

## Effects of Fullerene Derivatives on the Gas Permeability of Thermoplastic Polyurethane Elastomers

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**ABSTRACT:** In an effort to improve the gas barrier properties of thermoplastic polyurethane (TPU) elastomers, fullerene derivatives were added as fillers, and the resulting O<sub>2</sub> and CO<sub>2</sub> permeabilities were analyzed. The addition of 5 wt % polyhydroxylated fullerene {fullerenol [C<sub>60</sub>(OH)<sub>*n*</sub>] mixture, where *n* = 6–12} decreased the gas permeability by approximately 10–20%. According to the hole volumes computed with the results from positron annihilation lifetime spectroscopy, the addition of fullerene derivatives did not produce any changes in the hole volumes of the TPUs. Thus, the reduction in the TPU gas permeability was not caused by changes in the hole volumes. Instead, an inhibited diffusion of gas molecules by fullerene particles was deduced as the cause of the decrease in gas permeability from changes in the diffusion coefficient with temperature. The addition of urethanized fullerene, prepared through the chemical modification of fullerenol, markedly affected the TPU gas barrier properties. As compared to fullerenol addition, the gas barrier properties improved approximately fourfold for O<sub>2</sub> and approximately fivefold for CO<sub>2</sub>. These results suggest that the dispersibility of urethanized fullerene in TPU was higher than that of fullerenol. We found that the gas barrier properties were independent of the structure of polyol. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39986.

**KEYWORDS:** elastomers; polyurethanes; structure; property relations

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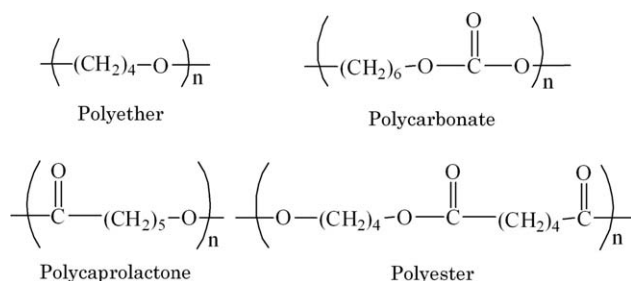
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### INTRODUCTION

Numerous options are available for polyols, polyisocyanates, and chain extenders that constitute thermoplastic polyurethane (TPU) elastomers. This broad selection enables molecular design according to the required performance. Furthermore, TPUs are highly recyclable industrial materials. We have studied mainly the physical property control of TPUs.<sup>1–3</sup> We have especially paid attention to the gas permeability of TPU because TPU is subject to oxidative deterioration caused by the permeation of oxygen included in the air. Lowering of the gas permeability, therefore, leads to an improvement of TPU's durability. Barrier ability for CO<sub>2</sub> is also useful as property of material used in the air. The chemical structure of the soft segment originating in polyols governs the gas permeability of TPUs, whereas the chemical structure of the hard segment originating in polyisocyanates and chain extenders has a smaller influence.<sup>1</sup> The improvement of the gas barrier for TPUs can be achieved by the use of a polyol possessing rigidity, but TPU loses flexibility instead. It seems to be difficult to make the gas barrier properties and flexibility compatible with each other. In recent years, researchers have reported an improvement in the superior gas

barrier properties with small additions of organoclay or graphene to TPUs.<sup>4,5</sup>

In this study, fullerene was adopted as a filler. Fullerene is soluble in many organic solvents, and its chemical modification is relatively simple. In addition, the dispersal of fullerene in TPUs is expected to form polyurethane nanocomposites with reinforcing effects<sup>6</sup> and oxidation-preventing performances.<sup>7</sup> In practice, fullerenol has been used with consideration of the affinity between polyurethane and fullerene. To further enhance the fullerene affinity, urethanized fullerene, prepared by the reaction of fullerenol with phenyl isocyanate, was also used. There has been little study on the influence of fullerene on the polymer's gas permeability. Research has been reported for fullerene-containing polymers, poly(phenylene oxide),<sup>8</sup> and star-shaped polystyrene.<sup>9</sup> The reports do not necessarily give a thorough discussion of the effect of fullerene on the mechanism of gas permeability. We expected to obtain new information about the gas barrier properties by fullerene. The chemical structure of the soft segment originating in the polyols governs the gas permeability of the TPUs, as mentioned previously. Therefore, four types of polyol were adopted to examine the relationship



**Figure 1.** Chemical structures of the polyols.

between a difference in the chemical structure of the soft segment and the addition of fullerene.

