Void Morphology in Polyethylene/Carbon Black Composites

D. W. M. Marr*

Chemical Engineering and Petroleum Refining Department, Colorado School of Mines, Golden, Colorado 80401

M. Wartenberg and K. B. Schwartz

Raychem Corporation, Menlo Park, California 94025

M. M. Agamalian and G. D. Wignall

Solid State Division, Oak Ridge National Laboratories, Oak Ridge, Tennessee 37830

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ABSTRACT: Through the use of small angle neutron scattering (SANS), we have determined the size and quantity of voids incorporated during fabrication of polyethylene/carbon black composites. Analysis of such systems via X-ray scattering is difficult because of their three-phase nature, being composed of polymer matrix, filler, and any trapped voids. Through a combination of SANS on deuterated and protonated composites, however, the scattering contrast can be varied to reflect either a two or three phase morphology and the size and quantity of voids determined. The scattering analysis used to extract void morphology is based on the three-phase model of microcrack determination via small angle X-ray scattering (SAXS) developed by W. Wu (*Polymer* **1982**, *23*, 1907) as applied to particulate reinforced composites.

Introduction

Carbon black has been blended with polyolefins for many years and used as a reinforcing filler in a number of applications, with automotive tires probably being the best known. Carbon black (a relatively conductive material) can also be blended with polyethylene (a semicrystalline polymer and an insulator) to produce a conductive composite used in electrical products, e.g. circuit protection devices, self-regulating heaters, sensors, and corrosion protection devices such as sacrificial anodes. In the circuit protection example, the concentration of carbon black is, at room temperature, above the percolation threshold and the composite is conducting; however, under conditions of high current flow, the composite heats. The heating induced by this overcurrent melts and expands the polyethylene matrix, lowering the effective concentration of the carbon black. As the composite approaches the percolation threshold, it becomes highly resistive.[1] This results in a significantly lower current and the device cools to its original state. Therefore, a simple mixture of carbon black and polyethylene acts as a resettable fuse. In another application using a similar system, carbon black is blended with mixtures of polymers and the resulting device is used continuously as a heater. If an overtemperature condition occurs, the network resistance increases, resulting in a lowered current. In this application the mixture of carbon black and polyethylene is used as a self-regulating heater.

In principle these products are quite simple; however, the electrical properties of the composites are affected by the microstructure formed during processing. Changes in the processing conditions can lead to significant variations in morphology and changes in the electrical performance. The ability to characterize these systems is therefore important for the design of these materials, though determining the morphology is extremely difficult due to the length scales involved (1−100 nm, too small to be investigated via typical light-based methods) and the absorption of visible light by carbon black. Other techniques such as scanning and transmission electron microscopies suffer from difficulty in both sample preparation and interpretation of the resulting images. Positron annihilation[2,3] has been used to examine void issues in polyethylene and polyethylene composites, though this technique is focused on subnanometer length scales. Small angle X-ray and neutron scattering (SAXS and SANS), however, probe a much wider range of dimensions and are sensitive to the length scales of interest for defining the properties of this particular composite system.

SAXS uses radiation of much smaller wavelength than visible light (∼1 Å) and is therefore sensitive to significantly smaller size scales than light scattering. X-rays are scattered by fluctuations in electron density (ED) within a given sample, and thus carbon black/polyethylene composites have substantial SAXS cross sections due to the large ED difference between the components. The problem, however, is that there is strong ED contrast between carbon black, polyethylene, and voids, making interpretation of scattering data more complex. Due to the unique capabilities of small angle neutron scattering, including high bulk penetrating power and the ability to manipulate local scattering amplitudes via isotopic labeling (deuteration), we can overcome these difficulties. SANS uses neutrons of wavelength (5−10 Å) comparable to SAXS and therefore probes similar length scales. Neutrons, however, are scattered by nuclei (as opposed to electrons), and thus the SANS contrast can be changed via isotopic substitution, which has little effect on the chemistry of the blend.[4,5] Because of the large difference in the scattering lengths between hydrogen and deuterium, we can substitute one for the other to tune the scattering length density (SLD) of the polyethylene matrix to approach that of the filler particles, thus accentuating the low concentration phase. Previous SANS experiments[6] have suggested the presence of a third phase (voids), and in this paper, we focus on a set of experiments designed

