were observed by transmission electron microscopy (TEM).

RESULTS AND DISCUSSION

In the matrix of polymer blends which are incompatible with each other, CB particles distribute unevenly to each component of the polymer blend. There are two types of distribution. (1) One is 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 the interface of two polymers. In our previous paper,[5] it was found that the dispersion state of CB particles in polymer blend matrices can be predicted qualitatively from the value of the wetting coefficient which is defined as eq 1.

$$\omega_{A\text{-}B} = \frac{\gamma_{CB\text{-}B} - \gamma_{CB\text{-}A}}{\gamma_{A\text{-}B}} \quad (1)$$

where $\gamma_{i\text{-}j}$ is the interfacial free energy of i–j interface.

The next phenomenon is predicted[5]: when

$$\omega_{A\text{-}B} > 1 \qquad \text{CB particles distribute within the A phase}$$
$$-1 < \omega_{A\text{-}B} < 1 \qquad \text{CB particles distribute at the interface} \qquad (2)$$
$$\omega_{A\text{-}B} < -1 \qquad \text{CB particles distribute within the B phase}$$

For this calculation, components of surface free energy of each CB and polymer matrix at molding temperature of 190°C are listed in Table I and Table II.[6] In Table I, CB0 represents unoxidized CB, and CB25 and CB50 represent oxidized CB by oxidation for 3 h in 25% and 50% boiling nitric acid respectively. The dispersive components of the surface free energies (γ^d) of these CB particles were estimated by IGC (inverse gas chromatography) and the polar components of them (γ^p) were estimated by ESCA (electron spectroscopy for chemical analysis). Further details for this measurements are described in our

Table I. Surface free energy of CB (190°C)

	γ	γ^d	γ^p
	mJ m^{-2}		
CB0	42.5	41.9	0.6
CB25	45.6	42.9	2.7
CB50	47.7	43.4	4.3

Table II. Surface free energy of polymer (190°C)

	γ	γ^d	γ^p
	mJ m^{-2}		
HDPE	25.9	25.9	0
PP	20.2	19.8	0.4
PMMA	28.1	20.2	7.9

Table III. Wetting coefficient ($\omega_{A\text{-}B}$)

	CB0	CB25	CB50
HDPE/PP	2.00	0.75	0.25
HDPE/PMMA	0.66	0.10	−0.19
PP/PMMA	0.83	0.04	−0.38

other paper.[7] The values of γ at 190°C were obtained by using the relation: $-d\gamma/dT = 0.06$, which was general value for polymers.[6] By using these values of γ^d and γ^p, the interfacial free energies (γ_{12}) of each CB/polymer interface can be calculated. In these calculations, the following equation was used.[8]

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^d \gamma_2^d} - 2\sqrt{\gamma_1^p \gamma_2^p} \qquad (3)$$

Further, by using the values of γ_{12}, the wetting coefficients can be calculated by eq 1 and are listed in Table III. From these calculations, for the HDPE/PP/CB0 composite, CB is predicted to be dispersed in the HDPE phase, and for the other composites, CB is predicted to be dispersed at the interface of each polymer.
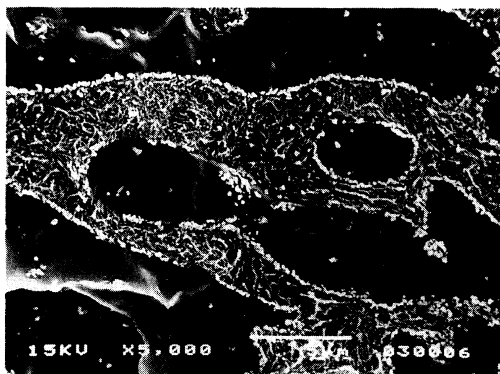
Figure 1(a), (b), and (c) are SEM photographs of 5% volume CB0, CB25, and CB50-filled HDPE/PP blends respectively. In SEM photographs, CB particles are recognized as white points, and the two polymer phases were distinguished each other from the SEM photographs of the blends which have various blend ratio (HDPE/PP = 20/80, 40/60, 60/40, 80/20). The HDPE phase appears as white textures on the fracture surface. For the HDPE/PP/CB0 composite, CB is almost predominantly distributed in the HDPE phase and in this phase CB is relatively homogeneously distributed. For the HDPE/PP/CB25 and HDPE/PP/CB50 composites, the majority of CB particles are distributed at the interface of the two polymers. Figure 2(a), (b), and (c) are TEM photographs of the same samples as in Figure 1. In TEM photographs, CB particles are recognized as black points. In case of HDPE/PP blends, the HDPE phase is liable to
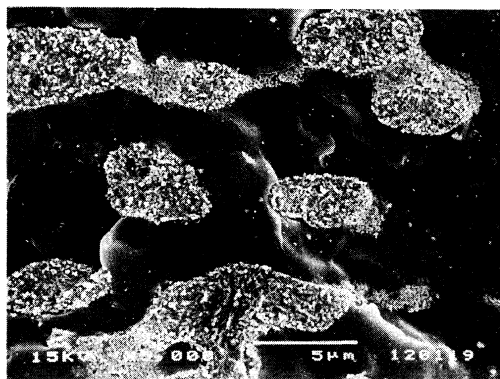
(a) CB0
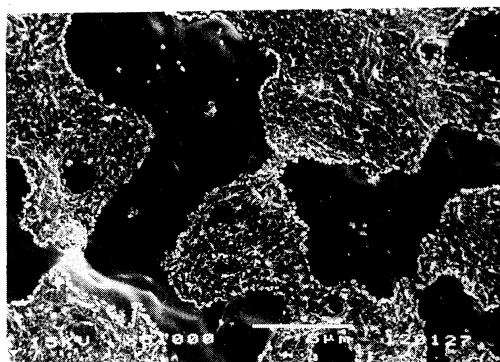
(b) CB25

