Halogenated Polyethylenes as Electron-Sensitive Resists

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Synopsis

Irradiation of a layer of halogenated polyethylene with an electron beam at 10-kV accelerating potential brings about crosslinking of brominated and chlorobrominated polyethylenes, but the chlorinated polyethylenes undergo either crosslinking or degradation, depending on the electron charge delivered. The limiting charge value which separates these two effects was found to be ca. 1×10^{-3} C/cm^2. The minimum useful dose was found to increase in the order brominated, chlorobrominated, chlorinated polyethylene.

INTRODUCTION

During the fabrication of various microelectronic devices a very high precision at every stage of production must be maintained. One of the newest techniques used to attain this goal is electron beam lithography. Among the most important parameters characterizing this process one may include the sensitivity of the polymeric resist layer to the electron beam.[1,2] This problem is a subject of many recent reports,[3–8] in which both fundamental properties of such layers and various methods to attain their highest possible sensitivities are described. One can expect that the presence of electron-sensitive sites in the polymer chain will ensure an enhanced sensitivity of the polymer to crosslinking or degradation. One such sensitizing factor is the presence of halogen. The use of poly(vinyl chloride)[2,3] and chlorinated polyethylene[3] has already been reported. These studies showed that poly(vinyl chloride) possessed a sensitivity of 3×10^{-5} C/cm^2, and that of chlorinated polyethylene was 2×10^{-6} C/cm^2. These results indicate that it may be of interest to study the electron beam sensitivity of halogenated polyethylene, for it is known that the kind, amount, and distribution of halogen in the chain affect the sensitivity of the polymer.

This paper presents the results of our studies on the effect of the halogen content in chlorinated, chlorobrominated, and brominated polyethylenes on their electron beam sensitivity.

EXPERIMENTAL

Materials

Polyethylene, a low-density polyethylene (LPE) having $\overline{M}_n = 34.460$, branching number 41.5 per 1000 methylene units, and specific density $d_0 = 0.914$ g/cm^3 was used throughout this study.

Chlorinated polyethylenes were obtained by methods developed in our labo-

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ratory; they had the following halogen contents: chlorinated polyethylene, 19.1–53.3 wt % Cl[9]; brominated polyethylene, 24.8–71.5 wt % Br[10]; chlorobrominated polyethylene, 19.1–58.8 wt % Cl and 4.7–44.6 wt % Br.[11] The structural chain characteristics of halogenated polyethylenes investigated in this work are shown in Table I.[12]

Electron Beam Exposure

Polymer resist layers less than 1 μm thick were used on silicon supporting disks. The samples were prepared by dripping a 4–7 wt % polymer solution onto spinning silicon disks followed by drying at 50°C for 30 min. Polymer resist layers were irradiated with an electron beam microlathe (built at the Institute of Electron Technology, Technical University of Wrocław, Wrocław, Poland). The accelerating potential used was 10 kV. The surface charge density, expressed in C/cm^2, was controlled by current density and exposure time. Irradiation effects were studied by polymer resist solubility determinations in benzene at 50°C for 60–120 sec. After drying, the size and thickness of the film were measured.

RESULTS AND DISCUSSION

Results of irradiation of halogenated polyethylenes with the electron beam are shown in Figures 1–3. Irradiation of the brominated and chlorobrominated polyethylenes leads to crosslinking of the polymer resist layer (Figs. 2 and 3), but in the case of chlorinated polyethylene, after some value of the surface charge density is exceeded, degradation begins to prevail over crosslinking (Fig. 1). The critical value separating these two effects lies at about 1×10^{-3} C/cm^2. These results suggest that chlorobrominated and brominated polyethylenes belong to the class of so-called negative polymer resists. Chlorinated polyethylene may also be included in this class, but only if the charge density is lower than 1×10^{-3} C/cm^2.

Irradiation sensitivity of halogenated derivatives of polyethylene in relation to the chlorine content in the polymer resist is shown in Table II. These data indicate that the higher the halogen content in the polymer, the lower the minimum useful dose of radiation needed to crosslink the resist. Sensitivity of the chlorobrominated polyethylene increases along with increase of the bromine content in the resist, the chlorine content simultaneously decreasing. Changes of the minimum useful radiation dose in the case of chlorinated and chlorobrominated polyethylenes are relatively small, up to 40 wt % of the bromine content. Significant differences in the values of the minimum useful dose were observed for brominated polyethylene containing up to 60 wt % bromine.

