Plasma-Deposited Polymer Films. I. Low-Angle X-Ray Study

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Synopsis

A low-angle x-ray scattering technique has been applied to determine the submicrostructure of plasma-formed polyethylene and polystyrene. The plasma-formed polymers appear to closely approximate a "filler–binder" structure where polymer spheres constitute the filler material and a lower-density polymer, the binder. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) micrographs confirm the spherical diameters predicted by the low-angle x-ray scattering data.

INTRODUCTION

Conventional analyses of the physical and chemical properties of plasma-formed polymer films are usually hampered by their general insolubility arising from a high degree of crosslinking. Accordingly, other techniques have been used in attempts to more fully characterize their unique properties and morphology.

In the course of a mechanistic and structural study of plasma-polymerized ethylene, a low-angle x-ray scattering technique[1] was employed to determine the submicrostructure of the polymer films. The data were consistent with a morphology of closely packed globular particles.

Several investigators have examined plasma-formed polymers with scanning electron microscopy (SEM) and observed spherical powders on the surfaces.[2–13] Thompson observed plasma-formed polystyrene spheres with diameters of 0.2–1.7 microns which varied with power to the reactor.[2] Liepens and Sakaoku determined that their plasma-formed polystyrene spheres were closely sized around 2360 Å for the reactor conditions used.[3] Kobayashi et al. found plasma polyethylene globules of an average size of 1–2 microns with their energetic polymer formation.[4] Niinomi et al. reported plasma polyethylene powders formed on several substrates to contain spheres 0.2–1.2 microns in diameter.[5] They observed that powder formation was favored by lower flow rates and pressure. However, other researchers considered this phenomenon as separate from film-forming processes.[2,4–7,9,11] This conclusion was based largely on SEM observation that spheres were no longer visible. However, the problem with this conclusion is that the sphere size corresponded roughly to the smallest resolution limits of the SEM instruments employed.

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The low-angle x-ray technique has some advantages over SEM techniques. The x-rays probe the bulk volume of the sample and do not destroy or even appreciably alter the sample being investigated. (Some micrographs of plasma-formed polymers have shown evidence of the electron beam attacking the surface.[2]) Furthermore, the x-ray technique is capable of resolving dimensions of the order of, and smaller than, SEM. For these reasons, the low-angle x-ray technique provides a unique and complementary tool for probing plasma-formed polymer films.

EXPERIMENTAL

The design and operating parameters of the rf-induced plasma reactor have been described in the literature.[14]

Samples for scattering analysis were obtained from several sources. Plasma-deposited polyethylene was scraped from the walls of the rf coil reactor section used to prepare the films. The film was formed during a 24-hr, 5-W, 20-micron (partial pressure of monomer) run. For comparison purposes, a piece of commercial polyethylene sheet was used. Plasma-deposited polystyrene samples were prepared similarly.

Low-angle x-ray scattering data for the samples were obtained with a Kratky camera over angles from about 0.003–0.2 radian. A copper target was the source of x-rays, the scattering of which was detected by a proportional counter. A linear amplifier and pulse height analyzer ensured that only x-rays in a narrow wavelength band around the CuK_α wavelength were recorded. The scattering data were corrected for instrumental background. Collimation corrections were performed by the method of Lin et al.[15]

RESULTS AND DISCUSSION

A convenient method of data analysis is a log–log plot of the corrected scattered intensity versus the scattering angle. For the plasma-formed polymer samples at most scattering angles, this plot yielded a straight line with a slope of -4. This kind of scattering curve, corresponding to a scattered intensity proportional to the inverse fourth power of the scattering angle, is characteristic of samples containing globular, nearly equidimensional inhomogeneities.[1,16] However, the possibility of nonglobular particles cannot be excluded from consideration.

The results for plasma-deposited polyethylene are shown in Figure 1. As can be seen in comparing Figures 2(a)–2(c) with Figure 1, the scattering curves for three orientations of conventional polyethylene are completely different from those for plasma-deposited polyethylene. Conventional polyethylene exhibits none of the structure types discussed.

