

Evaluation of Particle Dispersion in Polymer Solids by Oxygen Plasma Etching

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SYNOPSIS

A new technique using oxygen plasma etching was developed for studying the dispersion of filler particles in polymer solids. With this method, the organic polymer matrix is selectively etched from the top surface down into the bulk, revealing the dispersion state of the filler particles upon scanning electron microscopic analysis. A polymer composite, comprised of zinc oxide particles and a linear styrene-*n*-butylmethacrylate copolymer, was used to investigate the particle dispersion as a function of filler volume fraction. Preliminary data on the effect of a surfactant on filler dispersion is also discussed. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

The modification of polymer properties by particulate filling is commonly used to design and manufacture polymer composites with tailor-made mechanical, conductive, or magnetic properties.¹ The structure of the particle dispersion in the composite critically effects the material properties.^{2,3} For example, the fracture properties of a particulate-filled polymer can be dramatically altered by a change in degree of dispersion because the particles can act as stress concentrators to control microscopic fracture.⁴⁻⁶ In the case of conductive particles, the percolation thresholds of thermal and electric conductivity also are very sensitive to the structure of the particle dispersion, which obviously will significantly influence the thermal and electric behavior of the composites. However, it is often difficult to unambiguously determine the three-dimensional structure of the particles' dispersion as they are buried deep inside the polymer matrix. The polymer matrix usually is not transparent to light and the sizes of the commonly used particles generally are too large for X-ray analysis. Here, we present a simple technique for investigation of particle dispersion in polymers based upon selective etching by a plasma. By se-

lecting a plasma etchant that optimizes the etching rate difference between the polymer matrix and the filling particles, the structure of the dispersed particles can be revealed after etching by high-resolution scanning electron microscopy (SEM) on the etched surfaces. The three-dimensional structure of particle dispersion can be obtained by serial etchings to different depths or from various etching directions.

As a general example, we selected an oxygen plasma to investigate the structure of zinc oxide particles in a styrene-*n*-butylmethacrylate copolymer. The oxygen plasma⁷ can be considered a highly reactive, surface-specific, oxidizing agent. The plasma chamber operates in a vacuum; thus, the produced oxide species, usually volatile for polymers, are swept out of the chamber. Since the zinc oxide particles are generally much less reactive to the plasma etching compared to the polymer matrix, the structure of particle dispersion can be revealed. In this article, the dispersion of the zinc oxide particles in the polymer resin is studied as a function of filler loading and as effected by an added nonionic block polymer surfactant.

EXPERIMENTAL

Sample Preparation

The samples of the polymer composite consist of particles of zinc oxide (Aldrich Chemical Company,

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Milwaukee, WI) dispersed in a polymer matrix resin. The polymer we used for this study is a styrene-*n*-butylmethacrylate copolymer, Figure 1, tradenamed PICCO 1200 (Hercules). The polymer has a glass transition temperature around 65°C. As revealed by SEM, the shape of the zinc oxide particles is random but can be approximated as spheres. The size of the zinc oxide particles, measured from the SEM micrographs up to 100 particles, is distributed between 0.05–0.5 μm and averages approximately 0.2 μm. The organic and inorganic materials were mixed in a Banbury mixer (HBI Rheomix 600, Saddle Brook, NJ) at 170°C. For the purpose of comparison, the mixing was done by using a constant blade rotation speed, 100 rpm, for every sample until the viscosity of the melt decreased to a plateau level. The plateau viscosity indicates that the disintegration of the filler aggregates has reached a saturation level and thus the filler has mixed well with the polymer matrix under this mixing condition. The mixing time usually ranges from 20–45 min, with a longer mixing time for specimens with a higher zinc oxide volume fraction. After being cooled to room temperature, the mixed material was ground by a Wiley mill to coarse particles, ca. 1 mm in diameter, and the coarse powder was fused on an aluminum wafer, approximately 1 mm thick and 1 × 1 cm lateral dimension, at 130°C on a hot plate. The thickness of the sample is between 1–2 mm, much larger than the size of the particles or the particle aggregates.

To observe the effect of a surfactant on the composite structure, a nonionic triblock surfactant (Pluronic L-61) (BASF, Holland, MI) was used in a 3% loading (wt) and mixed with the zinc oxide and the PICCO polymer together in the Banbury mixer.