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Table 1

species	density (g/cm^3)	amorphous (10^{10} cm^{-2})	crystalline (10^{10} cm^{-2})	average (10^{10} cm^{-2})
h-polyethylene (hPE)	0.953 ± 0.001	-0.30 (ρ^{a}_{hPE})	-0.36 (ρ^{x}_{hPE})	-0.34 (ρ^{t}_{hPE})
d-polyethylene (dPE)	1.080 ± 0.002	7.30 (ρ^{a}_{dPE})	8.58 (ρ^{x}_{dPE})	8.13 (ρ^{t}_{dPE})
carbon black (CB)	1.917 ± 0.002			6.40 (ρ_{CB})
voids				0.0

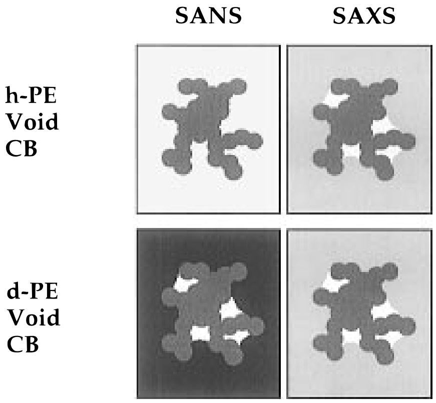

Figure 1. Illustration of contrast matching experiments.

to quantitatively determine the volume fraction and dimensions of voids incorporated during carbon black/polyethylene composite preparation. Contrast variation methods have also been used[7] in a complementary study to probe the internal structure of the carbon black particles.

Figure 1 illustrates the proposed experiments schematically for the three-phase system (polymer, carbon black, and voids) and makes it clear that one cannot resolve void morphology solely with SAXS. However, if one examines a normal protonated composite via SANS, the sample is essentially two-phase because the scattering length densities of polyethylene and voids are virtually identical (see Table 1). If one blends carbon black with deuterated polyethylene, however, the presence of voids is highlighted within the carbon black/deuterated polyethylene matrix. Through a combination of these two experiments, one can now extract quantitative information about void size and quantity. We begin by discussing the two-phase system (carbon black in hydrogenated polyethylene) and the model used in its analysis. We then progress to the fully three-phase deuterated polyethylene composites, their analysis, and finally the results of this approach.

Experiment Section

Four composites were prepared at carbon black volume fractions of 0.360 and 0.429 using a furnace black of intermediate size and shape. Two different polymer matrices were used, protonated polyethylene at a density of 0.953 ± 0.001 g/cm^3 and an analogous fully deuterated polyethylene at a density of 1.080 ± 0.001 g/cm^3. Composite samples were mixed in a DACA minicompounder,[8] a small scale twin-screw mixer/extruder (for compounding and extrusion of samples up to total volumes of approximately 5 cm^3). Carbon black and deuterated polyethylene were added in the appropriate ratios to a total weight of 1.5 g and processed at a temperature of 200 °C for 5 min in the twin-screw extruder.

The experiments were performed on the W. C. Koehler 30 m SANS facility at Oak Ridge National Laboratory.[9] The neutron wavelength was 4.75 Å ($\Delta\lambda/\lambda \sim 5\%$) and the source (3.5 cm diameter) and sample (1.0 cm diameter) slits (irises) were separated by a distance of 7.5 m. The sample−detector distances were 4.0 and 17.8 m, and the data were corrected for instrumental backgrounds and detector efficiency on a cell-by-cell basis, prior to radial averaging to give a q range of 0.04 $< q = 4\pi\lambda^{-1} \sin\theta < 1.5$ nm^{-1}, where 2θ is the angle of scatter. The net intensities were converted to an absolute (±4%) differential cross section [dΣ/d$\Omega(q)$] per unit sample volume (in units of cm^{-1}) by comparison with precalibrated secondary standards, based on the measurement of beam flux, vanadium incoherent cross section, and the scattering from water and other reference materials.[10] Procedures for transmission measurements and for subtracting the incoherent background, arising largely from the protons in the sample, have been described previously.[11]

