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EFFECT OF UV IRRADIATION ON GAS PERMEABILITY IN HETEROPHASIC ETHYLENE-PROPYLENE COPOLYMER FILMS[†]

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ABSTRACT

The permeability variations of carbon dioxide, oxygen, and nitrogen through isotactic polypropylene, heterophasic ethylene-propylene (E-P) copolymers, and polyethylene films were measured during photooxidation using polychromatic light at 60°C in air. For polypropylene-based samples the permeability decreases with increasing photooxidation, whereas for polyethylene and an elastomeric fraction from a heterophasic E-P copolymer an increase in permeability with photooxidation is observed.

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INTRODUCTION

A wide variety of organic polymers are used for vacuum/gas-filled systems as gaskets, seal lubricants, insulating materials, and so on. Transport of gases through membranes is also an important process in many industrial and biological applications. Knowledge of gas release behavior and permeation as well as thermal and photooxidation is required if they are to be applied in these systems [1, 2]. The permeation and diffusivity of gases through polymers has been measured by many investigators [3–6]. We previously studied the diffusion of oxygen in heterophasic ethylene-propylene (E-P) copolymers subjected to photo- [7] and thermal oxidation [8]. The extent of oxidation as a function of depth into the sample was measured by infrared spectroscopy using the carbonyl and hydroxyl band produced in photo/thermal oxidative degradation. The photo- and thermal oxidized samples showed very similar oxidation reaction profiles.

In this paper we report our results on the permeability of gases (CO_2 , O_2 , and N_2) through polymer films upon photoirradiation.

EXPERIMENTAL

Materials

Commercial samples of isotactic polypropylene (i-PP) from I.P.C.L., Baroda, India, linear low-density polyethylene (LLDPE, Du Pont, Canada), and heterophasic ethylene-propylene copolymer (EPQ 30R from Himont, Italy) were used in this study.

Procedure

The method of purification, fractionation, and sample preparation ($\sim 100 \mu\text{m}$ thick film) has been reported [7]. The copolymer EPQ 30R was fractionated as fractions A and B. The molar percentage of ethylene in copolymer samples EPQ 30R, EPQ 30R-A, and EPQ 30R-B are 15.1, 7.7, and 40.9, respectively. All samples were irradiated in an SEPAP 12/24 photoirradiation chamber for 30/50 hours at 60°C at $\lambda > 290 \text{ nm}$. The details of the equipment are described elsewhere [9].

Permeability Measurement

Permeability measurements before and after irradiation in SEPAP 12/24 were performed on a LYSSY GPM 200 instrument. A disk (50 cm^2) of each sample ($\approx 100 \mu\text{m}$ thick) was placed between the two chambers of a cell at isotactic pressure. One chamber was swept by an equimolar mixture of carbon dioxide, oxygen, and nitrogen; the other chamber was swept continuously by helium. The titration of each gas transferred into helium was performed by a GC chromatograph equipped by a molecular sieve column, a TCD detector, and a HP integrator. Figure 1 shows a schematic diagram of the apparatus. Measurements and standardizations were done at 23°C , and the accuracy was about 5%. A permeability coefficient is essentially estimated from the slope in the time-flux curve. For an easier comparison of the different compositions of polymer samples, the results have been normalized for

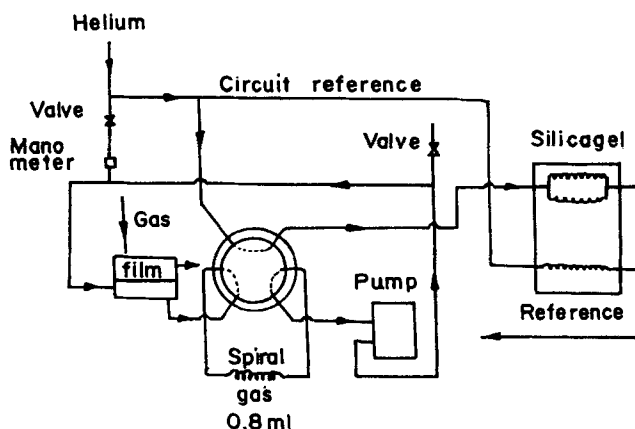


FIG. 1. Schematic diagram of gas permeability.

a 100- μm thickness, assuming that the permeability varies with the inverse of the thickness.