Etching and Dispersion Characterization

The fused specimen was then placed in a Plasmatherm plasma etching chamber for dry etching where a vacuum of 20 mtorr was maintained with oxygen

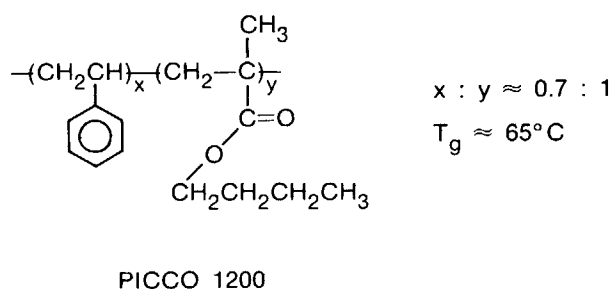


Figure 1 Chemical structure of the PICCO 1200 resin.

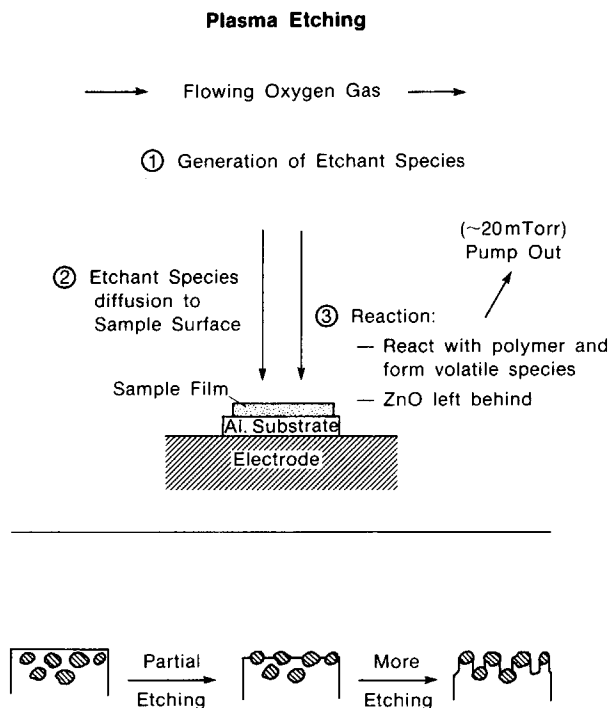


Figure 2 Oxygen plasma etching process.

gas flowing through at a controlled rate of around 40 cm³/s. The oxygen gas was converted into the reactive etchant species (plasma) and driven by a biased voltage (100 V) toward the electrode where the fused specimens were positioned. The oxygen plasma etching process is shown schematically in Figure 2. The etched sample was then analyzed by SEM.

RESULTS AND DISCUSSION

Effect of Etching Time

As shown in Figure 3, the morphologies of the etched area and the protected area (taped) demonstrate the effectiveness of the etching technique in unveiling the particle dispersion. However, excess etching could cause undercut beneath the inorganic particles and produce deep trenches within which the particle dispersion cannot be easily accessed due to the shadowing effect. Figure 4 shows the SEM micrographs of an etched sample, 40% by weight zinc oxide, for both 5 and 20 min etching time. It appears that fewer particles were observed and the topography became rougher for the longer etching time. The observation of fewer particles by SEM, however, is believed to be an artifact due to the shadowing effect in a very rough surface. Therefore,

**Effect of Etching:
20 min. on 50% ZnO in Picco 1200**

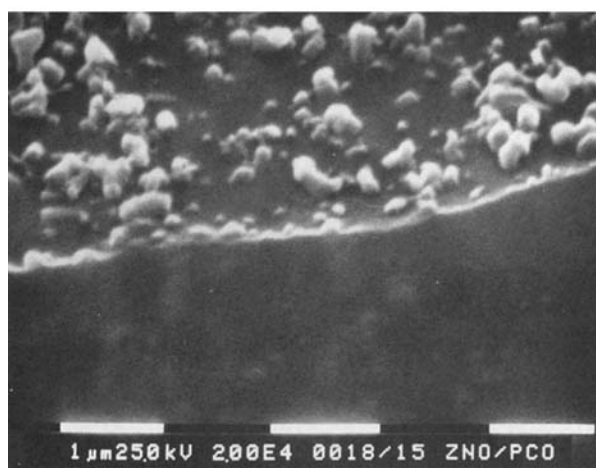
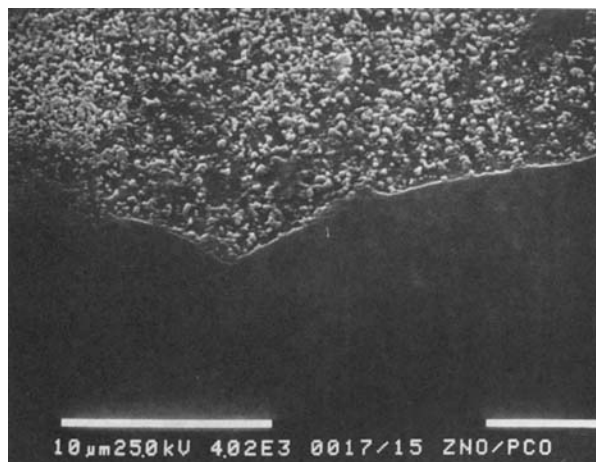