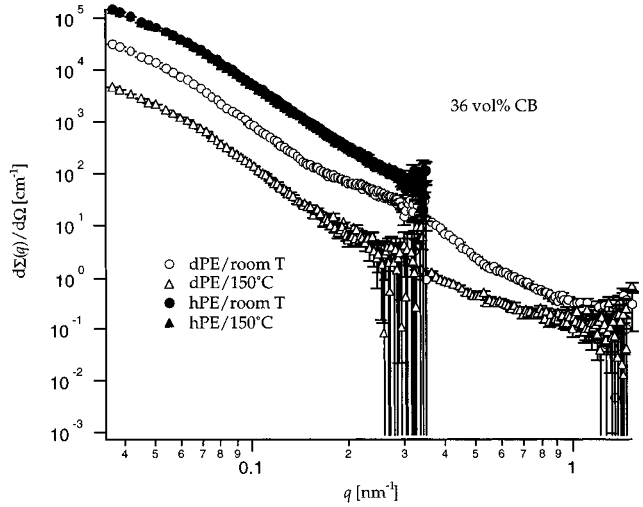

Figure 2. SANS scattering from 36 vol % CB samples at room and high temperatures.

Analysis

Figure 2 shows the SANS differential cross section dΣ/d$\Omega(q)$ for the two composite samples with a carbon black volume fraction of 36.0%. It may be seen that substituting dPE for hPE lowers the scattered intensity as expected. In addition, due to the difference in SLD between crystalline and amorphous regions in deuterated polyethylene (see Table 1) there is a “peak” associated with lamellar spacing in crystalline polyethylene around $q = 0.25$ nm^{-1} in the room temperature data for deuterated composites.

It may be seen that the cross sections of the protonated samples at room temperature and in the melt are very similar. The (SANS) contrast in this system is developed primarily from the difference in scattering length density between hPE and carbon black, neither of which change significantly with an increase in temperature. A small variation in total scattering is expected due to the change in volume fraction upon hPE melting and can be accounted for via the scattering invariant Q

$$Q = \int_0^\infty q^2 \frac{d\Sigma(q)}{d\Omega}\, dq \qquad \text{and} \qquad Q = 2\pi^2\phi_1\phi_2(\rho_1 - \rho_2)^2$$

for two-phase systems. Upon melting, we expect the effective volume fractions to change because of the expansion of the polyethylene phase. The relative change in volume fraction can be predicted from

Table 2

matrix	temp (°C)	ϕ_{CB}	$d\Sigma/d\Omega(0)$ (cm^{-1})	a_c (nm)	$10^{-22}Q^{exp}$ (cm^{-4})	$10^{-22}Q^{pred}$ (cm^{-4})	l_1 (nm)	l_2 (nm)
hPE	RT	0.360	(1.72 ± 0.02) × 10^6	40.7 ± 0.1	2.00 ± 0.04	2.06	63.6 ± 0.2	113.1 ± 0.3
hPE	150	0.335	(2.14 ± 0.03) × 10^6	43.7 ± 0.1	2.01 ± 0.04	1.97	65.7 ± 0.2	130.4 ± 0.3
hPE	RT	0.429	(1.43 ± 0.01) × 10^6	36.4 ± 0.1	2.34 ± 0.03	2.19	63.7 ± 0.2	84.8 ± 0.3
hPE	150	0.402	(1.67 ± 0.02) × 10^6	38.5 ± 0.1	2.29 ± 0.05	2.13	64.4 ± 0.2	95.9 ± 0.3

Table 3

matrix	temp (°C)	ϕ_{CB}	a_1 (nm)	a_2 (nm)	$10^{-5}A_1$ (cm^{-1})	$10^{-4}A_2$ (cm^{-1})	f	$10^{-22}Q^{exp}$ (cm^{-4})	$10^{-22}Q^{pred}$ (cm^{-4})
hPE	RT	0.429	33.4 ± 0.2	39.2 ± 0.2	9.06 ± 0.17	4.05 ± 0.11	0.889	2.15 ± 0.08	2.19
hPE	150	0.402	34.8 ± 0.2	40.0 ± 0.2	9.82 ± 0.21	4.51 ± 0.12	0.880	2.08 ± 0.08	2.13

