Surface Fluorination of Transparent Polymer Film

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Synopsis

Transparent polymer film was fluorinated by contacting with fluorine gas. The fluorinated layer depth was determined from the visual spectrum. The relation between fluorinated depth d and reaction time t was represented by $d = k \cdot t^{1/2}$. This result indicates that fluorine diffusion plays a predominant role in forming the diffusion profile. The apparent activation energy of fluorine gas diffusion into polystyrene (PS) and polycarbonate (PC) was 2.8 kcal/mole and 6.6 kcal/mole, respectively. The refractive index distribution from surface to center, which corresponds to the fluorine content in the layer, was determined by interference microscopy. PS and PC showed nearly stepwise change of refractive index. On the other hand, poly(methyl methacrylate) showed a gradual change. These results are compatible with fluorine analysis data and IR spectra of the fluorinated polymers. On the basis of these results, antireflecting layers on plastic lens or plate, plastic optical fiber, or fiber sheet were formed.

INTRODUCTION

Investigations of surface fluorination of polymer film or fiber have been undertaken mainly for improvement of adhesive properties or dyability. However, a unique property obtained by fluorination is lowering the refractive index of matrix polymer film. The present work was therefore undertaken to investigate the formation of refractive index distribution on a transparent plastic surface by fluorination and to investigate the possibility of application to optical guide formation or formation of antireflection layer on a plastic lens, etc.

There are few reports on the optical property changes of transparent polymer by fluorination and on information concerning fluorinated depth change by fluorination condition. Schonhorn[1] reported an indirect method to evaluate fluorinated depth from the crosslinked region determined from gel fraction after Soxhlet extraction. Because the application of this method to slightly fluorinated samples is difficult, evaluation of fluorinated surface was made by the optical method and the fluorination mode of the plastic film surface was clarified.

EXPERIMENTAL

Materials

Polycarbonate (PC), polystyrene (PS), and poly(methyl methacrylate) (PMMA) were employed as sample material. They were fluorinated in the

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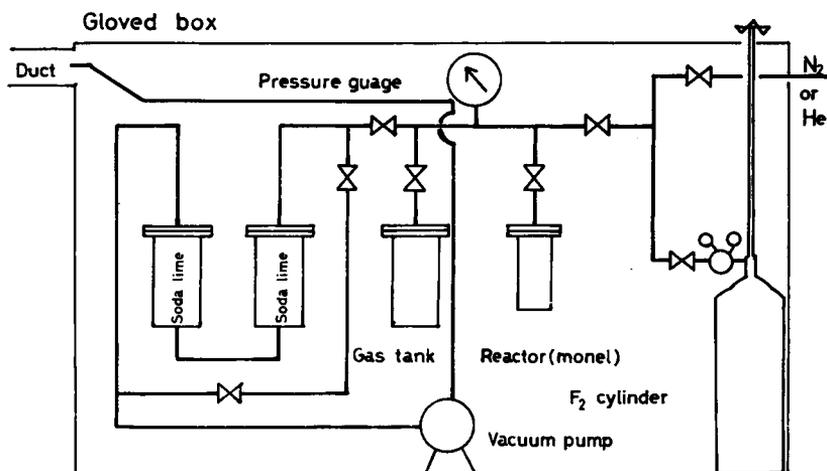
Fig. 1. Fluorination apparatus.

form of films which were prepared by casting or compression molding. Ditched films for fiber sheet were made by casting the polymer solution on a metal mold with a triangular ridged surface.

Fluorination

Fluorination was accomplished in the apparatus shown in Figure 1. Because of the high reactivity of fluorine gas, the reaction vessel, pressure control bulbs, and other important parts which contact the fluorine gas were made of Monel metal. A 5 cm × 1.5 cm polymer sheet was supported by nickel wire in a Monel reaction vessel having a 5 cm inside diameter and 25-cm length. Fluorine gas was carefully introduced and diluted by helium or nitrogen gas to avoid extreme reaction.