Figure 3 Effect of plasma etching on revealing the particle dispersion in the polymer matrix. SEM micrographs show the exposed areas compared with the area protected by tape. The top half of each micrograph is etched; the bottom half of each is taped.

an appropriate etching time should be selected and a constant etching time is preferred in comparing different samples. We have chosen, as a result of the initial etching time study, to etch all subsequent specimens for 5 min.

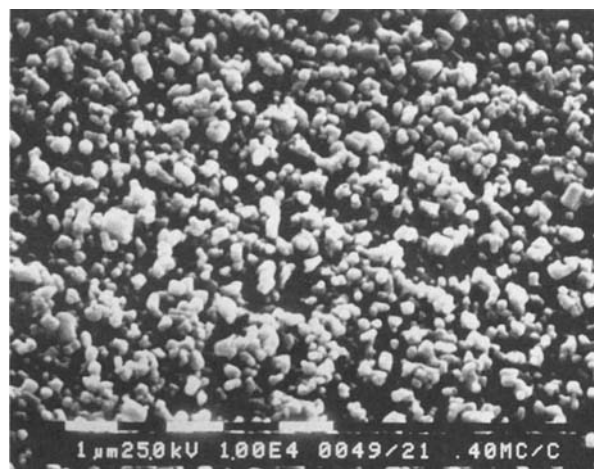
Effect of Particle Concentration

The particle dispersion as a function of filler weight fraction in the polymer solid was investigated by the oxygen plasma etching technique. At low filler concentration (< 20 wt %), loose clusters of a few par-

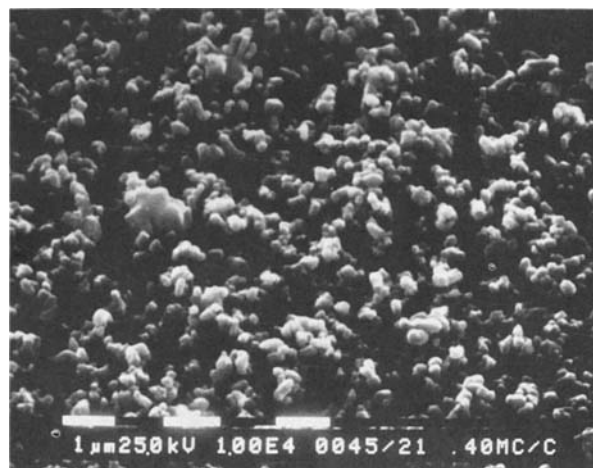
ticles (ca. 10) were observed. The clusters linked to each other, forming a vaguely defined chain structure. As the filler concentration increases, the clusters approach and contact each other and eventually coalesce. When the filler concentration increased above 60% by weight, the observed particles were uniformly packed. No large-scale fluctuation of the particle packing was observed. Figure 5 illustrates the particle dispersion as a function of the weight fraction of zinc oxide particles.

Since all specimens were prepared under the same mixing conditions until the viscosity plateau was reached, the variation of particle dispersion shown in Figure 5 is clearly due to the effect of filler frac-

40% ZnO in Picco 1200



5 minutes etching



20 minutes etching

Figure 4 Effect of etching time. Excess etching removes particles of the top layer and creates shadowing effect.