Table 4

matrix	temp (°C)	ϕ_{CB}	a_1 (nm)	a_2 (nm)	$10^{-4}A_1$ (cm^{-1})	$10^{-3}A_2$ (cm^{-1})	f	$10^{-20}Q^{exp}$ (cm^{-4})	$10^{-20}Q^{pred}$ (cm^{-4})
dPE	RT	0.360	40.3 ± 0.1	45.9 ± 0.3	22.9 ± 01.4	17.5 ± 0.6	0.811	33.9 ± 03.4	13.1
dPE	150	0.336	38.7 ± 0.1	44.9 ± 0.1	3.20 ± 0.33	2.58 ± 0.15	0.812	5.36 ± 0.95	3.57
dPE	RT	0.429	37.0 ± 0.1	43.8 ± 0.3	19.0 ± 0.9	17.3 ± 0.5	0.801	36.8 ± 02.9	14.0
dPE	150	0.403	36.0 ± 0.1	41.1 ± 0.3	2.91 ± 0.23	2.82 ± 0.12	0.796	6.16 ± 0.83	3.85

$$\phi^{new} = \frac{1}{1 + \frac{d^{t}_{PE}}{d^{a}_{PE}}\left(\frac{1}{\phi^{old}} - 1\right)}$$

where d^{a}_{PE} is the amorphous phase density and d^{t}_{PE} is the total density. When the above data for the protonated composites in the Debye–Bueche model[12] are interpreted with

$$\gamma(r) = e^{-r/a_c} \qquad \text{and} \qquad \frac{d\Sigma(q)}{d\Omega} = \frac{d\Sigma(0)}{d\Omega}(1 + q^2 a_c^{\,2})^{-2}$$

chord lengths (or domain sizes) of the individual phases can be determined via

$$l_i = \frac{1}{1 - \phi_i}\int_0^\infty \gamma(r)\, dr \qquad \text{or}$$

$$l_1 = \frac{a_c}{1 - \phi_1} \qquad \text{and} \qquad l_2 = \frac{a_c}{\phi_1}$$

To account for the lack of data at low and high q, experimental invariants were generated by integrating the model fits to the data. To obtain experimental values for Q at higher concentrations, the data were fit to the two-correlation length Debye–Bueche model.[13–15]

$$\frac{d\Sigma(q)}{d\Omega} = \frac{A_1}{(1 + q^2 a_1^{\,2})^2} + A_2 \exp\left(-\frac{q^2\, a_2^2}{4}\right)$$

where

$$\frac{d\Sigma(0)}{d\Omega} = A_1 + A_2 \qquad \text{and} \qquad f = \frac{A_1}{A_1 + \frac{8A_2}{\sqrt{\pi}}\left(\frac{a_1}{a_2}\right)^3}$$

Our results for these model fits are shown in Tables 2 and 3. In Table 2 the domain size l_1 corresponds to the phase at volume fraction ϕ_1 (carbon black), as confirmed by the fact that it does not vary as the sample is brought through the melt transition. Note also the domain size of the polyethylene phase behaves as expected. As the samples are melted, the domain size increases, indicating the polyethylene expansion; also, the domain size decreases as the polymer volume fraction is lowered. With a knowledge of the SLDs and volume fractions of the components, we have generated predicted invariants for comparison to those determined experimentally. As seen in Tables 2 and 3, the agreements are very good, indicating that we have a good handle on the analysis for protonated polyethylene/carbon black composites and that this system effectively behaves as two phases.

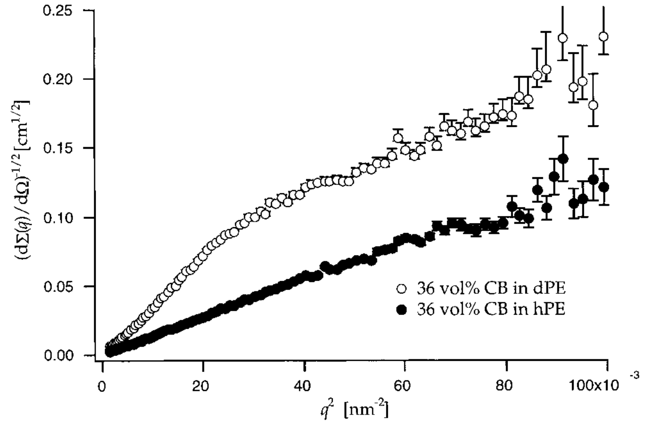

Figure 3. Debye–Bueche plot of a deuterated and protonated composite showing the linear behavior of the protonated sample.