Data obtained from these two types of polyethylene samples suggested an extension of the low-angle x-ray analysis to two samples of plasma-deposited polystyrene. The resulting low-angle curves are shown in Figure 3. As with the plasma-formed polyethylene, the plot is characteristic of material containing globular inhomogeneities.

The presence of sets of subpeaks in the higher-angle scattering regions of Figures 1 and 3 may be associated with diffraction effects. The Bragg spacings range from 30 to 90 Å, but their relationship to the polymer segments is unknown.

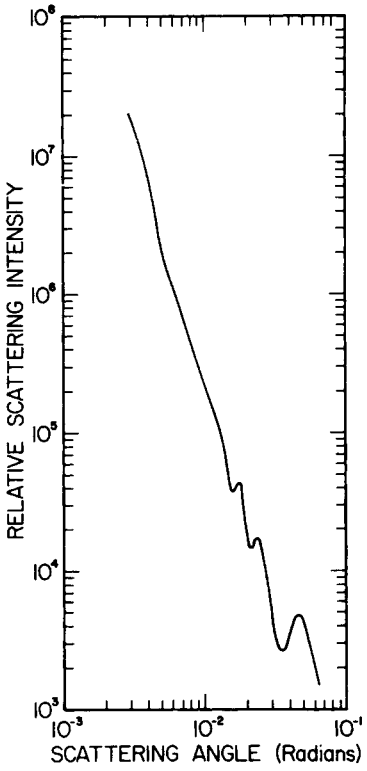

Fig. 1. Small-angle x-ray scattering of a plasma-formed polyethylene.

It was assumed that two phases contributed to the scattering—a higher-density spherical polymer material embedded in a binder of lower-density polymer. For the purposes of analyzing the small-angle x-ray scattering data, the two phases were considered to have uniform but different electron densities. There was reason to believe that the interstitial phase material was a lower-density polymeric material since SEM studies by Thompson[2] gave evidence of erosion of the "film" material around and below the surface spheres. This erosion uncovered what appeared to be more spheres buried in the film.

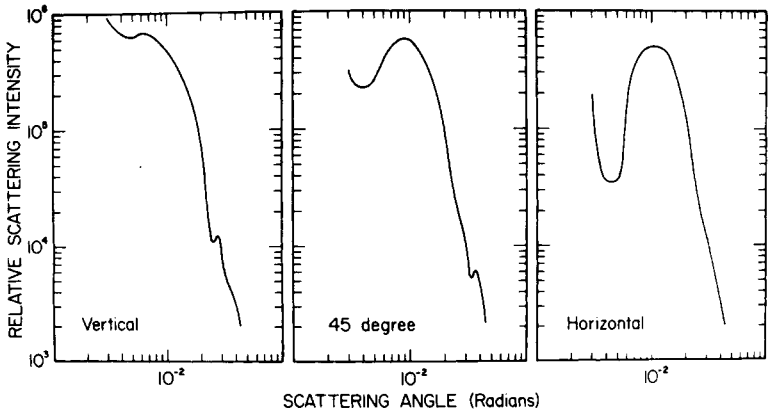

Fig. 2. Small-angle x-ray scattering of three orientations of a conventional polyethylene.

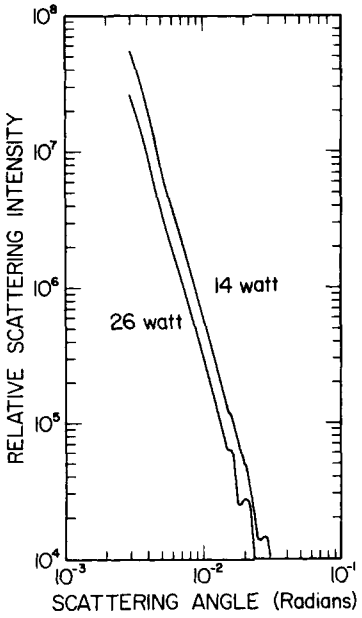

Fig. 3. Small-angle x-ray scattering of two plasma-formed polystyrene samples.