In general, the product of the gas diffusion coefficient and gas solubility coefficient ( $S$ ) in a polymer represents its gas permeability coefficient ( $P$ ) as an equation ( $P = DS$ ). Sufficient free space [free volume ( $V_f$ )] around gas molecules is a prerequisite for gas transfer within a polymer film. The following formula was submitted to explain how the free volume fraction ( $f_v$ ) of the polymer constituting the film determines the probability of the transfer.<sup>10,11</sup>

$$\ln D = A - B/f_v \quad (1)$$

where  $A$  and  $B$  are constants. In our research, the  $V_f$  values in samples subjected to gas permeability were measured with positron annihilation lifetime spectroscopy (PALS), and the relevance to gas permeability was examined.

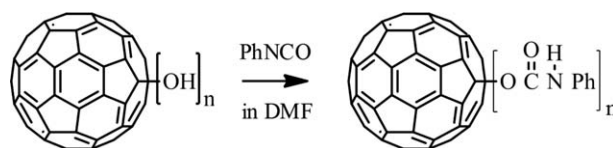
## EXPERIMENTAL

### Materials

For the soft segment of TPU, the following materials were used after nitrogen drying at 80°C under 0.3 kPa: polyetherdiol [PEt; poly(tetramethylene glycol) (PTMG); number-average molecular weight ( $M_n$ ) = 2000; Mitsubishi Chemical, Japan], polycaprolactone diol (PCL; PLACCEL220N,  $M_n$  = 2000, Daicel Corp., Japan), polycarbonate diol (PC; NIPPOLAN980R;  $M_n$  = 2000; Nippon Polyurethane Industry Co., Ltd., Japan), and polyesterdiol (PEs; NIPPOLAN4010,  $M_n$  = 2000, Nippon Polyurethane Industry Co., Ltd. Japan). The structures of the various polyols are illustrated in Figure 1. For the diisocyanate and chain extender, 4,4'-diphenylmethane diisocyanate (MDI; purity = 99.9%; Nippon Polyurethane Industry Co., Ltd.) and 1,4-butanediol (BD; Kanto Chemical Co., Inc., Japan) were used. For TPU synthesis, dehydrated  $N,N$ -dimethylacetamide (DMAc) was used as a solvent, and dibutyltin dilaurate (Tokyo Chemical Industry Co., Ltd., Japan) was used as a catalyst. Fullereneol [ $C_{60}(\text{OH})_m$  mixture, where  $n = 6-12$ ], phenylisocyanate (PhNCO), and dehydrated  $N,N$ -dimethylformamide (DMF) were obtained from Kanto Chemical Co., Inc.

### Synthesis and Analysis of Fullerene Derivatives

In accordance with the synthesis procedure of Stankovich et al.,<sup>12</sup> PhNCO was added via a dropping funnel into a 1% dehydrated DMF solution of  $C_{60}(\text{OH})_m$  vacuum-dried over  $P_2O_5$  for 24 h, and allowed to react under a nitrogen atmosphere at 60°C for 48 h [ $C_{60}(\text{OH})_m/\text{PhNCO}$  molar ratio = 1:12 calculated as  $n = 12$ ; see Scheme 1]. The product was washed



**Scheme 1.** Reaction of  $C_{60}(\text{OH})_n$  with PhNCO.

with toluene and dried under reduced pressure for 72 h at room temperature.

The structural identification of urethanized fullerene [ $C_{60}(\text{OCONHPh})_n$ ] was performed by Fourier transform infrared spectroscopy (model IR-Prestige-21 spectrophotometer, Shimadzu, Japan) and <sup>1</sup>H-NMR [model JNM-4000 (400 MHz) spectrometer, JEOL, Ltd., Japan, hexadeuterated dimethyl sulfoxide ( $\text{DMSO}-d_6$ ), containing 0.03% tetramethylsilane, accumulation count = 8, analysis temperature = 25°C]. The following results were obtained.