(c) CB50

Figure 1. SEM photographs of 5% volume (a) CB0-, (b) CB25-, and (c) CB50-filled HDPE/PP.
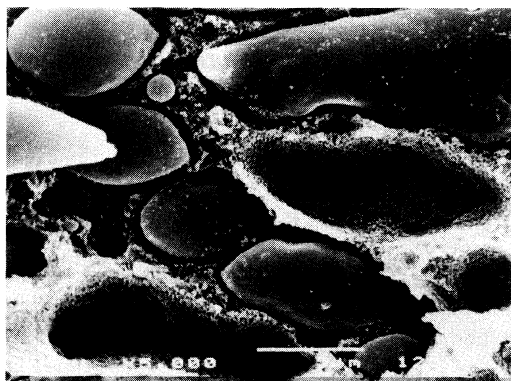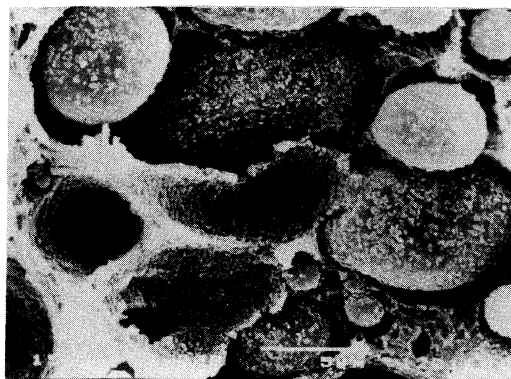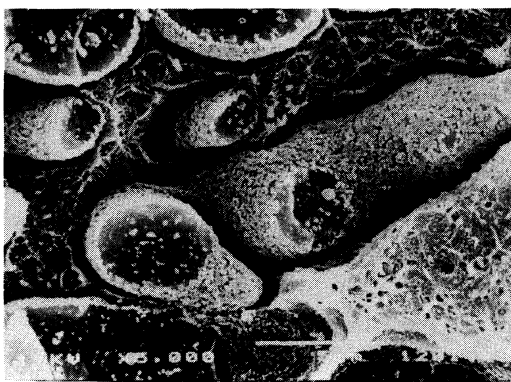
(a) CB0

(b) CB25

(c) CB50

Figure 2. TEM photographs of 5% volume (a) CB0-, (b) CB25-, and (c) CB50-filled HDPE/PP.

