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Dopeable styrenic foams used in inertial fusion targets

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Low density polymer foams have been an integral part of targets used in Inertial Confinement Fusion (ICF) experiments. In order to accomplish this the formulation of the High Internal Phase Emulsion (HIPE) foam had to be optimized. Along with a change in density and the incorporation of fillers into a foam, there is also a change in the pore size and the distribution of pore sizes. The emulsion technique used to produce these foams is amenable to modification providing foams with a wide range of densities, 15 mg/cm^3 to 500 mg/cm^3, and metal loadings up to 90 percent by weight. A qualitative distribution of pore size can be seen visually with scanning electron microscopy (SEM). At low metal loadings SEM did not observe the submicron metal particles. The distribution of these particles in the foam matrix was seen with near-infrared imaging. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

Polymeric foams comprised of only carbon and hydrogen have been the main focus in the Inertial Confinement Fusion (ICF) targets at Los Alamos National Laboratory (LANL) for the past five years. The method used to make foams for the ICF program by Williams [1] is an extension of work developed at Unilever [2]. Polystyrene HIPE foams have received a lot of attention at LANL outside the ICF program. High internal phase emulsions are defined as emulsions containing an internal phase volume greater than 74% [3]. High Internal Phase Emulsion (HIPE) foams can be modified with bismaleimides for use in high temperature applications, >200°C [4], or with various functional groups for use as monolithic separation columns [5]. Target designs have become more complex over the years, which places more demands on the foams themselves. Parts that have dimensions less than 50 μm need to retain their dimensional stability to within 2–3 μm. These stringent demands have now been placed on metal containing foams that have a metal content greater than several weight percent.

Densities of undoped foams prepared at LANL usually range from 30 mg/cm^3 to 650 mg/cm^3. This is achieved by varying the ratio of the oil phase to the water phase. As the density of the foam increases there is a thickening of the struts of the cell along with a closing of the window of the cell wall between adjacent cells. Metals can be incorporated into foams over this entire range of densities. The resulting density of these metal composite foams is of course greater than that of the base foam and has approached 1,000 mg/cm^3. The metal doped foams have been of interest in components of hohlraums for Inertial Confinement Fusion [6] and the metal oxide foams have been used in targets in a study in fluorescent imaging as a diagnostic for imaging [7].

There has been much debate as to the type of polymers that are acceptable for use in targets. The general consensus is that a hydrocarbon-based polymer is preferred over those containing nitrogen and oxygen like polyimides and polyacrylates. Depending on the design of the target there is a loss in the gain of the target that contains nitrogen and oxygen. Metals can be readily incorporated into acrylate

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systems. These are polymers that are based on metal salts of polyacrylic acids. These systems have not been considered at this point due to their high oxygen content and the realtively low metal loading. The polymethylpentene (TPX) system has been doped with metals in the past at LANL [8, 9]. Although it is a CH_2 system, the levels of loading were on the order of a few weight percent, far too low for the desired level of doping in the hohlraum components. For these reasons we have focused on the styrenic HIPE foams.

2. Experimental

2.1. Materials

Styrene, divinylbenzene (DVB), sodium persulfate, metals, metal oxides, and scandium isopropoxide were purchased from Sigma-Aldrich Fine Chemicals, USA, and were used without any further purification. The sorbitan monooleate (SMO) samples were provided by Lonza, Inc., USA.

2.2. Preparation of foams

An oil phase, consisting of the monomers and surfactant, and an aqueous phase, consisting of water and the initiator, were prepared, followed by mixing using the standard emulsification techniques [1]. Once the emulsion was formed it was cured at 58°C for 24 h. The resulting foam was extracted with ethanol to remove the surfactant. The foam was then dried under ambient conditions. The pores formed during the emulsification process are open cell, on the order of one to tens of micrometers in diameter as determined by mercury porosimetry and scanning electron microscopy.