Fourier transform infrared spectroscopy (KBr;  $\nu$ ,  $\text{cm}^{-1}$ ): 3325 (N—H stretching), 1651 (C=O stretching), 1593 (C=C stretching), 1543 (N—H deformation), 1496 (C=C stretching), 1315 [C—N stretching aromatic], 1230 [C—O stretching (urethane bond)], 1049 (C—O stretching, fullerene), 754 [C—H deformation aromatic]. <sup>1</sup>H-NMR (400 MHz,  $\text{DMSO}-d_6$ , 25°C,  $\delta$ , ppm): 6.96 (2H, aromatic), 7.26 (2H, aromatic), 7.44 (2H, aromatic), 8.63 (1H, urethane)

C=O stretching due to the urethane group was observed at a low wave number compared to that of TPU or other carbonyl compounds (1710–1730  $\text{cm}^{-1}$ ). The intramolecular or intermolecular hydrogen bonding of the amide group belonging to the fullerene derivative is considered to have an influence on C=O stretching; this is known to be a feature of fullerene derivatives with amide groups.<sup>13,14</sup>

### TPU Synthesis and Preparation of the TPU-Containing Fullerene Derivative

TPU synthesis followed the prepolymer method (polyol/MDI/BD molar ratio = 1:2:1). An isocyanate-terminated urethane prepolymer was obtained by the mixing of MDI with vacuum-dried polyol at 60°C for 4 h in DMAc. A chain extender, BD, and a catalyst, dibutyltin dilaurate, was added to the prepolymer solution, and the mixture was stirred at 40°C for 2 h. The end of the chain-extending reaction was confirmed by the disappearance of the isocyanate group peak in the IR spectrum. A fullerene derivative dissolved in DMAc was added to the TPU solution, and the mixture was stirred at 40°C for 30 min. This

**Table I.** Physical Characteristics of the TPUs

Polyol type	$M_n^a$	$M_w/M_n$	$T_g$ (°C) of the TPUs
PEt	73,000	1.26	-78.1
PCL	98,000	1.22	-58.7
PC	93,000	1.22	-49.7
PEs	87,000	1.23	-26.7

$M_w$  = weight-average molecular weight.

<sup>a</sup>Polystyrene-reduced  $M_n$ .

S1

**Table II.** Coefficients of Permeability, Diffusivity, and Solubility of TPU<sub>PEt</sub>/C<sub>60</sub>(OH)<sub>n</sub>

Temperature (°C)		C <sub>60</sub> (OH) <sub>n</sub> (wt %)			
		O <sub>2</sub>		CO <sub>2</sub>	
		0	5	0	5
15	<i>P</i> (barrer) <sup>a</sup>	5.95	5.40	29.9	26.5
	<i>D</i> (10 <sup>-7</sup> cm <sup>2</sup> /s)	11.5	7.32	9.63	6.67
	<i>S</i> (10 <sup>-4</sup> cm <sup>3</sup> cm <sup>-3</sup> cmHg <sup>-1</sup> )	5.17	7.38	31.0	39.7
25	<i>P</i> (barrer) <sup>a</sup>	9.47	8.26	49.0	36.8
	<i>D</i> (10 <sup>-7</sup> cm <sup>2</sup> /s)	18.0	12.4	16.4	11.1
	<i>S</i> (10 <sup>-4</sup> cm <sup>3</sup> cm <sup>-3</sup> cmHg <sup>-1</sup> )	5.26	6.66	29.9	33.2
40	<i>P</i> (barrer) <sup>a</sup>	17.9	14.5	75.9	62.6
	<i>D</i> (10 <sup>-7</sup> cm <sup>2</sup> /s)	38.8	28.2	33.4	21.1
	<i>S</i> (10 <sup>-4</sup> cm <sup>3</sup> cm <sup>-3</sup> cmHg <sup>-1</sup> )	4.61	5.14	22.7	29.7
50	<i>P</i> (barrer) <sup>a</sup>	24.2	21.5	108	80.9
	<i>D</i> (10 <sup>-7</sup> cm <sup>2</sup> /s)	44.5	42.2	42.8	32.9
	<i>S</i> (10 <sup>-4</sup> cm <sup>3</sup> cm <sup>-3</sup> cmHg <sup>-1</sup> )	5.44	5.09	25.2	24.6

