

## Polymeric Ultraviolet Absorber

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### Synopsis

Polymeric fine powder, prepared by polymerization of glycidylmethacrylate-divinylbenzene, was reacted with 2,4-dihydroxybenzophenone. The resultant polymer was effective as a polymeric ultraviolet absorber, and no migration was observed in polypropylene.

### INTRODUCTION

Polyolefins are susceptible to oxidation promoted by heat or light, and stabilizers such as antioxidants and ultraviolet absorbers (UV-absorber) are used to make polyolefins more durable. However, there is the drawback that the stabilizers are apt to migrate out of the substrate during practical uses. Therefore, polymeric stabilizers have been studied in order to overcome this drawback.<sup>1-4</sup> However, the polymeric stabilizers should be not so well blendable with high crystalline polyolefin, due to poor compatibility of the polymeric stabilizers with the polyolefin. Then, the polymeric stabilizers should be finely dispersed in the substrate, as presumed by the fact that poly(styrene-glycidylmethacrylate) or poly(vinyltoluene-glycidylmethacrylate) is dispersed in the shape of small particles in the substrate when they are blended with polypropylene (PP).<sup>5</sup>

On the other hand, we have prepared a fine powdery polymer of glycidylmethacrylate-divinylbenzene (PFPC) which is used as a mordant by making use of the reactivity of the glycidyl group to improve the poor dyeability of PP.<sup>6-8</sup> We have also studied the anchoring effect of PFPC for antioxidants having plural phenolic hydroxyl group in a molecule.<sup>9</sup> This paper is concerned with preparation of a polymeric UV-absorber by reacting the epoxy group of PFPC with the 4-hydroxyl group of 2,4-dihydroxybenzophenone (DBP, an UV-absorber), as shown in the previous paper.<sup>2</sup> It was elucidated that the polymeric UV-absorber (PFPC-DBP) was effective in overcoming the drawbacks described above.

### EXPERIMENTAL

#### Preparation of PFPC-DBP

PFPC was prepared by the method in the previous paper<sup>10</sup> and the composition of PFPC, divinylbenzene/(glycidylmethacrylate + divinylbenzene), was 0.1 by weight. PFPC, DBP, and a solvent were put into a glass autoclave and

TABLE I  
Structural Formulas of Stabilizers

BEC	
HOBP	
DBP	
DLTDP	$S-(CH_2CH_2COOC_{12}H_{25})_2$
PFPC-DBP	

were kept at 120°C for 3 hr with vigorous shaking. The resultant mixture was poured into excess methanol and PFPC-DBP produced was filtered, washed with methanol and petroleum ether successively, and dried under vacuum.

### Photodegradation Test

PFPC-DBP was blended with PP powder under 30 mesh (melt index, at 230°C, load 2.16 kg/cm<sup>2</sup>: 0.5 g/10 min). The stabilizers used are shown in Table I. Then, BBC and DLTDP were added and the resultant mixture was extruded at 230°C and pelletized. Films 0.5 mm thick were molded, and the films were exposed to light from a carbon arc at 60 ± 3°C under 60% humidity by the aid of Shimazu Weather Tester CW-DV-3 from Shimazu Seisakusho Co., Ltd. Time to embrittlement by bending (180°) was measured at intervals of 20 hr.

### RESULTS AND DISCUSSION

First, the reaction of PFPC with DBP was studied as shown in Table II, and an IR spectrum of PFPC-DBP is shown in Figure 1. The absorption bands at

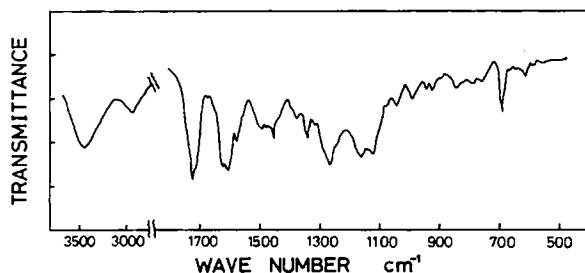


Fig. 1. IR Spectrum of PFPC-DBP.

TABLE II  
Preparation of PFPC-DBP

Sample no.	Solvent, ml	DBP, g	PFPC, g	$A_{1625 \text{ cm}^{-1}}/A_{1725 \text{ cm}^{-1}}$
1	<i>n</i> -Butanol, 40	1.5	1	0.36
2	Toluene, 40	1.5	1	0.34
3	Dimethylformamide, 40	1.5	1	0.55

TABLE III  
Results of Photodegradation Test<sup>a</sup>

Sample no.	UV-Absorber, wt-%	DLTDP, wt-%	BBC, wt-%	Time to embrittlement, hr	
				Untreated	Treated <sup>b</sup>
I	PFPC-DBP, 3.0	0.7	0.2	240	80
II	PFPC-DBP, 1.5	0.7	0.2	240	60
III	PFPC-DBP, 0.5	0.7	0.2	160	60
IV	None	0.7	0.2	100	40
V	HOBP, 0.5	0.7	0.2	260	40

<sup>a</sup> PFPC-DBP prepared from the following recipe: PFPC, 10 g; DBP, 35 g; and 500 ml dimethylformamide.

<sup>b</sup> Dipped in trichloroethylene at room temperature overnight (1 g film/100 ml trichloroethylene).