2.3. Preparation of metal doped foams

Two approaches were used to produce a doped polystyrene (PS) HIPE foam with scandium. The first was prepared by adsorbing the organometalic scandium isopropoxide onto the surface of the foam. Since the scandium isopropoxide contains only 2.9 atom% scandium, scanidium oxide (40 atom% Sc) was used to dope the foams in order to get a higher scandium content. Metal doped foams were prepared by dispersing the metal or metal oxide in the aqueous phase before making the emulsion. The tungsten powder had an average particle size of 0.8 μm and the gold powder had an average particle size of 85 nm. The densities of these metal being much greater than that of water lead to a rapid settling of the particles. Once the emulsion is formed the viscosity is sufficiently high enough to prevent the particles from migrating. Unfortunately the nanoparticulate gold tends to form aggregates that do not break up in the emulsification process. In order to get a uniform distribution of gold in the foam the aqueous phase needed to be placed in an ultrasonic bath for two hours. Once the aggregates were broken up they were not observed to reform upon polymerization of the foam.

2.4. Analysis of foams

Mercury Intrusion Porosimetry experiments were performed using a Micromeritics PoreCore-III. Mercury is a non-wetting liquid that does not wick into a substance by capillary action. Pressure needs to be applied on the mercury in order for it to fill a pore. The diameter of a pore can be calculated using the Washburn equation [10]:

$$D = -4\gamma \cos\theta / P \tag{1}$$

where γ is the surface tension, θ is the contact angle, and P equals the applied pressure. Incremental pore volume/pore area vs. pore diameter can readily be obtained. Pore sizes that could be measured ranged from 750 μm at a pressure of 1.4 kPa to 3 nm at a pressure of 414 MPa. Median pore diameter is defined to be the 50th percentile of the volume or area curve. The median values found for the volume average and the area average are not the same since larger pores contribute less to the pore area than they do the volume. The average pore diameter is calculated assuming that the pores are right cylinders. For these HIPE foams this only gives us an approximate value of the pore sizes since the Scanning Electron Micrographs (SEM) in Fig. 1 clearly shows that the pores for these foams are spherical rather than cylindrical. SEM micrographs were obtained using a S-520LB Scanning Electron Microscope (Hitachi High Technologies America).

Skeletal density measurements were obtained by helium pycnometry using an Acupyc-1330 (Micromeritics, Inc., USA). Envelope density measurements were made using a Micromeritics Geopycnometer. Skeletal density refers to the density of the material that makes up the foam whereas the envelope density represents the aereal density of the foam. To determine the envelope density of a material, neither a liquid nor a gas was used; instead, a free-flowing powder consisting of small, hard, spherical particles was used. The volume of a compacted bed was measured before the volume of the same bed was measured with the sample included. The volume displaced by the sample then was used to calculate the density of the foam.

Laser experiments conducted on the Trident laser were used to evaluate the feasibility of fluorescence-based imaging using a scandium doped foam. The major improvement that fluorescence-based imaging offers over traditional radiography is the enhanced measurement localization. This technique utilizes a standard backlighter illuminating a target causing a strategically placed dopant to fluoresce. Images were taken using a four-strip microchannel plate framing camera with an eight hole pinhole array. Time integrated spectroscopic data were obtained using a Bragg crystal spectrometer [7].

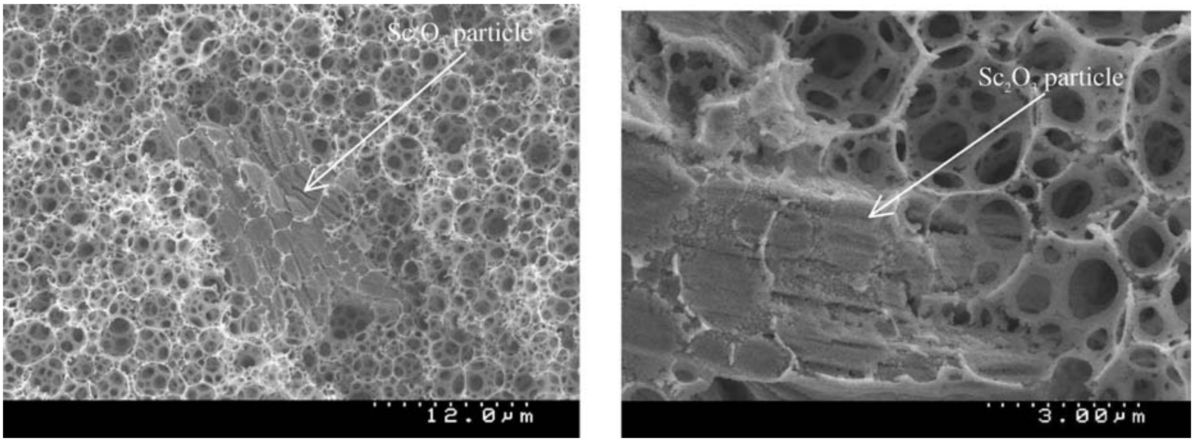

Figure 1 Sc_2O_3 particles incorporated in HIPE foam. (SEM).