*d* = 0.5 mm.

solution was poured into a Teflon-coated tray, and the solvent was carefully removed under 0.7 kPa at 50°C for 72 h. An elastic film of brownish red or brown color was obtained. The TPU molecular mass (*M<sub>n</sub>*) was measured via gel permeation chromatography with degassed DMF as an eluent (model GL7410 pump model RI 704 detector, model GL7432 column, GL Sciences, Inc., Japan). The TPU glass-transition temperatures (*T<sub>g</sub>*) were measured by differential scanning calorimetry (model DSC220, Seiko Instruments, Inc., Japan, nitrogen flow = 50 mL/min, heating rate = 5°C/min, temperature range = -130 to 150°C). A comparison of the fullerene derivatives' dispersability in TPU was performed by transmittance measurements in the UV-vis region (V-650 series UV-vis spectrophotometer, Jasco Co., Ltd., Japan). The *M<sub>n</sub>* and *T<sub>g</sub>* values for the TPUs are shown in Table I.

#### Gas Permeability Measurements

The prepared sheets were mounted on a differential-pressure gas permeability apparatus (model MT-C1, Toyo Seiki Seisaku-Sho, Ltd., Japan). The analytical system was de-aerated for no less than 12 h under a vacuum pump. The *P* values for O<sub>2</sub> and CO<sub>2</sub> were measured, and the *D* values were computed from eq. (2):<sup>15</sup>

$$D = \frac{d^2}{6t} \quad (2)$$

where *D* is the diffusion coefficient (cm<sup>2</sup>/s), *d* is the film thickness (cm) and *t* is the time (s) taken for diffusion. Dividing *P* by *D*, we obtained *S*.

**Table III.** *E<sub>p</sub>*, *E<sub>D</sub>*, and  $\Delta H$  Values in the Gas Permeability of Oxygen and Carbon Dioxide for TPU<sub>PEt</sub>/C<sub>60</sub>(OH)<sub>n</sub>

C <sub>60</sub> (OH) <sub>n</sub> (wt %)	<i>E<sub>PO2</sub></i> (kJ/mol)	<i>E<sub>DO2</sub></i> (kJ/mol)	$\Delta H$ (kJ/mol)	<i>E<sub>PCO2</sub></i> (kJ/mol)	<i>E<sub>DCO2</sub></i> (kJ/mol)	$\Delta H$ (kJ/mol)
0	31.4	31.6	-0.18	27.6	33.7	-6.12
5	30.3	39.3	-9.01	25.1	34.9	-9.83

#### Positron Annihilation Lifetime

The *V<sub>f</sub>* values of the samples used in the gas permeability test were analyzed via PALS. From the *ortho*-positronium (*o*-Ps) lifetime ( $\tau_3$ ; ns), the hole radius (*r*; Å) was calculated from eq. (3):<sup>16-18</sup>

$$\tau_3 = \frac{1}{2} \left[ 1 - \frac{r}{r_0} + \frac{1}{2\pi} \sin \left( \frac{2\pi r}{r_0} \right) \right]^{-1} \quad (3)$$

where *r*<sub>0</sub> = *r* +  $\Delta r$ , where  $\Delta r$  is the empirical thickness of the electron layer (1.66 Å). *V<sub>f</sub>* was calculated with eq. (4):

$$V_f = \frac{4\pi r^3}{3} \quad (4)$$

Furthermore, the intensity of *o*-Ps (*I*<sub>3</sub>), which is indicative of hole density, was measured.