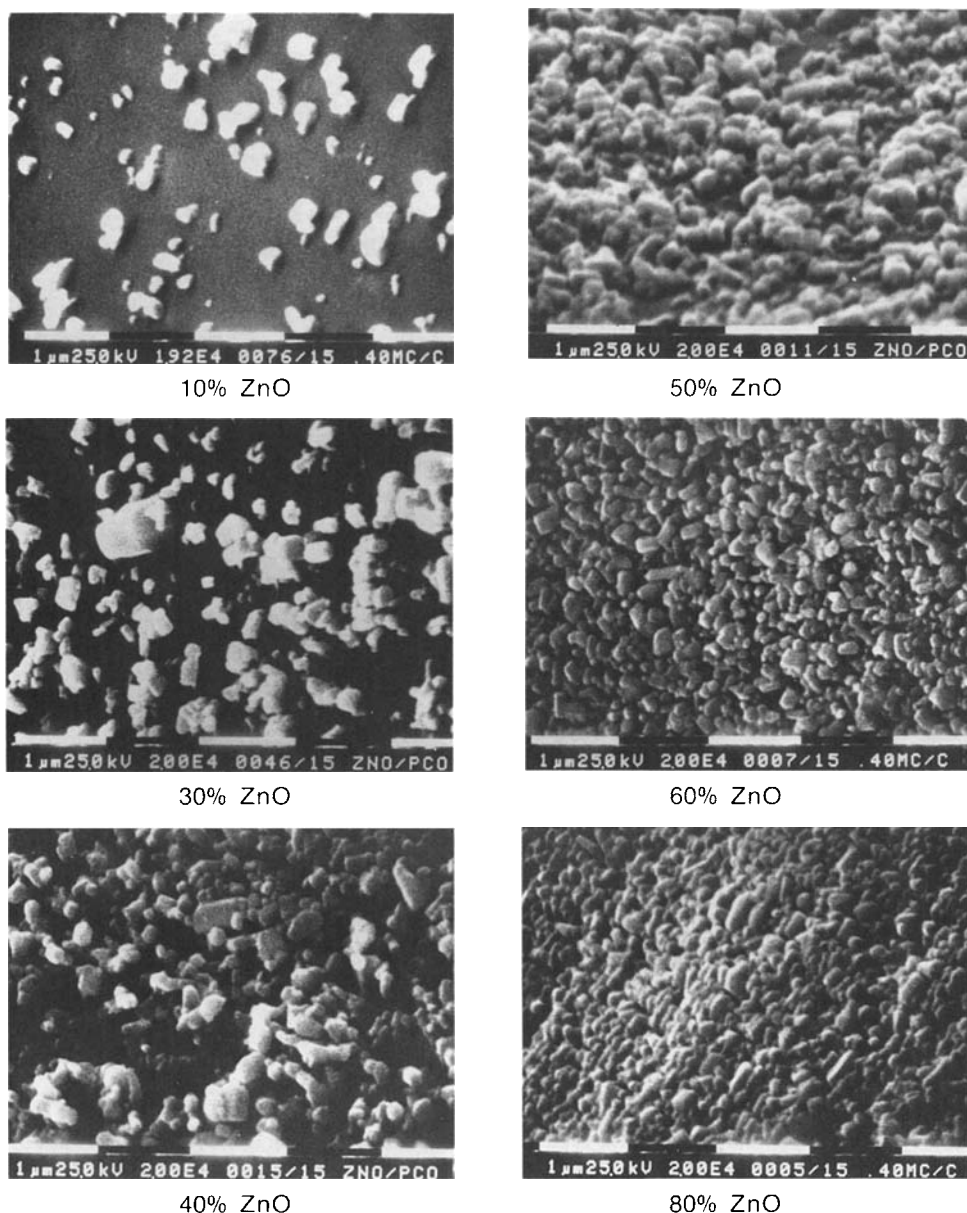


Figure 5 Zinc oxide particle dispersion in PICCO 1200 matrix as a function of zinc oxide weight fraction.

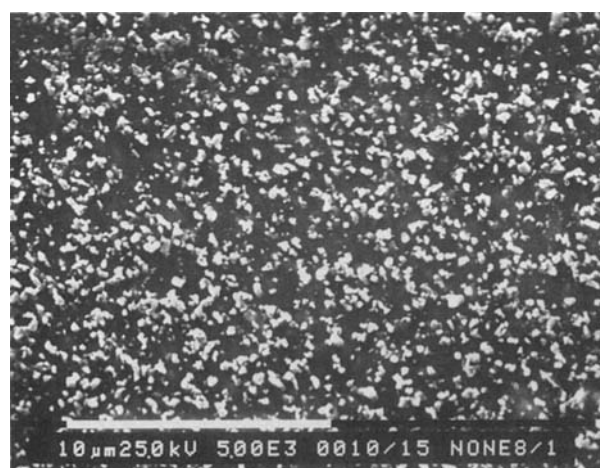
tion, not to the effect of mixing time. The loose clusters and sometimes chain-like structures formed by the zinc oxide particles at low filler fractions (< 40 wt %) suggest that an attraction exists between particle surfaces, presumably due to the hydrophilicity of the zinc oxide surface relative to the polymer matrix. As the filler fraction increases, these small aggregates start to break down and show packing uniformity when the filler fraction is higher than 60 wt %. The breakdown of the filler aggregates is probably due to the increase of the plateau viscosity at higher filler fraction in which the shear force dur-

ing mixing becomes sufficient to break up the filler aggregates that were clustered by the attraction between the hydrophilic particles.