Near-infrared (NIR) images were measured using the MatrixNIR NIR Chemical Imaging System(Spectral Dimensions, Inc., USA). For this study, two samples were examined and included a HIPE foam with a density of 30 mg/cm^3 and a tungsten-doped HIPE foam with a density of 80 mg/cm^3. The field of view for the imaging experiment was 14.9 mm × 11.9 mm and the spectral range was 950 cm^{-1} to 1,750 cm^{-1}. Images were measured in 10 nm steps with 16 frames averaged for a total collection time of 2 min. For a single data set the total number of spectra per set were about 82,000.

The near-infrared data were analyzed using principal component analysis (PCA). Since PCA is scale dependent, the data were processed with a background correction, spatial masking, and mean centering with normalization to unit variance. PCA is utilized to assess the variance in the two data sets.

3. Results and discussion

The initial scandium doped foams were prepared by adsorbing organomettalic scandium isopropoxide onto the surface of the foam. The density of the foam increased from 65 mg/cm^3 to 88 mg/cm^3, a 29% increase in envelope density. The skeletal density increased from 1.08 g/cm^3 to 1.20 g/cm^3. Scanning electron micrographs of this foam showed a uniform coating of scandium isopropoxide on the surface of the cell walls without any gross agglomeration present in the sample. Although these targets provided sufficient fluorescence to be successfully imaged a higher scandium loading was desired to improve the resolution of the image and to enhance the contrast. By changing the dopant from scandium isopropoxide to scandium oxide, higher loadings of scandium are possible since the weight percentage increases from 20 weight% to 65 weight% (3 atom% and 40 atom percent, respectively). If the particle size of Sc_2O_3 is small enough, the fluorescence should be averaged across the sample. A mechanical grinder was used to grind the Sc_2O_3 to a smaller more uniform particle size. The foam prepared by this method consisted of a 50 mg/cm^3 foam doped with 30 mg/cm^3 scandium oxide. The resulting density of the foam was 84 mg/cm^3, which is in good agreement with the calculated density. The micrograph of this foam, Fig. 1, shows distinct crystals of the scandium oxide embedded through several of the cell walls of the foam due to the large size of the scandium oxide particles.

The images acquired on the Trident laser shown in Fig. 2 for the doped and undoped foams were done using a titanium backlighter pumped at identical energies. The emission from the scandium doped foam, Fig. 2b, is clearly visible, where there is no discernable emission from the undoped foam. The midplane lineouts in Fig. 2d clearly show the additional peak from the fluorescence of the scandium in the doped foam along with that of the backlighter in Fig. 2c. Two further experiments were performed to confirm that these emissions were due to the Kα fluorescence of the scandium [7].

The incorporation of particles into the foam seems to have an affect on the surface tension of the aqueous phase in the emulsion. A dramatic change in the structure of the struts can be seen. Fig. 3 shows scanning electron micrographs of a standard HIPE foam, a foam with 2 atom percent gold, and a foam with 2 atom percent tungsten and the highly loaded tungsten foam. This change in structure is seen as a change in the pore size distributions in these foams as determined by mercury porosimetry shown in Fig. 4. The metal doped foams have significant amount of pores larger than 10 μm that are not present in the undoped material. Aggregates of the particles in either the struts or pore walls are not seen in the SEMs of the foams with two atom percent loading. The aggregation of tungsten particles seen in the 86 wt.% tungsten loaded foam can be seen in Fig. 4d. The emulsions for these low density foams have very high viscosities that prevent the higher density metal particles from settling. Skeletal densities of the metal loaded foams are constant along the 6 cm length of the cylinder, which are cured in an upright position. If the metal particles within the foam monolith were to be