## RESULTS AND DISCUSSION

#### Gas Barrier Effects of C<sub>60</sub>(OH)<sub>n</sub> for TPU with PEt

For validation of the gas barrier effects, we used ether polyol thermoplastic polyurethane (TPU<sub>PEt</sub>). Because the gas permeability of TPU<sub>PEt</sub> was higher than the others, we considered that TPU<sub>PEt</sub> was most appropriate for examining the gas barrier effects of fullereneol. Table II shows the results of the gas permeability test for O<sub>2</sub> and CO<sub>2</sub> with the C<sub>60</sub>(OH)<sub>n</sub>-additive TPU<sub>PEt</sub> [TPU<sub>PEt</sub>/C<sub>60</sub>(OH)<sub>n</sub>] at several temperatures. All of the data changed exponentially with increasing temperature. *P* decreased with the addition of C<sub>60</sub>(OH)<sub>n</sub>, and this tendency became marked with increasing temperature. *D* showed a similar

**Table IV.**  $V_f$  and  $I_3$  Values of TPU/C<sub>60</sub>(OH)<sub>*n*</sub>

C <sub>60</sub> (OH) <sub><i>n</i></sub> (wt %)	$\tau_3$ (ns)	$r$ (Å)	$V_f$ (Å <sup>3</sup> )	$I_3$ (%)
0	2.55	3.32	153	30.5
5	2.54	3.31	151	27.2

tendency. Consequently, the gas barrier properties obtained with the addition of C<sub>60</sub>(OH)<sub>*n*</sub> were considered to be caused by the inhibition of diffusion.

#### Temperature Dependence of the Gas Permeability for TPU<sub>PEt</sub>/C<sub>60</sub>(OH)<sub>*n*</sub>

As noted previously,  $P$  is described as the product of  $D$  and  $S$ . Arrhenius eqs. (5) and (6) were applied to obtain the activation energy of the gas permeability ( $E_p$ ) and activation energy of diffusion ( $E_D$ ), respectively. Because  $S$  is expressed in eq. (7) with the Van't Hoff equation, the heat of dissolution ( $\Delta H$ ) was calculated with eq. (8) (Table III):

$$P = P_0 \exp(-E_p/RT) \quad (5)$$

$$D = D_0 \exp(-E_D/RT) \quad (6)$$

$$S = S_0 \exp(-\Delta H/RT) \quad (7)$$

$$E_p = \Delta H + E_D \quad (8)$$

where  $P_0$ ,  $D_0$ , and  $S_0$  are constants,  $R$  is the gas constant (in this equation only), and  $T$  is the absolute temperature.

With respect to oxygen diffusion, the addition of C<sub>60</sub>(OH)<sub>*n*</sub> made  $E_D$  larger; this suggested that movement of oxygen molecules between holes was less likely to occur. The same tendency was seen for carbon dioxide, but the increase in  $E_D$  was slight. The differences in the molecular size or molecular agglomeration between the gases were assumed to reflect the observed results in some form.  $\Delta H$  decreased with the addition of fullerene. This indicated an increase in the solubility of the gases. Fullerene might have enhanced the affinity of the gases to TPU<sub>TEt</sub>. It was evident that the decrease in  $P$  with the addition

of fullerene was caused by the decrease in  $D$  because  $S$  increased with the addition of fullerene.  $E_p$  for 5 wt % addition was slightly lower than that for no addition. This was due to the fact that the degree of increase in  $E_D$  was larger than that of the decrease in  $\Delta H$  because  $E_p$  is expressed as a sum of  $\Delta H$  and  $E_D$ , as shown by eq. (8).

#### Positron Annihilation Lifetime of TPU/C<sub>60</sub>(OH)<sub>*n*</sub>

The results of PALS for TPU<sub>PEt</sub>/C<sub>60</sub>(OH)<sub>*n*</sub> are shown in Table IV. The 5 wt % addition of C<sub>60</sub>(OH)<sub>*n*</sub> as compared to no addition, provided a very slight decrease in the  $V_f$  of TPU<sub>PEt</sub>/C<sub>60</sub>(OH)<sub>*n*</sub>. Thus, the decrease in  $V_f$  was unlikely to have contributed to the decrease in the gas permeability. The introduction of C<sub>60</sub>(OH)<sub>*n*</sub> led to a decrease in  $I_3$ . The decrease in  $I_3$  was assumed to reflect a drop in the hole density; this suggested a contribution to a decrease of diffusion. It was hard to judge, however, because the possibility could not be ruled out that the many  $\pi$  electrons present in the fullerene molecules suppressed  $o$ -Ps generation.

