USAXS Imaging of Carbon Black/PMMA Composites

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Introduction

A new imaging technique that makes use of ultrasmall-angle x-ray scattering (USAXS) as a contrast mechanism was used to study carbon black/poly-methylmethacrylate (CB/PMMA) composite materials. CB is a common polymer additive that is used for reinforcement and for its ability to enhance physical properties such as conductivity. It is of particular interest in that its percolation volume fraction is exceptionally low. CB/PMMA has been observed to become conductive at loadings as low as 0.133%, whereas other fillers require 2-3% or even 6-8% loading. Earlier USAXS measurements [1] of 1% CB in PMMA displayed fractal-like scaling, indicative of surface roughness. A low-*q* knee [where $q = (4\pi/\lambda)\sin\theta$, λ is the x-ray wavelength, and 2θ is the scattering angle] was taken to correspond to the largest aggregate radius of gyration in a polydisperse aggregate model of this composite material. In the present research, USAXS scans and images were made of CB/PMMA composites ranging from 0.1 to 1.0% loading in an attempt to observe the underlying mechanism responsible for the unique behavior of these materials.

Methods and Materials

Although USAXS provides quantitative, statistical, volume-averaged microstructural information about bulk specimens, it provides almost no information on how the scattering objects are distributed in the scattering volume. USAXS imaging greatly expands the usefulness of USAXS in four main ways. First, it provides direct images of the shapes and 3-D arrangements of the scattering objects. Second, it enables the local scattering intensity to be measured as a function of the scattering vector *q* by comparing images produced at different *q*'s. From these *q*-dependent scattering data, it becomes possible to extract shape and size information, even when the scattering objects are smaller than the spatial resolution of the imaging (although the determination of their locations is still limited by the resolution). Third, USAXS imaging extends the size range over which microstructural information can be obtained. The UNI-CAT USAXS at the APS measures over three orders of magnitude in size of real-space structures from about 1 nm to a little over 1 µm. USAXS imaging extends this range to millimeter-sized structures by imaging them directly. Fourth, USAXS imaging can identify the source of the observed scattering and thus verify that it arises from the expected microstructural features. In this research, USAXS imaging was used together with USAXS in an attempt to observe the relationship between the features in the amorphous PMMA matrix and the CB additive, which may account for this composite material's remarkable properties.

Compositions ranging from pure PMMA to samples containing up to 6.5% CB were fabricated and measured. Complex impedance plots were used to calculate the resistance of each sample and then converted to resistivity using the sample dimensions. Conductivities of the samples were obtained by fitting the experimental data with an equivalent circuit and normalizing by the sample dimensions.

Results and Discussion

The electrical impedance data show that percolation begins almost immediately and that the threshold is at 0.133% CB by volume. This is in contrast to other PMMA/CB composites [2], which were found to display percolation at approximately 8% loading. The present results suggest that the high surface area and branching of the CB used may be responsible for the dramatic increase in the conductivity. The unexpectedly low value of the percolation threshold is thought to be due to a combination of effects brought about by the low CB particle size, its high branching, and the possible presence of tunneling conduction. Evidence for this was obtained by fitting the conductivity to the volume fraction raised to the negative 1/3 power [2]. Atomic force microscope (AFM) studies were performed on the samples with higher CB concentrations in an attempt to observe the CB network in the composites more closely, where those results indicate that some agglomeration occurs even at 0.4%.

USAXS scans of the 0.1%, 0.2%, 0.4%, 0.6%, 0.8%, and 1.0% PMMA/CB materials showed the same features that were seen in the earlier work [1]. A knee in the scattering was found in the vicinity of $q = 0.006$ Å^{-1}, below which the power-law slope was ≈ -2.7 and above which it was ≈ -3.3. A USAXS image of the scatterers taken at $q = 0.0005$ Å^{-1} is shown in Fig. 1. Quite remarkably, the amorphous PMMA appears to form very large grains that seem to be surrounded by the filler material. This network could not be seen with the optical microscope, but it may well be responsible for the remarkable properties at low-concentration of CB in PMMA.

FIG. 1. USAXS image taken at $q = 0.0005$ *Å*$^{-1}$ *of PMMA/CB with 0.8% loading. The field of view is 0.57-mm wide × 0.28-mm high.*

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