Fluorinated Depth Evaluation

Fluorinated depth was evaluated by visible region spectrum of the fluorinated sample plate. A typical visible region spectrum of the polymer is shown in Figure 2. If the refractive index distribution from surface to center can be as-
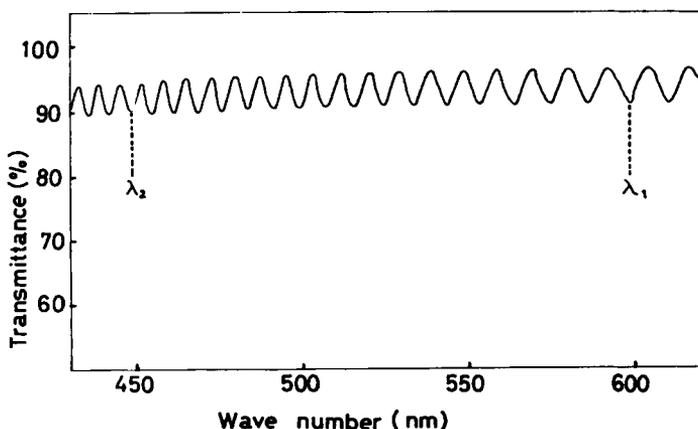
Fig. 2. Visible region spectrum of fluorinated polymer.

sumed to be a stepwise function, the fluorinated depth is calculated from the number of peaks N in the spectrum between wavelengths λ_1 and λ_2, according to eq. (1).

$$d = \frac{N}{n}\left(\frac{\lambda_1 \cdot \lambda_2}{\lambda_1 - \lambda_2}\right)$$ (1)

where n is the refractive index of the original polymer.

Visible and Infrared Spectra Measurement

The visible region absorption spectra were determined by a Hitachi Model EPS-3T spectrometer, and the infrared absorption spectra were determined by a Shimadzu IR-27G spectrometer.

Chemical Analysis of Fluorine Content

The fluorinated samples were digested in potassium carbonate according to Noshiro et al.[2] leached with distilled water, and diluted to 1 liter using an ion buffer solution. The electrode potential of the solution was determined by using a Corning Model 10 pH meter equipped with fluoride electrodes Cat. No. 476042, and fluorine contents were determined by the Nernst equation.

RESULTS AND DISCUSSION

Fluorinated Depth and Reaction Time

As can be seen from Figure 3, the fluorinated depth was directly proportional to the square root of reaction time. This relation is represented by the following equation:

$$d = k \cdot t^{1/2}.$$ (2)

The proportionality constant k is 13.2 and 5.6 for PS and PC, respectively. This result indicates that, in spite of the accompanying rapid reaction of fluorine and polymer, the surface fluorination reaction proceeds under the control of fluorine gas diffusion.
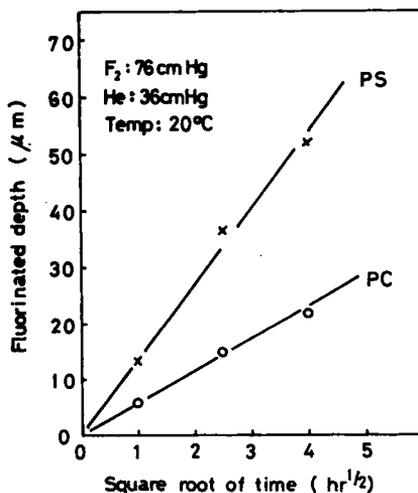
Fig. 3. Fluorinated depth time dependence. Conditions: 76 cm Hg F_2, temp. 25°C.

Weight Increase and Reaction Time

The increase in weight is the result of the exchange of hydrogen in the polymer for fluorine. So, as can be seen in Figure 4, the weight increment is proportional to the square root of reaction time, in the same way as the fluorinated depth.

The weight increment by fluorination is related to the fluorinated depth by calculating the weight increment due to replacement of hydrogen by fluorine in the fluorinated layer, as given in Table I. The ratio of observed weight increase to calculated weight increase is related to the fluorine atom distribution and degree of replacement of hydrogen by fluorine.

Poly(tetrafluoroethylene) showed no weight increase by contact with fluorine gas since there was no hydrogen atom in the polymer molecule. The weight in-

TABLE I
Fluorinated Depth and Weight Increase

Polymer	Fluorinated depth, μm	$\Delta W_{cal.}$,[a] mg/cm^2	$\Delta W_{obs.}$,[b] mg/cm^2	$\Delta W_{obs.}/\Delta W_{cal.}$
Polycarbonate	1.7	0.30	0.09	0.30
	2.4	0.42	0.14	0.33
	6.0	1.05	0.35	0.33
	40.0[c]	7.1	2.2	0.31
Polystyrene	2.2	0.3	0.23	0.77
	6.3	0.86	0.62	0.72
	13.9	1.89	0.96	0.51
	17.0	2.31	1.45	0.63