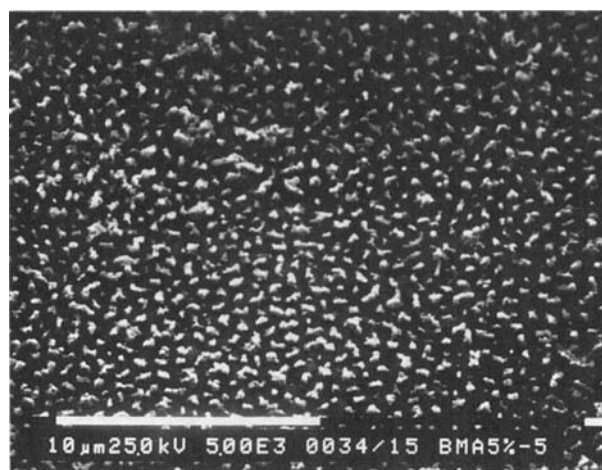
Effect of Triblock Surfactant

To further investigate the effect of surface properties of filler particles, we examined the effect of the addition of a block copolymer surfactant that could provide a bridging segment between the hydrophobic matrix and the hydrophilic filler. Because zinc oxide particles are hydrophilic relative to the polymer ma-

trix, a triblock copolymer (Pluronic L-61) of short end segments of hydrophilic polyethylene oxide (PEO) attached to a long central block of hydrophobic polypropylene oxide (PPO) was selected as the surfactant to test this hypothesis. As shown in Figure 6, the surfactant significantly improved the dispersion. The zinc oxide clusters were reduced in size and distributed more uniformly in the polymer matrix. This indicates that the surfactant successfully modified the surface of the particles and in fact may have acted as a bridging agent between the hydrophilic zinc oxide particles and the hydrophobic polymer matrix, resulting in a very uniform distribution of the initially aggregated filler particles. A full discussion on surfactant effects in filled polymers as studied by the oxygen plasma etch/SEM analysis will be the subject of an upcoming article.



No Surfactant



3% Triblock Surfactant

Figure 6 Effect of a triblock surfactant (Pluronic L-61) on particle dispersion (30% by weight zinc oxide).

The analysis of particle dispersion described in this work, although qualitative, demonstrates the ability of using plasma etching to study particle dispersion in particulate polymer composites. By further using advanced image analysis routines and combining data from different etching directions, useful information of a full three-dimensional structure of particle dispersion in polymer can be obtained. This technique not only allows us to study the effect of surfactant molecular structure of surfactants on particle dispersion but also provide an experimental tool for studying the relationship between particle dispersion and material behavior of polymer composites. Recently, this method has also been used to elucidate the solid-state structure of phase-separated polymer blends⁸ and dispersion level of organometallic compounds in photoresistant films.⁹

CONCLUSIONS

1. A simple technique using oxygen plasma etching has been developed for revealing particle dispersion in polymer-based composites. The oxygen plasma preferentially etches the organic polymer matrix, forming volatile oxide species, and leaves behind the stable, nonvolatile oxides of the inorganic filler. This technique can be applied to a wide variety of polymeric composite systems where the filler particles exhibit markedly lower etching rates than the organic matrix, i.e., high etch selectivity exists.
2. In zinc oxide/PICCO composites, the particles tend to form loose aggregates (chain structure) at low concentration. At higher concentration, particles tend to pack together tightly, and the dispersion appears to be uniform. This behavior is probably due to the increase in shear force during mixing, which becomes sufficiently large at higher filler fractions to break up the particle aggregates.
3. Block copolymer surfactants can be effective in improving the particle dispersion. Specifically, surface-active Pluronic L-61 triblock polymer aided in the distribution of zinc oxide particles in PICCO resin, as determined by the oxygen plasma etching/SEM analysis.

The authors thank Hoa Truong for help with the oxygen plasma etching.

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Received December 10, 1990

Accepted December 10, 1991