A tortuosity factor was proposed in semicrystalline polymers.<sup>19</sup> This factor is a geometrical impedance factor accounting for the reduction in  $D$  and forces gas molecules to follow a longer path. It appears as a divider of  $A$  in eq. (1). Because TPU is considered a quasi-semicrystalline polymer, an increase in this factor with the addition of fullerene would result in a decrease in  $D$ . The increase in this factor may have caused the decrease in  $D$ .

The results of the gas permeability measurements and PALS showed that the change in the gas barrier properties of the TPU<sub>PEt</sub>/C<sub>60</sub>(OH)<sub>*n*</sub> composite with the addition of C<sub>60</sub>(OH)<sub>*n*</sub> did not originate from a decrease in  $V_f$  but was probably due to the increase in the tortuosity factor with the addition of fullerene, which acted as a blocker.

The results of PALS for TPU/C<sub>60</sub>(OH)<sub>*n*</sub> with different polyols are shown in Table V. The addition of C<sub>60</sub>(OH)<sub>*n*</sub> did not lead to a change in TPU  $V_f$ , although large differences were

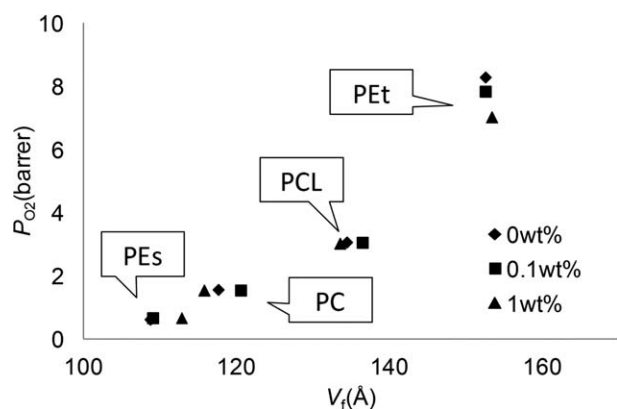
**Table V.**  $V_f$  of TPU/C<sub>60</sub>(OH)<sub>*n*</sub>

Polyol type	C <sub>60</sub> (OH) <sub><i>n</i></sub> (wt %)	$\tau_3$ (ns)	$r$ (Å)	$V_f$ (Å <sup>3</sup> )	$P_{O_2}$ (barrer <sup>a</sup> )	$P_{CO_2}$ (barrer <sup>a</sup> )
PEt	0	2.55	3.32	153	8.30	29.0
	0.1	2.55	3.32	153	7.85	22.8
	1	2.56	3.31	151	7.04	24.9
PCL	0	2.38	3.18	134	3.07	10.0
	0.1	2.40	3.19	136	3.06	7.94
	1	2.37	3.17	133	3.03	8.56
PC	0	2.20	3.04	118	1.57	4.62
	0.1	2.24	3.07	121	1.55	4.31
	1	2.19	3.02	115	1.55	4.09
PEs	0	2.12	2.96	109	0.629	2.39
	0.1	2.12	2.96	109	0.674	2.34
	1	2.16	3.00	113	0.678	2.54

$d = 0.5$  mm.

<sup>a</sup>Barrer = 10<sup>-10</sup>(cm<sup>3</sup> cm cm<sup>-2</sup> s<sup>-1</sup> cmHg<sup>-1</sup>)

$P_{O_2}$  and  $P_{CO_2}$  are permeability coefficients of oxygen and carbon dioxide, respectively.



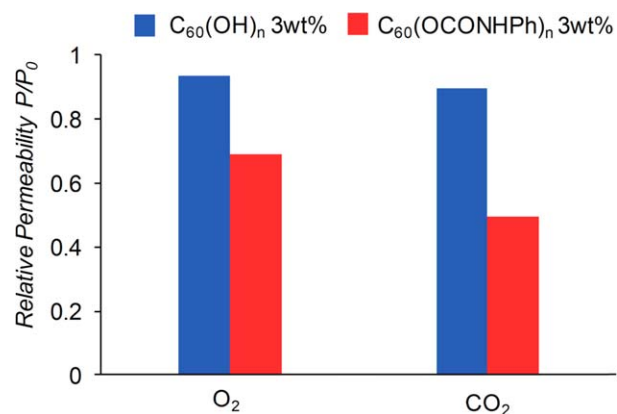
**Figure 2.** Plot of  $V_f$  of TPU/ $C_{60}(OH)_n$  versus oxygen  $P$  at 25°C ( $d = 1.0$  mm).