[a] Weight increase calculated from fluorinated depth.
[b] Observed weight increase.
[c] Obtained from interference microscopy observation.
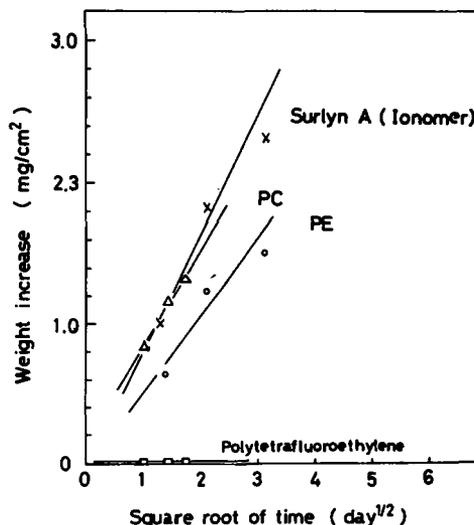
Fig. 4. Weight increase time dependence. Conditions: 40 cm Hg F$_2$, temp. 25°C, 36 cm Hg He.
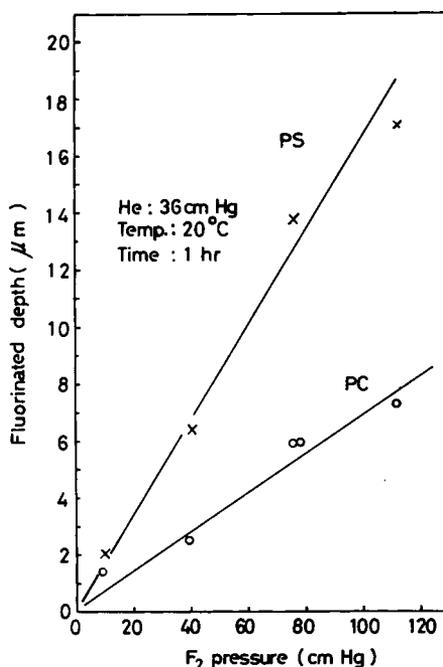
Fig. 5. Relation between F_2 pressure and fluorinated depth.

crease of polyethylene is smaller than that of polycarbonate. This is considered to be the difficulty of gas diffusion into the crystalline part.

Fluorinated Depth and Fluorination Pressure

As can be seen in Figure 5, fluorinated depth of the polymer films was affected by fluorine gas pressure, and the amount of fluorination is directly proportional to the fluorine gas pressure.

Fluorinated Depth and Reaction Temperature

Plots of logarithm of fluorinated depth versus reaction temperature $10^3/T$ (°K) are shown in Figure 6.

Fluorinated depth d is related to the square root of the diffusion constant D by the assumption that the rate of fluorine gas diffusion is faster than the rate of replacement reaction between the hydrogen atoms in the polymer and the diffused fluorine (cf. Appendix). From this assumption, the activation energy of fluorine gas diffusion was determined to be 2.8 and 6.6 kcal/mole for PS and PC, respectively. Shinohara[3] gave 6.8 kcal/mole as the activation energy of poly-(vinyl fluoride).

Dilution Gas Effect

The effect of dilution gas was shown in Figure 7 in the case of polycarbonate. The results show that fluorine gas in helium gas is more easily diffused into the polymer film than fluorine gas in nitrogen gas. As the molecular radius of helium gas (5 Å) is smaller than that of nitrogen gas (14 Å), helium gas more easily diffuses into polymer than nitrogen. The dilution gas effect can be considered to be operating by prediffused gas.
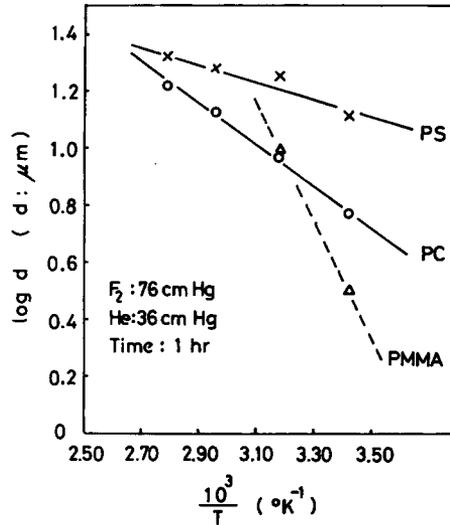
Fig. 6. Relation between reaction temperature and fluorinated depth. Conditions: 76 cm Hg F_2, 36 cm Hg He, time 1 hr.
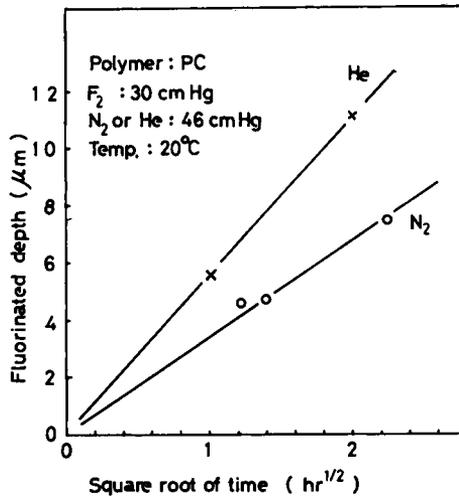
Fig. 7. Effect of dilute gasses on fluorinated depth. Conditions: polymer PC, 30 cm Hg F_2, 46 cm Hg N_2 or He, temp. 20°C.

Fluorinated Polymer Structure

Structures of fluorinated polymer were investigated by infrared spectra and fluorine analysis. The fluorinated sample films were dissolved in methylene chloride and separated into soluble and insoluble parts. The fluorine contents of each part are given in Table II.

The insoluble part of fluorine content of fluorinated PS and PC is closely equal to the theoretical value which was calculated by assuming that all hydrogen atoms in the polymer were replaced by fluorine atom. However, the soluble part of the fluorine content of PS and PC was zero. On the other hand, the soluble part of PMMA contained 1.6% fluorine, and the insoluble part con-

TABLE II
Fluorine Content in the Fluorinated Polymer

Polymer	Solubility in CH_2Cl_2	Fluorine Content, %		
		$F_{obs.}$	$F_{cal.}$	$F_{theo.}$[a]
PTFE[b]	—	78.0	76.0	—
PVF[c]	—	59.3	59.4	—
PS	insoluble	64.3	—	61.3
	soluble	0.0	—	
PC	insoluble	55.2	—	58.7
	soluble	0.1	—	
PMMA	insoluble	18.4	—	62.1
	soluble	1.6	—	

[a] Fluorine content when all hydrogen atoms are replaced by fluorine atoms.
[b] Poly(tetrafluoroethylene).
[c] Poly(vinylidene fluoride).
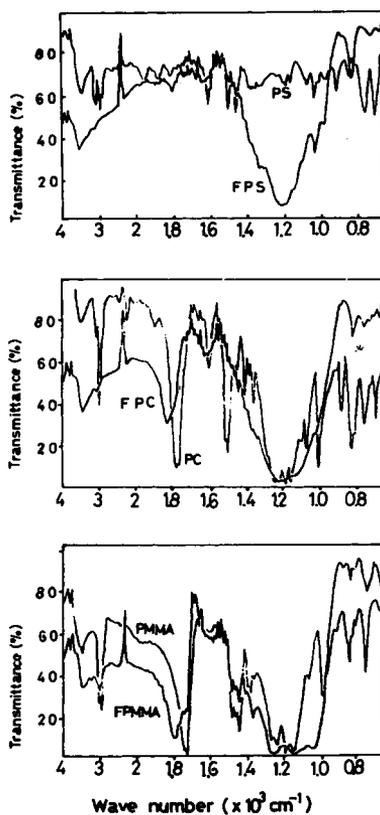
Fig. 8. Infrared spectrum of fluorinated polymers.

tained only 30% fluorine of the theoretical value. These results show good agreement with the refractive index distribution of each polymer.

The infrared spectra of the fluorinated polymer film are shown in Figure 8. The spectra of the soluble part showed almost no change compared with the initial spectra. This means that the soluble parts contained almost no fluo-

rinated components. However, the insoluble part showed a remarkable change in spectra. The broad absorption due to stretching vibration of the C–F bond was observed at 1000–1300 cm^{-1} in each polymer. On the other hand, the 2800–3000 cm^{-1} absorption band due to the C–H bond disappeared. Absorption bands 1780 and 1750 cm^{-1}, due to carbonyl group shifted to the higher wavenumber side by 50 and 60 cm^{-1} for polycarbonate and poly(methyl methacrylate), respectively.

These results show that the hydrogen atoms in the polymer were replaced by fluorine atoms at random by free-radical process in the same way as in the usual fluorination reaction of organic molecules in fluorine gas.[1]

Refractive Index Distribution

Refractive index distribution from surface to center was observed by interference microscope. The results were given in Figure 9. The fluorinated polycarbonate and polystyrene showed a nearly stepwise change in refractive index. However, the fluorinated poly(methyl methacrylate) showed a gradual change in refractive index from surface to center. The refractive index change corresponds to the amount of hydrogen replaced by fluorine in the polymer. These results are compatible with the fluorine analysis data, which show that the fluorine content of the insoluble part of fluorinated poly(methyl methacrylate) is smaller than that of fluorinated polycarbonate or polystyrene, and that the fluorine content of the soluble part of fluorinated poly(methyl methacrylate) is larger than that of polycarbonate or polystyrene. The reason for this difference is not obvious, but may be due to the effect of the benzene ring in their structure.

