

The Anchoring Effect of the Fine, Powdery Copolymer of Glycidyl Methacrylate-Divinyl Benzene for Antioxidants in Polypropylene

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The anchoring effect of the fine, powdery copolymer of glycidyl methacrylate-divinylbenzene, blended in polypropylene, for phenolic antioxidants was studied by the oxygen absorption method and by studying the infrared spectrum. As a result, the anchoring effect was recognized, and it was confirmed that the effect came from the reaction between the phenolic hydroxyl groups of antioxidants and the epoxy groups of the fine, powdery copolymer and that, furthermore, the anchoring effect was related to the molecular structure of the antioxidants. It is interesting to note that these results suggest that polymeric antioxidants practically overcome the defect of the migration or the volatility observed on low-molecular-weight antioxidants.

In a previous paper,¹⁾ we reported that the fine, powdery copolymer of glycidyl methacrylate-divinylbenzene was useful as a mordant for the dyeing of polypropylene fiber, and showed the anchoring phenomena of the dye with the amino group in the substrate, a phenomena resulting from the reaction between the epoxy group of the fine, powdery copolymer and the amino group of the dye.

The reaction between the phenolic hydroxyl group and the epoxy group is well known.²⁾ These facts suggest that the fine, powdery copolymer might be effective in anchoring the phenolic antioxidant in polypropylene. This effect was studied by the oxygen-absorption method and by infrared spectroscopy.

Experimental

Materials. The polypropylene (PP) powder used contains no antioxidant. The properties were as follows: melt index (at 230°C, load; 2.16 kg/cm²): 0.25 g/10 min, specific gravity (at 23°C): 0.912 g/cm³, and grain size: under 30 mesh.

Fine, powdery copolymers (PFPC) of glycidyl methacrylate (GMA)-divinylbenzene (DVB) [PFPC-GD] and styrene (St)-DVB [PFPC-St] were prepared by the procedure described in the previous paper.³⁾ The synthetic conditions of PFPC and the epoxy values are shown in Table 1. The epoxy value was determined by the HCl-dioxane method.⁴⁾

TABLE 1. SYNTHETIC CONDITIONS AND EPOXY GROUP CONTENT OF PFPC

PFPC	Condition		Epoxy group content
PEPC-GD	GMA	: 180 g	6.21 mmol/g-powder
	DVB	: 20 g	
	BPO	: 10 g	
	<i>n</i> -Heptane	: 2.8 l	
	at 70°C	5 hr	
PFPC-St	St	: 225 g	—
	DVB	: 25 g	
	BPO	: 10 g	
	<i>iso</i> -PrOH	: 2.5 l	
	at 70°C	4 hr	

1) Y. Mizutani, *This Bulletin*, **39**, 1088 (1966).

2) P. E. Parker, *Chem. Rev.*, **59**, 737 (1959).

3) Y. Mizutani, K. Yamamoto, and S. Matsuoka, *This Bulletin*, **39**, 1792 (1966).

4) G. King, *Nature*, **164**, 1106 (1949).

TABLE 2. STRUCTURAL FORMULAS OF ANTIOXIDANTS

	Structural formula
DVMP	
MTVP	
VHMP	
MDTP	
TTBP	
DLTDP	$S(CH_2CH_2COOC_{12}H_{25})_2$

The antioxidants used are shown in Table 2.

Preparation of Samples. PP powder and PFPC were mixed in a sufficient amount of methanol with a mixer. The polymer mixture thus obtained was filtered and dried in a vacuum at room temperature. Then, the polymer mixture was dipped into an acetone solution of the antioxidant, after which the acetone was evaporated at room temperature under reduced pressure. The mixture was extruded at 200—230°C with an extruder (Type MK-1, from the Modern Machinery Co., Ltd.) and then pelletized.

In order to obtain the specific surface area of the sample over the safe limit of the specific surface area for an oxygen-absorption reaction⁵⁾ and in order to eliminate the unreacted antioxidant, the pellets were dissolved in hot *p*-xylene under a nitrogen atmosphere, poured into methanol, filtered out, extracted with acetone for about 16 hr, and then dried in a vacuum at room temperature.

5) Y. Mizutani, H. Ihara, K. Yamamoto, and S. Matsuoka, *Kobunshi Kagaku*, **21**, 437 (1964).

The Measurement of Oxygen Absorption. The measurements were carried out with an apparatus previously described.⁵⁾ The reaction temperature was maintained by means of a vapor bath. As a vapor bath, monochlorobenzene, *p*-xylene, and a mixture of them with a trace of ethanol were used. The amount of oxygen absorbed was transformed into the value at 25°C and 760 mmHg.

The amount of oxygen absorbed gradually increased in the initial stage, and then it increased steadily. The oxygen absorption rate at the steady state (K_c , ml/min·g) was determined by the slope of the linear part of the oxygen absorption curve, and the induction period (P , min), by the extrapolation of the slope.⁵⁾

The Measurement of the Infrared Spectrum. The spectrum was measured on a filmy sample with a Hitachi model EPI-G₂ spectrometer. For the accuracy of the experiment, an equimolar antioxidant (MTVP) to the epoxy-group of PFPC-GD was added, and the absorption intensity of the hydroxyl group of MTVP ($(\log I_0/I)/d$; where $\log I_0/I$ was the absorbance and d was the thickness of the film) was calculated. This value was used as a measure of the concentration of the antioxidant.

Results and Discussion

Anchoring Effect of PFPC-GD in the Practical Recipe.

The compositions of the samples used are summarized in Table 3. DLTDP was used as a co-inhibitor.⁶⁾ P-1

TABLE 3. COMPOSITIONS OF SAMPLES IN PRACTICAL RECIPE

Sample	Added material,	wt %
P-1	MTVP	0.056
	DLTDP	0.110
P-2	PFPC-St	4.55
	MTVP	0.056
	DLTDP	0.110
P-3	PFPC-GD	4.55
	MTVP	0.056
	DLTDP	0.110

contains no polymeric, fine powder, and P-2 contains PFPC-St, which has no reactive group. These two samples were used as the reference samples. P-3 contains PFPC-GD, which has an epoxy group. Examples of the

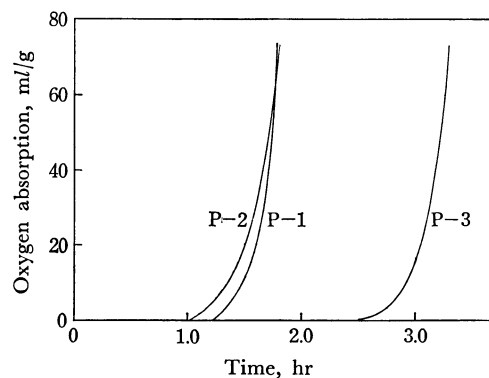


Fig. 1. Oxygen absorption curves in practical recipe at 133°C.

6) N. P. Neureiter and D. E. Bown, *Ind. Eng. Chem., Prod. Res. Develop.*, **1**, 236 (1962).

oxygen absorption curves of these three samples are shown in Fig. 1. It was observed that the induction period of the oxygen absorption curve of P-3 was longer than that of either reference sample, P-1 or P-2. The co-inhibitor (DLTDP) was not detected in these samples by studying the infrared spectrum. Therefore, the difference in the induction period shows that the antioxidant (MTVP) was anchored in PP resin and was not extracted with acetone. In P-2, the anchoring effect was not observed, because PFPC-St had no reactive group. These results suggest that the anchoring effect comes from the reaction between the epoxy groups of PFPC-GD and the phenolic hydroxyl groups of the antioxidant (MTVP).

The reciprocal of the induction period ($1/P$) and oxygen absorption rate at the steady state (K_c) were obtained from the oxygen absorption curves at various

TABLE 4. THE VALUES OF $1/P$ AND K_c AT VARIOUS TEMPERATURE IN THE PRACTICAL RECIPE

Sample		Reaction temp., °C			
		133	128.6	125	121
P-1	$(1/P) \times 10^2$, min ⁻¹	1.11	0.781	0.602	0.417
	K_c , ml/min·g	4.3	3.5	2.2	1.0
P-2	$(1/P) \times 10^2$, min ⁻¹	1.36	0.877	—	0.426
	K_c , ml/min·g	4.3	2.8	—	0.9
P-3	$(1/P) \times 10^2$, min ⁻¹	0.549	0.444	0.355	0.448
	K_c , ml/min·g	4.6	2.6	2.1	0.68

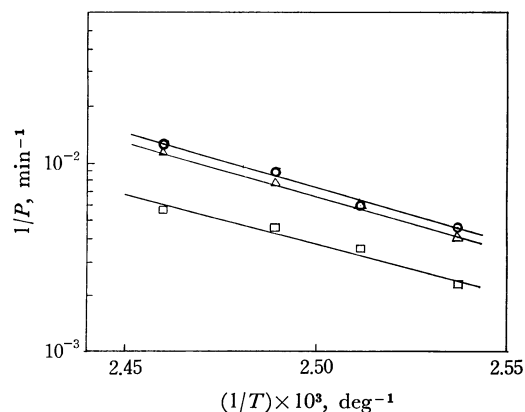


Fig. 2. Arrhenius plot of $1/P$ in practical recipe. Δ : P-1, \circ : P-2, \square : P-3

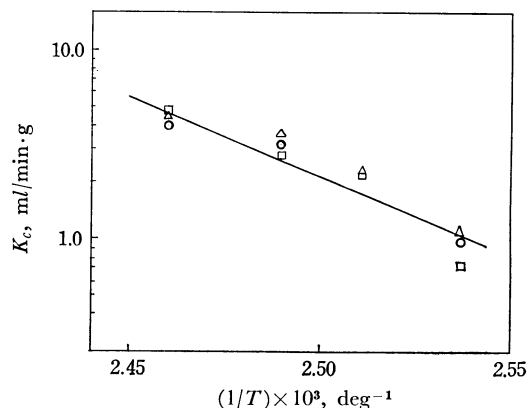


Fig. 3. Arrhenius plot of K_c in practical recipe. Δ : P-1, \circ : P-2, \square : P-3

temperatures, as is shown in Table 4. The activation energy of the reaction in the induction region (E_i) and that in the steady state (E_s) were calculated from the Arrhenius plots shown in Fig. 2 and Fig. 3. The values of the activation energies were as follows: $E_i=25-28$ kcal/mol and $E_s=40$ kcal/mol. These values almost correspond with those reported in a previous paper⁵⁾ ($E_i=22$ kcal/mol, $E_s=43$ kcal/mol).

Confirmation of the Reaction between PFPC-GD and MTVP by Studying the Infrared Spectrum in a Model Recipe. The polypropylene powder in a model recipe contains 4.6 wt% of PFPC-GD and 3.2 wt% of MTVP.

The infrared spectra of the samples investigated are shown in Fig. 4. P-4-1 consisted of pellets obtained by

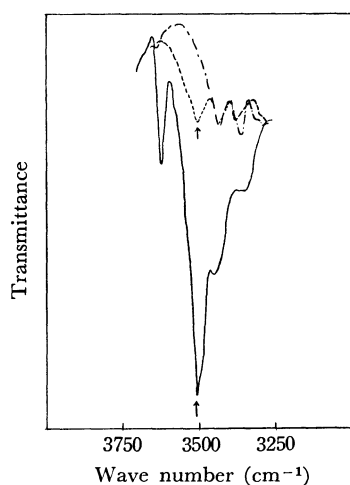


Fig. 4. Infrared spectra in model recipe.

----- Reference, — P-4-1, ---- P-4-2, P-4-3, P-4-4

extruding the PP powder of the model recipe, P-4-2 consisted of the powder obtained by treating the pellets with hot *p*-xylene, and P-4-3, and P-4-4 consisted of the powder extracted with acetone. As the reference sample, pellets without any added MTVP were used. The infrared spectra of P-4-2, P-4-3, and P-4-4 were identical. The absorption band at 3510 cm^{-1} was assigned to the characteristic band of the phenolic hydroxyl groups of MTVP, and the absorption intensities of the band were calculated. The results are shown in Table 5. The constancy of the value under treatment

TABLE 5. THE CHANGE OF ABSORPTION INTENSITY IN THE MODEL RECIPE

Sample ^{a)}	Time of acetone-extraction (hr)	$(\log I_0/I)/d^{(d)}$
P-4-1 ^{b)}	—	20.3
P-4-2 ^{c)}	—	2.7
P-4-3	6	2.8
P-4-4	16	2.8

a) PFPC-GD: 4.6 wt%, MTVP: 3.2 wt%.

b) Pellets after extruding.

c) Powder obtained by treating with hot *p*-xylene.

d) Based upon the value of reference sample, PP+PFPC-GD.

with hot *p*-xylene (P-4-2) and the extraction time with acetone shows that the antioxidant (MTVP) reacted with PFPC-GD and was anchored in PP resin. The decrease in the absorption intensity upon treatment

with hot *p*-xylene or upon extraction with acetone shows that the degree of the reaction of MTVP with PFPC-GD was low. For reference, the induction period of the oxygen-absorption reaction of P-4-3 at 128°C was over 10 hr.

Influence of the Molecular Structure of Antioxidants on the Anchoring Effect.

If the reactivities of the phenolic hydroxyl groups are equal, it seems that quantity of antioxidants to be anchored will be greater as the numbers of the hydroxyl groups in a molecule increases. Also when the numbers of the hydroxyl groups are equal, it seems that the quantity will be mainly due to the reactivity of the hydroxyl group. In order to confirm the above suppositions, oxygen absorption curves on various antioxidants are compared in Fig. 5. The anti-

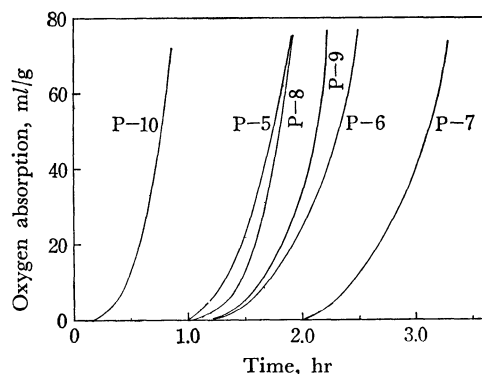


Fig. 5. Influence of the molecular structure of antioxidants on anchoring effect. (at 129°C)

oxidants used and the quantities added, which were so fixed that the quantities of the phenolic hydroxyl groups were equal, are shown in Table 6. