DISPERSION OF PARTICLES IN POLYMER COMPOSITES FILLED WITH CARBON BLACK STUDIED BY SCANNING ELECTRON MICROSCOPY OBSERVATION

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ABSTRACT: The degree of dispersion of carbon black (CB) particles in a polymer matrix is known to be a determining factor in the physical properties of the composites. In this study, we discuss the effect of the oxidation treatment of CB, the chemical modification of the chain-ends and main chain of the polymers and molding time on this dispersion in detail, through a study using scanning electron microscopy (SEM) observation. The oxidation of CB changed the state of its distribution in some polymer matrices: in a nonpolar polymer the fillers was aggregated, but, in a polar polymer the dispersion of the fillers was improved. The chemical modification of chain-ends causes a regular distribution of CB particles, but the chemical modification of the main chain caused the CB particles to be aggregated. Also, this distribution state was changed in accordance with the molding time.

1. INTRODUCTION

The degree of dispersion of carbon black (CB) particles in a polymer matrix is known to be a determining factor in the physical properties of the composites, to a certain extent [1–3], and therefore, it is important to use a reliable technique when assessing the CB dispersion. The changes in overall dispersion mode are strongly correlated with the percolation phenomena in electrical conductivity of CB filled polymers [4]. The SEM photographs of the section were taken to be subjected to a statistical treatment to characterize the mode of dispersion of CB. The states of dispersion of CB of these samples were well characterized by statistical processing using the quadrat method and Morishita’s IQ values [5]. In the quadrat method the total area of SEM pattern is divided small elemental parts of the same area and the number of the points in each element is calculated [4]. In CB filled polymers, a structure consisting of three to five primary particles behaves like one point in the two dimensional SEM photograph. So, in this type of analyse, SEM photograph is more convenient than TEM photograph. In our previous studies [6], we used electron microscopy extensively, to observe the state of the dispersion of CB particles in the polymer blends. In the present paper, the dispersion of CB particles in some polymer matrices is determined by scanning electron microscopy observation. We also discuss the effect of the oxidation treatment of CB, the chemical modification of the chain-ends [7] and main chain of the polymer, and the molding time on this dispersion, in detail.

2. EXPERIMENTAL

Carbon Black, Seast 300, having a particle-diameter of 27 nm, was used as a conductive filler. In order to vary the surface free energy of the filler, CB was oxidized for 3 h in 50% boiling nitric acid. High density polyethylene (HDPE), poly (methyl methacrylate) (PMMA), polystyrene (PS) and chain-ends modified PS, isoprene rubber (IR) and main chain modified IR were used as the matrix polymers. The polymers and CB were mixed in a two roll mill. The sample was made molten for 5 min and then pressed for 10 min, and thereafter, the samples were cooled to obtain films having a thickness of about 0.8 mm. The polymer samples and composite preparation conditions are listed in Table 1. A section of the composite specimen was prepared by braking the specimen in liquid ni-
Table 1: Polymer Samples and Preparation Conditions of Composites

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Mixing temp. (time)</th>
<th>Molding temp. (time)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>180°C (15 min)</td>
<td>190°C (10 min)</td>
</tr>
<tr>
<td>PMMA</td>
<td>180°C (15 min)</td>
<td>190°C (10 min)</td>
</tr>
<tr>
<td>PS</td>
<td>180°C (15 min)</td>
<td>190°C (10 min)</td>
</tr>
<tr>
<td>Modified PS</td>
<td>180°C (15 min)</td>
<td>190°C (10 min)</td>
</tr>
<tr>
<td>IR</td>
<td>80°C (15 min)</td>
<td>120°C (10 min)</td>
</tr>
<tr>
<td>Modified IR (FPI)</td>
<td>150°C (15 min)</td>
<td>120°C (10 min)</td>
</tr>
<tr>
<td>Modified IR (AMI)</td>
<td>150°C (15 min)</td>
<td>120°C (10 min)</td>
</tr>
</tbody>
</table>

Table 2: Interfacial Free Energy $\gamma_{ij} (\text{mJ/m}^2)$

<table>
<thead>
<tr>
<th>1-Polymer</th>
<th>2-Filler</th>
<th>CB</th>
<th>Oxidized CB</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td></td>
<td>2.5</td>
<td>6.5</td>
</tr>
<tr>
<td>PMMA</td>
<td></td>
<td>8.0</td>
<td>4.9</td>
</tr>
</tbody>
</table>

Then the fracture surface, which have etched with Eiko IB-3 under (400 V, 1 mA, 10 min) conditions, was coated with gold for SEM observation. SEM photographs were taken with a Nippon Electron JSM-T-220 under the following conditions: working distance 5 mm, tilting angle 15°, applied voltage 15 and 20 kV.

3. RESULTS AND DISCUSSION

3.1 Influence of Oxidation Treatment of CB Particles

Fig. 1 shows SEM photographs of HDPE, PMMA filled with 6% volume CB and oxidized CB particles, respectively, it was found that the oxidation of CB changed the state of its distribution in the polymer matrices: in nonpolar polymers such as HDPE the fillers were aggregated, but, in polar polymers such as PMMA, the dispersion of fillers was improved. On the other hand, the oxidation treatment of CB particles caused polar groups such as carboxyl and hydroxyl.

![SEM photographs](image)
groups to be incorporated in its surface. In comparison with unoxidized CB, the polar component of surface free energy of oxidized CB was greatly increased, but, its dispersive component was little changed. Namely, the interfacial free energies of nonpolar polymer composites increased with the oxidation of CB, whereas those of polar polymer composites decreased, as shown in Table 2. These results suggested that the dispersion of fillers in the polymer matrix is strongly related to the interfacial free energy of the polymer/filler interface.

3.2 Influence of Chemical Modification of the Matrix Polymers

Fig. 2 shows SEM photographs of 4% volume CB filled PS and modified PS respectively, and it can be seen that the dispersion of CB particles was improved by the chemical modification of the matrix. The above-mentioned chemical modification was developed by slightly modifying the chain-ends without changing the main chain structure. The chemical modification involves an addition reaction of some compounds such as N-alkylcaprolactam groups. In order to enhance strength of the interaction between the functional groups at the chain-ends and CB surface, which have some polar groups such as carboxyl, carbonyl and hydroxyl, the matrix polymer was strongly absorbed onto the surface of CB, and thus, suppress-
ed the transient-structure formation, or network formation, of interparticles.

Fig. 3 shows SEM photographs of 5% volume CB filled IR and modified IR, respectively, there it was found that, contrary to the case of chain-ends modified PS, CB particles were aggregated by the chemical modification of the main chain of the matrix. This suggests that the influence of the main chain modification on the filler dispersion is different from that of the chain-ends modification. In the main chain modification there are 10 functional groups in a chain, and because of the formation of combinations of cations in the main-chain and anions on the surface of CB particles, several CB particles were fixed to the same chain and a CB particle was taken by several chains simultaneously, and accordingly, the CB particles were forced to aggregate.

### 3.3 Influence of Molding Time

Fig. 4 shows SEM photographs of 4% volume CB filled PS composites at two different molding times and it can be clearly seen that the distribution state of CB particles was changed with a change of the molding time. At a temperature higher than Tg, CB particles were aggregated with a longer molding time, and this suggests that there is a characteristic time at which, as a result of the aggregation of CB particles, networks facilitating an electrical conduction can be formed. In practice, this time has been observed [5].

### REFERENCES