	PC	PS	PMMA
F_2 (cm Hg)	76	76	76
He (cm Hg)	36	36	36
Temp (°C)	20	20	20
Time (hr)	6.25	6.25	16
$10^3 \Delta n$	15	7.4	1.4
Δx (μm)	23	52	590
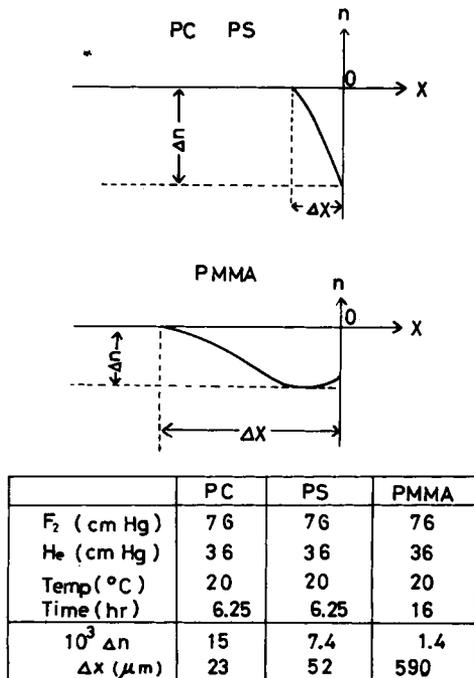
Fig. 9. Refractive index distribution curve.

The fluorinated depth can be determined from the refractive index distribution curve. The ratio of the observed weight increment to the weight increment calculated from this fluorinated depth agreed with the ratio calculated from the fluorinated depth obtained by eq. (1), as shown in Table I. This shows that the assumption used at the derivation of eq. (1) is acceptable.

APPLICATION

An antireflection layer can be formed by application of the fluorination reaction to a polymer or lens. For example, the transparency of poly(methyl methacrylate) plate was improved from 86.1% to 97.2% at 500 nm by reaction conditions 40°C, 76 cm Hg F_2 pressure, 1 hr.

Optical fiber was formed by applying the fluorination reaction to polymer fiber. For example, polycarbonate fiber was fluorinated at 20°C, 80 cm Hg F_2 pressure, 8 hr. An optical fiber whose sheath layer thickness was 17 μm was obtained, and refractive index difference between sheath and core was 15 × 10^{-3}.

An optical fiber sheet was also obtained by fluorinating the special form sheet film whose cross section consists of a triangular ridge arrangement. The fluorine diffused from the surface and formed a triangular ridge optical path.

CONCLUSIONS

The experiments indicated that the fluorine diffusion process plays a predominant role in the formation of diffusion profile and that the fluorination depth is proportional to the square root of the reaction time and to the fluorine gas pressure. The apparent activation energies of fluorine gas diffusion were 2.8 and 6.6 kcal/mole for polystyrene and polycarbonate, respectively.

Refractive index distribution from surface to center of fluorinated polymer film was stepwise for polystyrene and polycarbonate, and gradual for poly(methyl methacrylate). This tendency was consistent with the fluorine analysis data of the fluorinated layer.

The fluorination was applied to the formation of an antireflecting layer on plastic or lens, to optical fiber formation, and to optical sheet formation.

Appendix

The relation between diffusant amount M, diffusion time t, diffusion constant D, and sample thickness L in the case of a plane sheet is given by Park,[4] as shown in eq. (1A):

$$M_t/M_\infty = 4/\pi \cdot (Dt/L^2)^{1/2} \tag{1A}$$

where M_t is the diffusion amount at time t and M_∞ is the diffusion amount at equilibrium.

Since, as mentioned in this paper, the weight increase is directly proportional to the diffusion depth, M_t can be related to the diffusion depth d. M_∞ is a constant and independent of temperature in the case of polymer film fluorination. From these consideration, eq. (1) can be converted into eq. (2):

$$d = k \cdot (Dt)^{1/2} \tag{2}$$

where k is the constant containing L, M_∞, and the proportionality constant defining the relation between the diffusant amount and fluorinated depth. By differentiating eq. (2), eq. (3) is obtained at constant t:

$$\frac{d \ln d}{d\, 1/T} = \frac{1}{2} \cdot \frac{d \ln D}{d\, 1/T} \tag{3}$$

From these considerations, the activation energy of diffusion is obtained by multiplying by 2 the apparent activation energy obtained from the Arrehnius plot of d.

References

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