To avoid the complications added by the crystalline lamellae in dPE, the data here were fit over a range of 0.037 nm^{-1} < q < 0.126 nm^{-1}, corresponding to length scales greater than 50 nm. As shown in Figure 3, the data are not well fit by the single-parameter Debye–Bueche model. For two-phase systems, and as seen in the protonated composite case, this model should fit well. Such a deviation indicates that something else is present in these systems that has low contrast in the protonated polyethylene but shows up in the deuterated polymer case at low q, i.e. voids.[6] This inference is supported by the difference in the calculated and predicted scattering invariants shown in Table 4. Notice that in each of the cases, the experimental invariant is higher than that which one would predict for a simple two-phase system, indicating once again that there is another phase at low q contributing to the total scattering.

Assuming that the structure of this three-component composite (polyethylene, carbon black, and voids) is identical in the deuterated and protonated cases, we can extract quantitative information about void size and

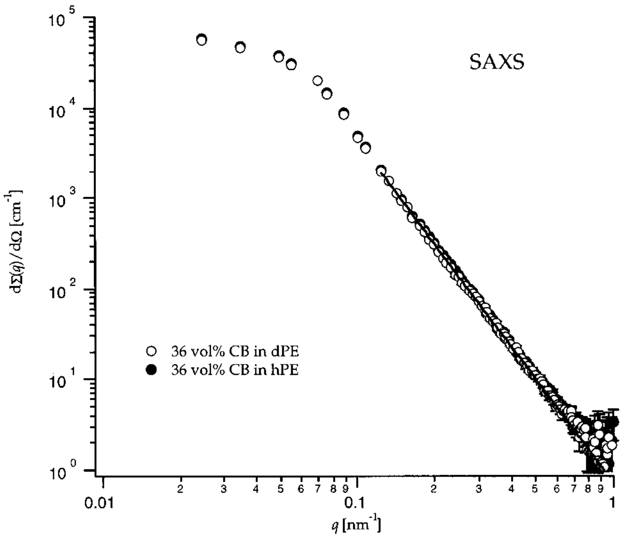

Figure 4. SAXS scattering from 36 vol % carbon black samples where the scattering from both deuterated and protonated composites overlap (the power law slope of this line is −3.79 ± 0.01).

Table 5

temp (°C)	ϕ_1 (CB)	ϕ_3 (voids)	l_1 (nm) (CB)	l_2 (nm) (PE)	l_3 (nm) (voids)
RT	0.360	0.0188 ± 0.0033	61.7 ± 1.0	109.7 ± 1.8	44.0 ± 24.0
150	0.335	0.0018 ± 0.0011	67.1 ± 1.2	133.1 ± 2.5	29.7 ± 152
RT	0.429	0.0212 ± 0.0032	57.9 ± 1.9	77.0 ± 2.6	42.0 ± 18.0
150	0.402	0.0025 ± 0.0010	57.0 ± 1.9	84.7 ± 2.8	40.0 ± 74.4

quantity. SAXS can be used to validate this hypothesis because of the sensitivity of X-rays to the scattering contrast between both polyethylenes (hPE/dPE) as well as carbon black. As displayed in Figure 4, the SAXS scattering patterns from the deuterated and protonated polyethylene composites overlap, showing the microstructures to be virtually identical over the length scales investigated. Thus, it is reasonable to use the scattering data from the protonated samples as a template for the expected SANS scattering curves of the deuterated materials if composed of only two phases. We will then attribute the excess scattering to the third phase.