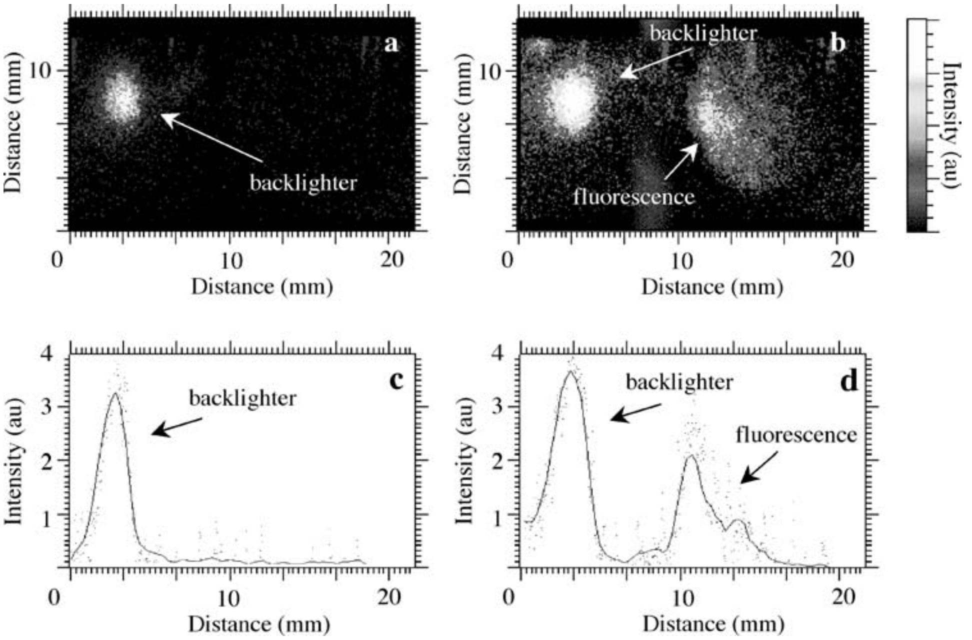

Figure 2 Measured emission from an (a) undoped HIPE foam, (b) and a Sc_2O_3 doped foam and (c) and (d) the corresponding midplane lineouts of (a) and (b), respectively.