RESULTS AND DISCUSSION

The permeability is the result of two distinct processes: solubility of the permeant and diffusion [10]. Significant changes in the gas permeability were observed for all samples subjected to photoirradiation. The apparent diffusion coefficients were calculated from the permeation curves and are given in Table 1. The data of

TABLE 1. Effect of Photoirradiation upon the Permeability of CO_2 , O_2 , and N_2 through E-P Copolymer Films

Sample	Irradiation time, hours	Permeability, $\text{L}/\text{m}^2/\text{day}/\text{atm}$			Apparent diffusion coefficient, $\times 10^9 \text{ m}^2/\text{h}$		
		CO_2	O_2	N_2	CO_2	O_2	N_2
i-PP	0	4.0	2.7	1.9	1.08	0.86	0.50
	30	0.9	0.3	0.1	0.91	0.71	0.28
EPQ 30R-A	0	3.70	1.53	0.34	0.50	0.32	0.11
	30	2.04	0.85	0.17	0.25	0.14	0.04
EPQ 30R	0	3.7	1.05	0.30	0.52	0.20	0.14
	50	2.4	0.75	0.27	0.32	0.13	0.10
EPQ 30R-B	0	11.0	3.6	2.0	1.43	0.85	0.31
	30	22.0	7.8	4.5	1.55	1.02	0.59
LLDPE	0	5.3	1.4	0.5	1.13	0.40	0.19
	50	9.2	2.5	1.2	1.87	0.72	0.34

Table 1 show two kinds of behavior. For propylene-derived polymers (i-PP, EPQ 30R, and EPQ 30R-A) the permeability and apparent diffusion coefficient decreases with increasing irradiation time. However, in the case of LLDPE and the elastomer fraction (EPQ 30R-B), the permeability and diffusion coefficient increase upon irradiation. Both the permeability and apparent diffusion coefficient were also found to increase with ethylene content. The decrease in gas permeabilities upon irradiation of EPQ 30R film is comparatively less when compared to i-PP and EPQ 30R-A. This implies that EPQ 30R shows a behavior similar to both polypropylene and polyethylene, but resembles i-PP more closely because there is decrease in permeability upon irradiation. The gas permeability is markedly dependent on the nature of the gas (0 hour value): $P_{\text{CO}_2} > P_{\text{O}_2} > P_{\text{N}_2}$. This trend and the permeability values for the pure components agree well with data reported in the literature [10]. These results show that the nature of photooxidation of a heterophasic E-P copolymer is very similar to that of i-PP [7-8]. We earlier provided evidence [7, 8] to show that photooxidation initiated in the amorphous portion is concerned mainly with the crystalline polypropylene phase in the case of E-P copolymers. The permeability results are in agreement with this conclusion.

It is more difficult to rationalize the changes in gas permeability with irradiation because of the macroscopic nature of this measurement. Several parameters, such as molecular weight, chain scission, crosslinking, crystallinity, oxidation products, etc., are modified by photooxidation and can be expected to result in a drastic change in gas permeability [11]. Peterlin [12] established that gas permeability is determined mainly by the amorphous regions. Therefore, a large reduction in gas permeability for irradiated i-PP can also be attributed to dramatic changes in crystallinity and photoproduct formation upon irradiation [13].

The decrease in gas permeability and apparent diffusion coefficient with irradiation in PP-based samples (i-PP, EPQ 30R, and EPQ 30R-A) is due to photooxidation of the polymer films. The photooxidation results in the formation of chemical crosslinks. Another reason for the decrease in permeability and diffusion is the existence of physical interactions between primary hydroperoxidic photoproducts. Contrary to PP-based samples, we observed an increase in gas permeability and apparent diffusion coefficient for photooxidized elastomeric films (LLDPE and EPQ 30R-B). This is because we did not find any appreciable crosslinking in LLDPE and EPQ 30R-B up to 50 hours of irradiation [7].

CONCLUSION

The present study shows two kinds of permeability (diffusion) behavior: 1) a decrease with irradiation in PP-based samples (i-PP, EPQ 30R, and EPQ 30R-A) and 2) an increase with irradiation in amorphous samples (LLDPE and the elastomeric fraction EPQ 30R-B). The changes in permeabilities are due to crosslinking upon irradiation. Crosslinking increases with irradiation in PP-based samples (i-PP, EPQ 30R, and EPQ 30R-A) whereas hardly any crosslinking reaction occurred in LLDPE and EPQ 30R-B up to 50 hours of irradiation.

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