This approach can be placed on firm theoretical ground via the theoretical formalism developed by Wu[16] to model microvoids (cracks) in composite materials. By comparing the SAXS scattering from undamaged (two phase) composites to damaged (three phase) composites, he was able to extract useful information about the size and quantity of the void phase. This approach is analogous to our comparisons of systems that are two phase (protonated composites) with those of similar morphology but with the addition of a small void component (deuterated composites). This approximation takes all three phases into account by expressing the correlation function for the entire system as a summation of the correlations for the individual phases $\gamma_i(\mathbf{r})$. For three-phase isotropic systems (phase 1 = filler, phase 2 = matrix, phase 3 = voids) the invariant can be determined via

$$Q = \int_0^\infty q^2 \frac{\mathrm{d}\Sigma(q)}{\mathrm{d}\Omega}\,\mathrm{d}q = 2\pi^2[\phi_1\phi_2(\rho_1 - \rho_2)^2 + \phi_2\phi_3(\rho_2 - \rho_3)^2 + \phi_1\phi_3(\rho_1 - \rho_3)^2]$$

If we denote Q^0 as the invariant for a system without voids (effectively blends of protonated polyethylene and carbon black), then

$$Q^0 = 2\pi^2\,\phi_1^0(1 - \phi_1^0)(\rho_1 - \rho_2^0)^2$$

and

$$Q - Q^0\left(\frac{\rho_1 - \rho_2}{\rho_1 - \rho_2^0}\right)^2 = 2\pi^2[(\rho_1 - \rho_2)^2(\phi_1(1 - \phi_1) - \phi_1^0(1 - \phi_1^0) - \phi_1\phi_3) + \phi_2\phi_3(\rho_2 - \rho_3)^2 + \phi_1\phi_3(\rho_1 - \rho_3)^2]$$

If one examines isothermal transitions from "damaged" to "undamaged" composites, the filler correlations and volume fractions will not vary (i.e., $\gamma_1(r) = \gamma_1^0(r)$, $\phi_1 = \phi_1^0$) and the volume fraction of the void phase can be calculated via

$$\phi_3 = \left[Q - Q^0\left(\frac{\rho_1 - \rho_2}{\rho_1 - \rho_2^0}\right)^2\right] / 2\pi^2\{\phi_1[(\rho_1 - \rho_3)^2 - (\rho_1 - \rho_2)^2 - (\rho_2 - \rho_3)^2] + (1 - \phi_3)(\rho_2 - \rho_3)^2\}$$

In addition, one can calculate the chord length (domain size) of this low volume fraction domain through definition of a function similar to the scattering invariant. For three-phase systems

$$\mathbf{Z} = \int_0^\infty q\,\frac{\mathrm{d}\Sigma(q)}{\mathrm{d}\Omega}\,\mathrm{d}q = 4\pi[(\rho_2 - \rho_1)(\rho_3 - \rho_1)\phi_1(1 - \phi_1)\int_0^\infty \gamma_1(r)\,\mathrm{d}r + (\rho_3 - \rho_2)(\rho_1 - \rho_2)\phi_2(1 - \phi_2)\int_0^\infty \gamma_2(r)\,\mathrm{d}r + (\rho_1 - \rho_3)(\rho_2 - \rho_3)\phi_3(1 - \phi_3)\int_0^\infty \gamma_3(r)\,\mathrm{d}r]$$

Assuming the volume fraction of voids is small (as justified in the results shown in Table 5), and that the chord lengths of phases 1 and 2 remain constant, the chord length of the void domain can be estimated via

$$l_3 = \frac{\mathbf{Z} - \mathbf{Z}^0\left(\frac{\rho_1 - \rho_2}{\rho_1 - \rho_2^0}\right)^2}{4\pi\phi_3(1 - \phi_3)(\rho_1 - \rho_3)(\rho_2 - \rho_3)}$$

Results and Discussion

Our investigations include four experiments where the composite has gone from two to three phases under conditions of constant filler volume fraction. Using the equations developed in the previous section, we can now determine the void volume fractions and associated chord lengths, the results of which are shown in Table 5. For the room temperature composites, we find a void size of 44 ± 24 nm and a void content of 1.9 ± 0.3 vol % for the 36.0 vol % sample. For the 42.9 vol % sample we obtain values of 42 ± 18 nm and 2.1 ± 0.3 vol %. Once the composites are heated above the melting point, there is a significant decrease in the void content, to a value of the same order as the experimental error. This decrease might be expected and suggests that the polyethylene domains grow at the expense of the voids as the temperature is brought above the melt. Also of note, and despite the limited data, is the apparent scaling of the void content with filler concentration at both room and high temperatures.