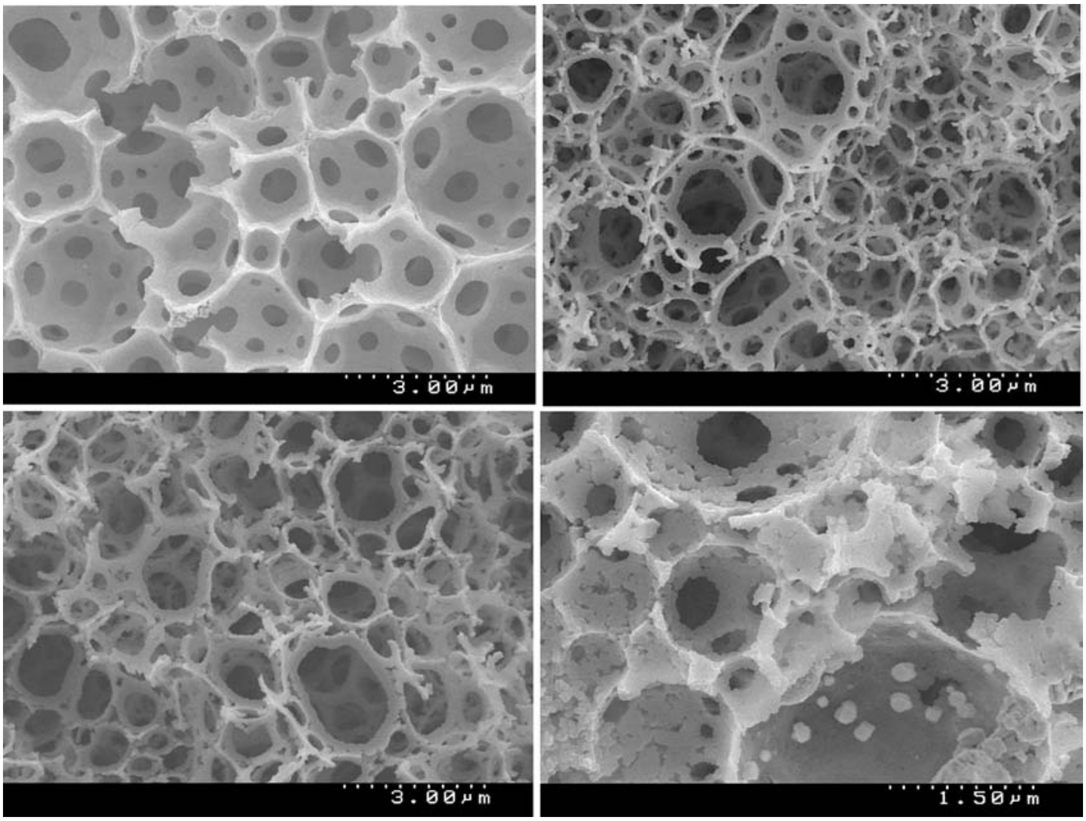

Figure 3 SEMs of four HIPE foams, clockwise from top left: undoped, plus 2 atom% gold, plus 2 atom% tungsten, and a highly loaded tungsten foam.

settling, the skeletal density at the top of the foam would be less than that at the bottom of the foam.

Density measurements of samples taken along the foam block do not show much of a difference in density indicating that there is relatively little settling of the metal particles once the emulsion forms. Table I shows both experimental and theoretical values for the skeletal densities of these metal composite foams. The composite foams

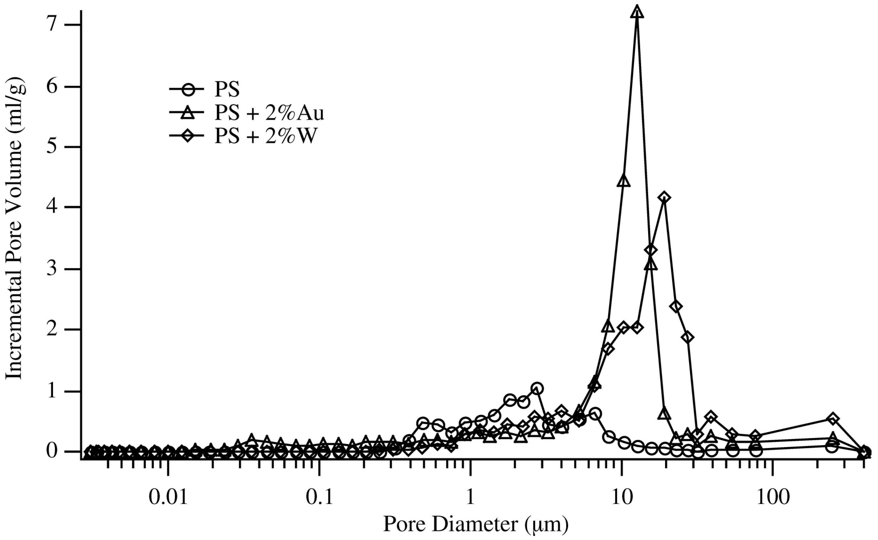

Figure 4 Pore size distributions for metal composite foams versus a standard HIPE foam as determined by mercury porosimetry.