The initial specific surface area of the plasma-formed polyethylene was calculated assuming the above model. The bulk density was determined in a gradient column. Closest packing of spheres was assumed for a model which would attribute 74% of the film volume to the spheres. The higher density was attributed to the spheres, and the lower-density binder material was assumed to have a density equal to that of the conventional polymer. This latter assumption is deemed reasonable in that we have prepared plasma-formed polyethylene of a more amorphous nature with densities approaching those of conventional polyethylene. The sphere density was determined from the equation

$$\rho_{\text{bulk}} = 0.74\rho_{\text{sphere}} + 0.26\rho_{\text{binder}}$$

This estimate of ρ_{sphere} and the assumed ρ_{binder} were combined to get the density difference term from which the specific surface area and spherical diameters were calculated (see Table I).

The calculated spherical diameters for the plasma-formed polymers in the right-hand column of Table I are in close agreement with data from other sources.

TABLE I
Average Spherical Diameters of Polymer Spheres Obtained from Small-Angle X-Ray Scattering

Polymer of	Bulk polymer density, g/cm³	Assumed second phase	ρ_{sphere}, g/cm²	Corrected specific surface, m²/g	d_{sphere}, μ
Ethylene (5 W, 20 μ)	1.186	amorphous polyethylene	1.303	17.4	0.26
Styrene (14 W)	1.370	amorphous polyethylene	1.486	21.7	0.19
Styrene (26 W)	1.370	amorphous polyethylene	1.486	9.4	0.43

For plasma-formed polyethylene, the x-ray data calculation yield a diameter of 0.26 micron, which has been verified by SEM techniques. Niinomi et al. reported spherical diameters for plasma-formed polyethylene ranging from 0.2 to 1.2 micron but did not refer them to rf power input.[5] However, both sets of data are in relatively close agreement.

For the plasma-formed polystyrene, the calculated diameters are 0.19 and 0.43 micron for 14- and 26-W plasmas, respectively. There data are compared with the SEM date of Thompson[2] (Table II). For the x-ray calculation on 26-W polystyrene, there is close agreement with Thompson's 22- and 36-W data. For the x-ray calculation of the 14-W polystyrene, the dimensions are smaller than those obtained by Thompson for a 13-W plasma. However, it should be pointed out that SEM-resolvable structures may still constitute agglomerates of smaller spheres.

The major assumption in the x-ray data treatment concerns the determination of the density difference of the two phases. For the plasma-formed polyethylene, the estimated sphere density is 1.31. This value is not at all unexpected in view of the fact that bulk densities of this magnitude or higher have been found for plasma-formed polyethylene.[19] Furthermore, the spheres appear to form in the UV- and ion-energetic volume of the plasma where dehydrogenation and/or crosslinking can significantly increase the density of the spheres.[2-12] Such reasoning has been used to explain the higher-than-conventional bulk densities of plasma polymers.

A minimum dimension for the spheres can also be calculated from the x-ray data, which does not require any assumptions about density.[1] Taking the minimum angle at which the negative fourth power proportionality of scattered intensity with scattering angle persists, a minimum scattering diameter (D_{min}) is calculated from

$$2\pi\theta D_{min}/\lambda \geq 4$$

where θ = minimum scattering angle (radians) and λ = x-ray wavelength (1.54 Å). For both plasma-formed polymers of this study, the scattering proportionality persists to about 0.003 radian, yielding a calculated D_{min} of 330 Å.

The significance of the x-ray analysis is that it shows the submicrostructure of plasma-formed polymers to consist of higher-density spheres distributed within a binder or polymer glue of lower density. The calculations indicate that approximately up to 70% of the film volume is made up of spheres. Using this technique as a probe, it should be possible to gain new insight into applications

TABLE II
Plasma Polystyrene Sphere Sizes as a Function of Power and Position in Reactor

Power	Minimum diameter, μ	Maximum diameter, μ	Average diameter, μ
8[a]	0.2	1.7	1.0
13[a]	0.5	1.0	0.7
22[a]	0.5	0.7	0.6
36[a]	0.5	0.5	0.5
36[b]	0.2	0.2	0.2

[a] Sample from bottom of sleeve 3.
[b] Sample from bottom of sleeve 8.

of plasma-formed polymer films where the composite structure would affect the desired properties. Such applications would include semipermeable membranes, barrier coatings, encapsulation films, and light guides.

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