1725  $\text{cm}^{-1}$  and 1625  $\text{cm}^{-1}$  are assigned to the ester group of the glycidyl group of PFPC and the carbonyl group of DBP, respectively.<sup>3</sup> The intensity ratio of the absorptions,  $A_{1625 \text{ cm}^{-1}}/A_{1725 \text{ cm}^{-1}}$ , shows the conversion of the epoxy group in PFPC. The value of sample 3 (0.55) shown in Table II corresponds to about 70% conversion. The UV-absorbing effect of PFPC-DBP is clearly understood by comparing samples I-III with IV in Table III. With regard to the samples untreated with trichloroethylene, PFPC-DBP showed nearly comparable effect to that of HOBP, a practically useful UV-absorber. The molar content of the DBP unit can be calculated by assuming that the conversion of the epoxy group was about 70% and the divinylbenzene content of PFPC was 10%. The quantity of PFPC-DBP equivalent to the HOBP content (0.5%) was calculated to be a little more than 0.5%, and both the molar contents of the DBP unit in PP were about 0.01 mole/kg PP. So, the efficacy of PFPC-DBP should be a little less than that of HOBP, probably due to the difference in the distribution of both the UV-absorbers in PP. However, the efficacy of PFPC-DBP after treatment with trichloroethylene was evidently superior to that of HOBP.

Figure 2 shows the changes in the IR spectra of the samples shown in Table III. The absorption band at 1750  $\text{cm}^{-1}$  is assigned to the ester group of DLTDP and the absorption bands at 1725  $\text{cm}^{-1}$  and 1625  $\text{cm}^{-1}$  to PFPC-DBP. Samples IV and V contain no glycidyl group of PFPC, so no absorption was observed at 1725  $\text{cm}^{-1}$ . The absorption bands at 1750  $\text{cm}^{-1}$  in all the cases and the absorption band at 1625  $\text{cm}^{-1}$  in the case of sample V disappeared by treatment with trichloroethylene. These facts showed that the stabilizers, not fixed in the substrate were excluded by the treatment. On the other hand, the absorption bands at 1625  $\text{cm}^{-1}$  and 1725  $\text{cm}^{-1}$  in the cases of samples I-III did not disappear by the treatment, as reasonably expected. The results shown in

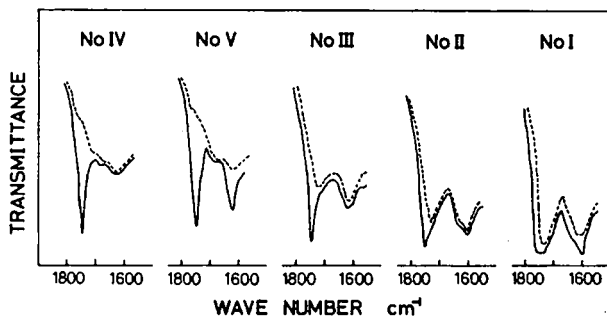


Fig. 2. Change in the IR spectra of PP films by the trichloroethylene treatment: solid lines, untreated; dotted lines, treated with trichloroethylene.

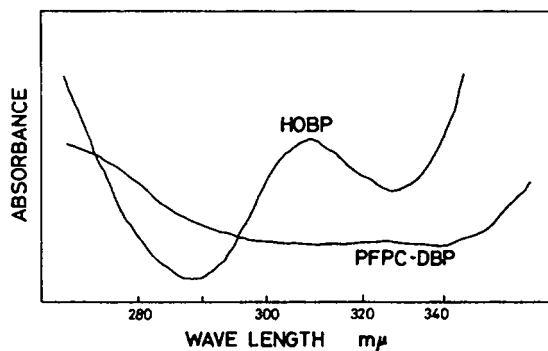


Fig. 3. UV Absorption spectra of PP films containing HOBP and PFPC-DBP: PP film, 0.01 mm thick.

Figure 2 could support the result shown in Table III, and the anchoring effect of PFPC<sup>9</sup> might be considered for BBC, though no evidence was obtained in this study. Figure 3 shows that the UV-absorption spectrum of the PP film containing PFPC-DBP was broader than that containing HOBP in the range of 250–340  $m\mu$ , the comparable wavelength of sunlight in the UV region.

As described above, PFPC-DBP was really effective in prolonging the exposing time to embrittlement. One of the most important factors with regard to the efficacy of PFPC-DBP should be its dispersibility in the substrate. The particle size of PFPC-DBP was about 0.2  $\mu$ , but it is not so easy a problem how uniformly to blend PFPC-DBP in PP with high crystallinity. The dispersion state of HOBP in PP (sample V) should be more uniform than that of PFPC-DBP (samples I–III). This difference can explain the more prolonged time of V without treatment by trichloroethylene in comparison with samples I–III. The time to embrittlement is different between the samples treated with trichloroethylene and untreated ones, due to elution of the stabilizers BBC, DLTD, and DBP. Therefore, not only polymeric UV-absorbers but polymeric antioxidants must be used to make PP more durable under more severe conditions.

There is another way to make PFPC-DBP: DBP is reacted with glycidyl-methacrylate in advance, and then the resultant monomer is copolymerized with divinylbenzene. We have tried this polymerization by using benzoyl peroxide as an initiator. However, the conversion was rather less, so this way would not be useful from a practical standpoint.

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