(a) CB0

(b) CB25

(c) CB50

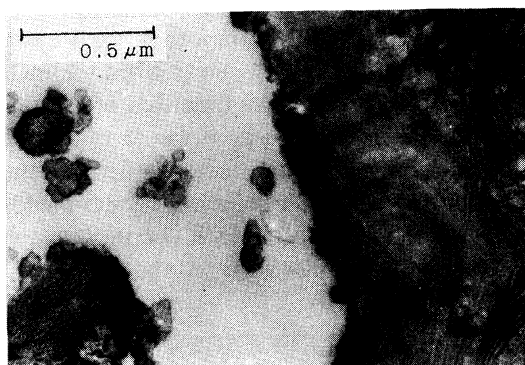**Figure 3.** SEM photographs of 5% volume (a) CB0-, (b) CB25-, and (c) CB50-filled HDPE/PMMA.
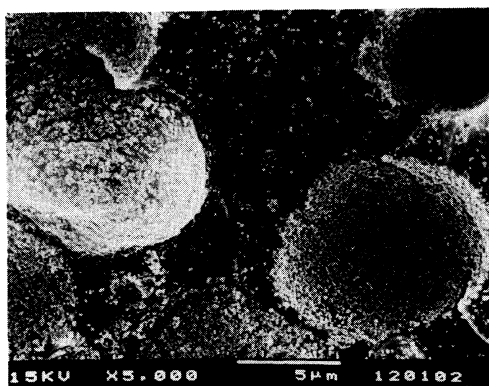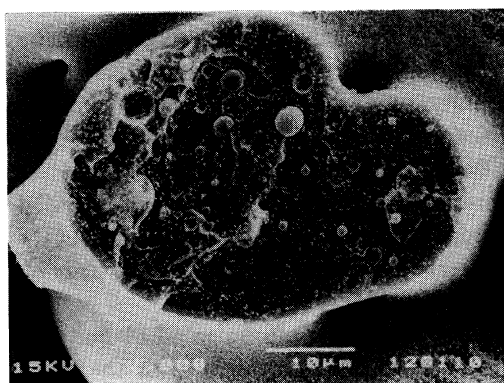
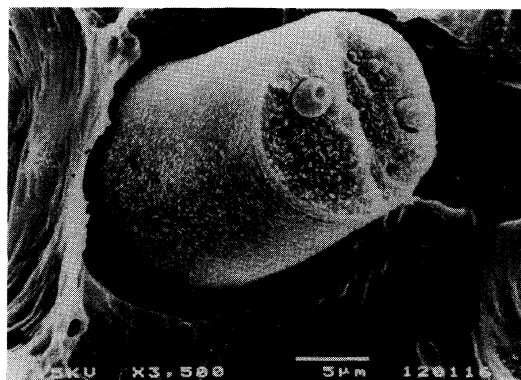**Figure 4.** TEM photograph of 5% volume CB50-filled HDPE/PMMA.

(a) CB0

be dyed by RuO_4. In the HDPE/PP blend CB0 is distributed in the HDPE phase, and CB25, CB50 are distributed at the interface of the two components. The similar distribution as in SEM photographs is observed in these TEM photographs.

Figure 3(a), (b), and (c) are SEM photographs of 5% volume CB0, CB25, and CB50-filled HDPE/PMMA blends, respectively. In these SEM photographs, the HDPE phase appears as white textures on the fracture surface and the PMMA phase appears as smooth surface. For these composites, because of the large interfacial free energies of HDPE/PMMA, debonding at the interface is observed, and the CB particles at the interface is clearly visible. In Figure 3(a), CB particles distribute at the HDPE surface from which PMMA phase was torn away, and they hardly distribute at the PMMA surface. In Figure 3(b) and (c), CB particles almost distribute at the surface of HDPE and PMMA phase. Figure 4 is TEM photograph of 5% voluem CB50-filled HDPE/PMMA blend, and the HDPE phase is dyed by RuO_4. It is also observed that CB particles distribute at the interface of the two polymers.

Figure 5(a), (b), and (c) are SEM photographs of 5% volume CB0, CB25, and CB50-filled PP/PMMA blends, respectively. For these composites, debonding at the

(b) CB25

(c) CB50

Figure 5. SEM photographs of 5% volume (a) CB0-, (b) CB25-, and (c) CB50-filled PP/PMMA.
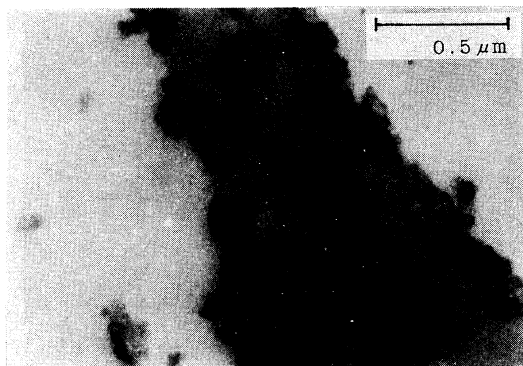
Figure 6. TEM photograph of 5% volume CB50-filled PP/PMMA.

interface is also observed, and the PMMA phase is observed as round lumps. In these photographs, CB particles almost distribute at the interface of the two polymers, but in Figure 5(b) and (c), it can be seen that they also exist in the PMMA phase. Figure 6 is TEM photograph of 5% volume CB50-filled PP/PMMA blend, and the PP phase is dyed by RuO_4. It is observed that CB particles almost distribute at the PP/PMMA interface.

These filler distribution in SEM and TEM photographs are coincident with the predic-tions by the values of ω_{A-B} in Table III. For the HDPE/PP/CB0 composites, CB also distributes in the HDPE phase when the melt viscosity of PP is smaller than that of HDPE. So, interfacial free energy is found to be one of the most important factors affecting the distribution of CB particles in polymer blends when the difference of the melt viscosity of each component is smaller than ten times.

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