The presented results indicate that the kind of halogen has the deciding effect on the sensitivity of modified polyethylene to the electron beam. Thus, one may suggest on this basis the introduction of a new sensitivity unit per unit molar content of the modifying element. We propose to name this unit "specific molar sensitivity." Figure 4 shows an approximate relationship between the specific sensitivity of halogenated polyethylenes and the molar content of halogen. The similar course of these relationships and the sequential structure of the brominated and chlorinated polyethylenes (Table I) indicate that the sensitivity of

TABLE I
Structural Characteristics of the Chain of Chlorinated and Brominated Polyethylenes[a]

Sample	Halogen content		Occurrence of elements in the sequential structure of the chain								
	wt %	mole/mole of PE units	00000	10000	10001	01001	01010	01020	00100	10101	20110
Chlorinated polyethylene	19.1	0.19	+	+	+	+	−	−	+	+	−
	34.2	0.42	+	+	+	+	+	−	+	+	−
	53.3	0.87	+	+	+	+	+	+	+	+	+
Brominated polyethylene	24.8	0.11	+	+	+	+	−	−	+	+	−
	39.0	0.22	+	+	+	+	+	−	+	+	−
	57.9	0.48	+	+	+	+	+	−	+	+	−
	71.5	0.78	+	+	+	+	+	+	+	+	+

[a] Symbols: 0 = $—CH_2—$, 1 = $—CHX—$, 2 = $—CX_2—$; X = Cl, Br.

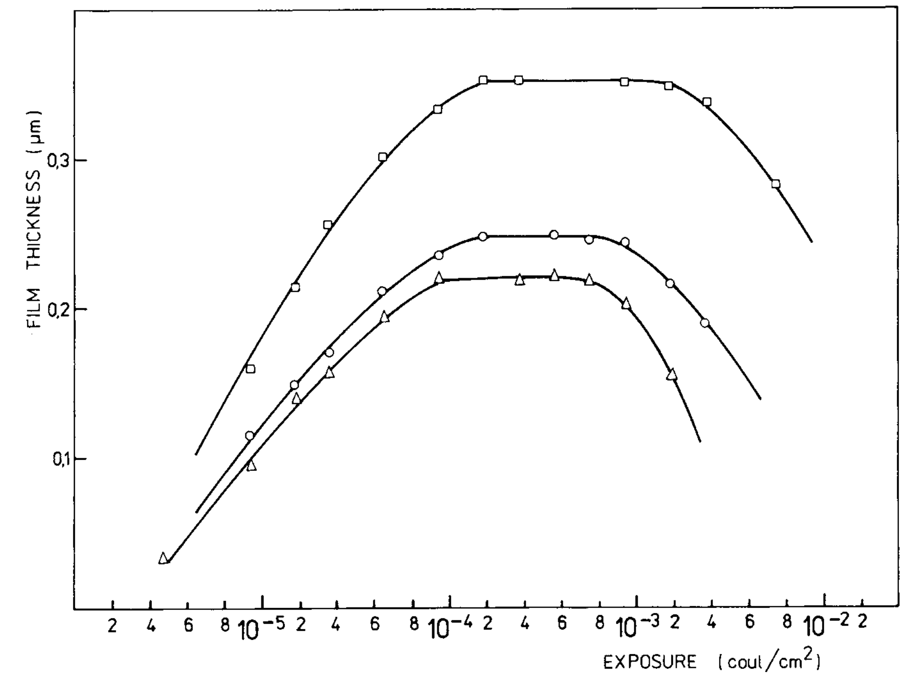

Fig. 1. Experimental development curves for chlorinated polyethylene: (□ 19.1% Cl; (O) 34.2% Cl; (Δ) 53.3% Cl.

the layer depends on the site of halogen substitution. The most active sites appear only in the later stages of halogenation. The changes in sensitivity result mainly from the differences in bonding energies of carbon and halogen atoms,

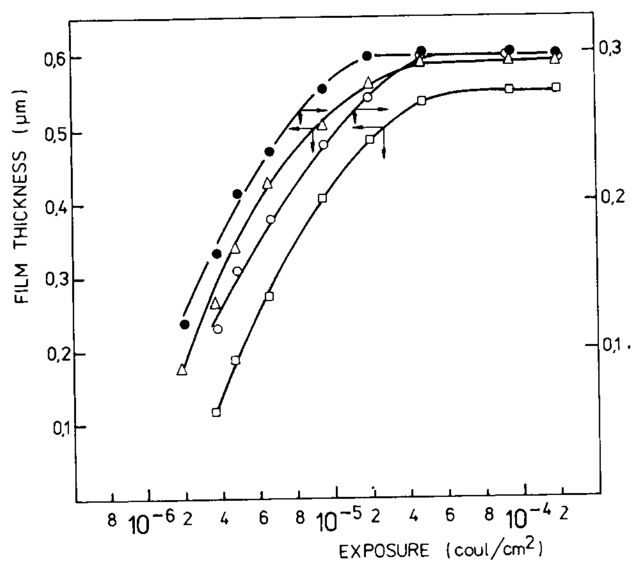

Fig. 2. Experimental development curves for brominated polyethylene: (□) 24.8% Br; (O) 39.0% Br; (Δ) 57.9% Br; (●) 71.5% Br.