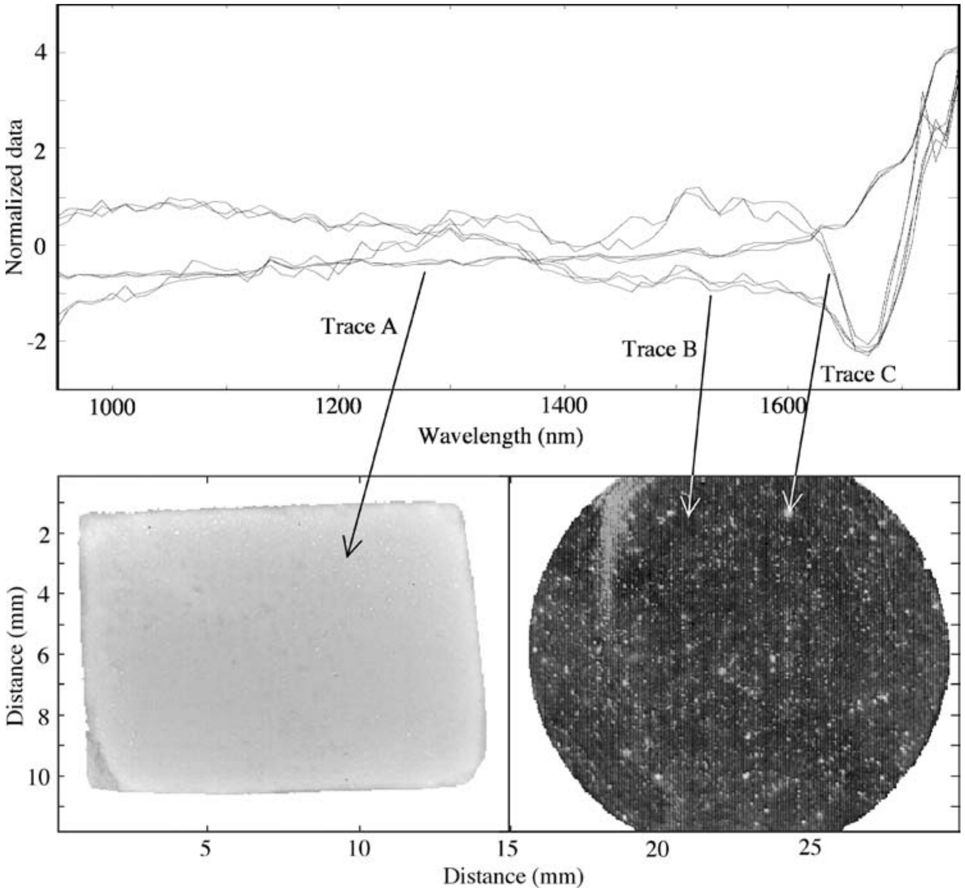

Figure 5 Single pixel spectra (top) and corresponding grayscale images for a HIPE foam (left) and a tungsten composite foam (right).

with the Y atom% metals are designated PSXMY, where X is the atom percent contributed by the foam. Calculations of the densities of the composite foam were done using the following simple mixing equation:

$$\frac{w_1}{\rho_1} + \frac{w_2}{\rho_2} = \frac{\overline{w}}{\rho}$$

where w_1 and ρ_1 are the weight percent and density of the PS and w_2 and ρ_2 are the weight percent and density of the metal. The agreement between the calculated value and experimental value of the densities shows that the syringe pump technique is an efficient way to incorporate the metal into the foam.

TABLE I. Skeletal density as determined by helium pycnometry

	Skeletal Density (g/cm^3)	
	Measured	Theoretical
Gold	19.2784	19.3(11)
Tungsten	18.6813	19.3(11)
PS Foam	1.0815	1.072(12)
PS98Au2	1.2944	1.359
PS98W2	1.2884	1.359
PS76W24	6.6810	6.995

Two foam samples were examined by near-infrared imaging to determine the distribution of the tungsten dopant in the HIPE foams. Near-infrared imaging is utilized extensively in the pharmaceutical industry to examine the distribution of components in pill samples. The two samples were an undoped HIPE foam with a density of 30 mg/cm^3 and an 80 mg/cm^3 foam with added tungsten. Imaging of these two samples allows for the examination of components within these samples. Single spectra from the PCA and corresponding images are shown in Fig. 5. The PCA analysis demonstrates a single component, as expected, for the undoped foam and two components for the tungsten-doped foam. Trace A in Fig. 5 represents the one component for the 30 mg/cm^3 HIPE foam, while trace B and trace C are from the analysis of the 80 mg/cm^3 doped foam. The undoped HIPE foam demonstrates an uniform distribution of the single component in the image. The near-infrared PCA image of the doped foam is able to distinguish the two components. The component identified as trace C in the image can be interpreted as the distribution of the tungsten dopant in the foam. The tungsten shows up as small inclusions distributed throughout the foam sample.

4. Conclusions

We have demonstrated that metal composite foams can be made. These foams are readily tailorable in terms of the composition and density of the foam along with the metal content. Scandium oxide composite foams were made and the targets fabricated from these foams provided a viable source for fluorescence diagnostics.

Imaging of these HIPE foams has provided a challenge over the years. Doping these foams with metals has added an extra dimension. SEM analysis has enabled us to look at the pore structure of these foams and as seen in this article, it does not necessarily catch micrometer size particles in the foam. Other techniques such as infrared imaging or other backscattering techniques [13] are necessary to resolve these dopants from their polymeric matrix.

Acknowledgments

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