recognized that were dependent on the polyol structure. The TPU  $V_f$  was not affected significantly by the addition of fullerene at least within the range of addition.  $V_f$  remained unchanged unless the soft segment structural changed. Figure 2 shows the tendency for the TPU  $V_f$  to increase depending on the polyol structure and the concomitant elevation in  $P$ .

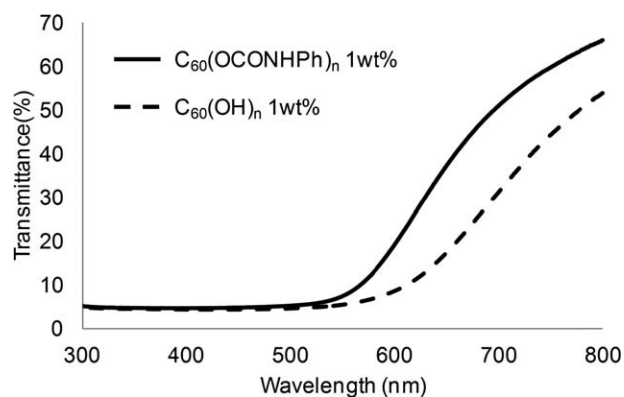
#### Effects of the Chemical Modification of $C_{60}(OH)_n$

The gas barrier properties of fullerene and urethanized fullerene were compared. As shown in Figure 3,  $P_0$  with urethanized fullerene achieved a reduction rate that was approximately four-fold higher for oxygen and fivefold higher for carbon dioxide compared to that of TPU<sub>PEt</sub> with fullerene.

As the dispersability of fillers in the polymers improved, the detour distance for gas molecules up to permeation generally became longer. To confirm the dispersability of fullerene derivative used in the experiments, the transmittance of the TPU<sub>PEt</sub> was measured. As shown in Figure 4, the transmittance rise wavelength of TPU<sub>PEt</sub> with urethanized fullerene was shorter than that of TPU<sub>PEt</sub> with fullerene, and consequently, the difference in the transmittance over wavelengths of 550–800 nm arose. It is qualitatively appropriate that the shorter the rise



**Figure 3.** Relative permeability of the TPU<sub>PEt</sub>-containing fullerene derivative ( $P$ ) at 25°C ( $d = 1.0$  mm).  $P_0$ : Permeability of TPUPET(control);  $P$ : Permeability of TPUPET containing fullerene derivative. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 4.** Light transmittance of the TPU<sub>PEt</sub>-containing fullerene derivative ( $d = 0.5$  mm).

wavelength of the transmittance of the translucent materials is, the smaller a size of part that scatters light. The higher dispersability of urethanized fullerene compared to fullerene presumably caused the shorter rise wavelength and, consequently, the higher transmittance. Thus, the superiority in gas barrier effect obtained through the introduction of urethane groups to fullerene was considered to result from the improved dispersability within TPU<sub>PEt</sub>. Although the possibility of change in the  $V_f$  of TPU<sub>PEt</sub> by the addition of urethanized fullerene should be discussed, no change was presumed from the results of the addition of fullerene.

#### CONCLUSIONS

Our investigation of the influence of fullerene derivatives as fillers on the TPU gas permeability elucidated the following:

1. The addition of fullerene to TPU caused the gas permeability to decrease for both  $O_2$  and  $CO_2$ .
2. Hole volumes according to PALS showed no significant differences between the fullerene derivative-added TPU and TPU without additive.
3. From the temperature change in  $D$  for gas permeability, the decline in gas permeability was presumed to be caused by the inhibited diffusion of gas molecules by fullerene particles.
4. The addition of urethanized fullerene through the chemical modification of fullerene improved the dispersability in TPU, and consequently, a distinct improvement in the gas barrier properties was observed.

#### ACKNOWLEDGMENTS

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