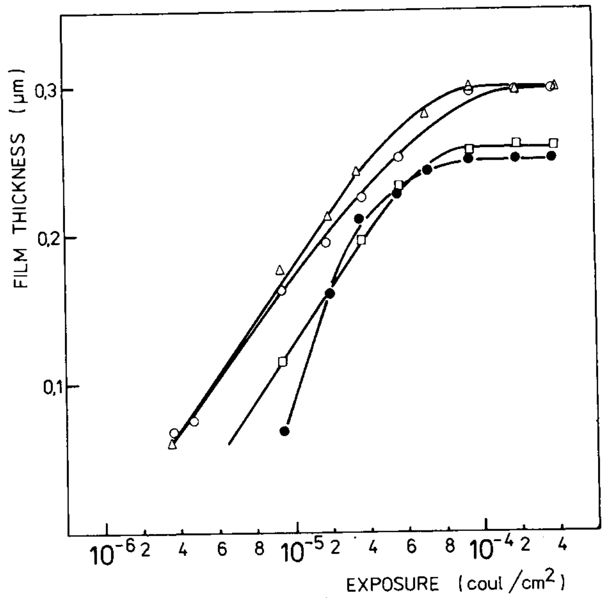

Fig. 3. Experimental development curves for chlorobrominated polyethylene: (□) 4.7% Br, 58.8% Cl; (○) 20.6% Br, 38.7% Cl; (△) 34.0% Br, 28.6% Cl; (●) 44.6% Br, 19.1% Cl.

which depend on the order of the carbon atom and the kind of halogen linked with it. The highest sensitivity, at similar molar content of halogens, is exhibited by brominated polyethylene, which is five times as sensitive as chlorobrominated and nine times as sensitive as chlorinated polyethylene.

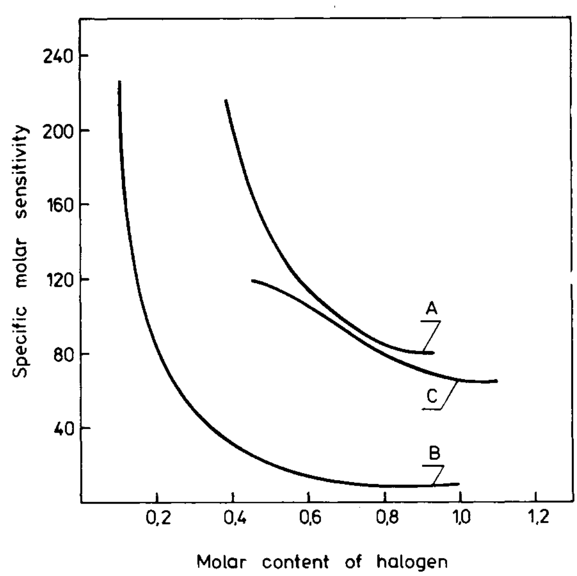

Fig. 4. Specific sensitivity of halogenated polyethylenes as function of molar content of halogen; A, chlorinated polyethylene; B, brominated polyethylene; C, chlorobrominated polyethylene.

TABLE II
Characterization of Resists from Halogenated Polyethylene (Pure Polyethylene 1 × 10^{-4} C/cm^2)

Chlorinated polyethylene		Brominated polyethylene		Chlorobrominated polyethylene		
Chlorine content, wt %	Electron sensitivity, 10^6 C/cm^2	Bromine content, wt %	Electron sensitivity, 10^6 C/cm^2	Chlorine content wt %	Bromine content, wt %	Electron sensitivity, 10^6 C/cm^2
19.1	81	24.8	24	58.8	4.7	72
34.2	78	39.0	16	38.7	20.6	65
53.3	72	57.9	9	28.6	34.0	58
—	—	71.5	8	19.1	44.6	40

CONCLUSIONS

(1) Modification of polyethylene through halogenation brings about a significant increase in the sensitivity of these polymer resists with the electron beam.

(2) Sensitivity of halogenated polyethylenes depends on the kind of substituent and, to a lesser extent, on the halogen content.

(3) The highest radiation sensitivity is exhibited by brominated polyethylene.

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