Though we currently do not have a technique that would allow us to corroborate our void size determina-

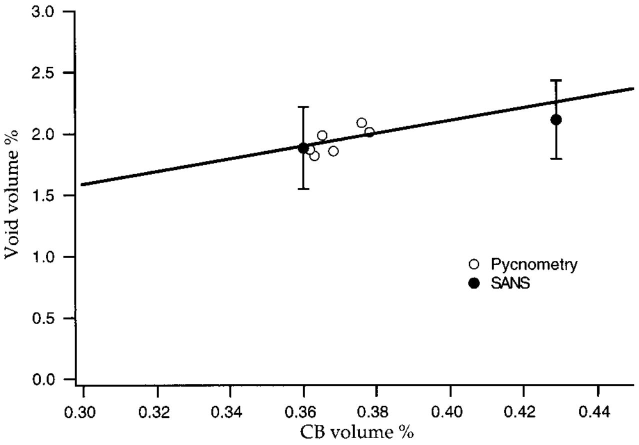

Figure 5. Void content determined via SANS and pycnometry at room temperature (the line is a fit through the pycnometry data that passes through 0,0).

tions, we have conducted a number of pycnometry measurements at room temperature on similarly prepared materials in order to compare to the void volume results. The void content was determined by comparing the measured densities with those predicted by assuming a lack of voids via *void content* $= (1 - \rho_{\mathrm{meas}})/\rho_{\mathrm{pred}}$ (see Figure 5). Despite the small range over which these pycnometry experiments were conducted, the results indicate that the void contents determined via the scattering studies are quite reasonable.

The analysis used in our scattering investigations is based on studies of materials where data could be taken before and after the formation of the void phase. Our approach relies quite heavily on the assumption that the three-phase morphology is identical in separately prepared composites, and thus we have made every attempt to maintain consistency in sample preparation. This postulate is supported by the SAXS data, which suggests that the morphology in these systems is only weakly dependent on processing conditions. We have also neglected the difference in SLDs between the crystalline lamellae and amorphous regions in dPE and used the crystallinity index to calculate an average SLD of 8.1×10^{10} cm^{-2}. Despite these approximations, we have achieved good agreement with independent estimates of the void content (Figure 5). An extension of these experiments involves the blending of hPE and dPE in a 20/80 mixture in order to closely match the SLD of the carbon black filler. As seen in dPE/hPE blend phase behavior studies, even relatively high molecular weights of these two polymers are miscible.[17] These studies will provide an independent determination of the void content without the assumptions inherent in the three-phase analysis and are currently underway to further improve our estimates of void content.

One can develop a number of hypotheses for the origin of voids in this system. These include the suggestion that incorporation could arise from incomplete wetting of the carbon black by the molten, amorphous polyethylene during high-temperature mixing.[6] It is also conceivable that voids could arise during the processing of highly structured fillers due simply to incomplete processing and the difficulty a viscoelastic fluid may encounter in penetrating very small domains, leading eventually to void entrainment. We have seen in these investigations, however, that the void volume fraction decreases to near zero above the melt, strongly suggesting that the system is nearly completely wetted during processing and that most of the void incorporation occurs post processing during composite cool. One hypothesis is that void formation could occur post processing as a mechanism for relieving stress as the composite cools below the matrix melt temperature. In polyethylene there are significant volume changes that occur upon crystallization, possibly leading to the formation of voids at the relatively weak interface between carbon black and the polymer matrix. Studies, therefore, using a polymer of similar chemistry but lower crystallinity (i.e., low-density polyethylene) could be used to help answer this question. This hypothesis does not explain the observed scaling of the void content with filler concentration, suggesting that entrainment may be involved and that carbon black structure will play a significant role in void quantity and morphology. This contradiction will serve as motivation for future studies into the influence of these factors on the system morphology.

Summary

These studies have shown that one can employ small angle neutron scattering to determine the size and concentration of voids incorporated in carbon black/polyethylene composites during processing. Approximately 2 vol % voids 40−50 nm in size were measured at room temperature for the systems and processing conditions we investigated. These voids decrease significantly in concentration during the melt transition, however, going from 2.0 to about 0.2 vol %. These results both prove the existence of voids and serve to motivate future investigation into the influence of processing and filler structure on void incorporation.

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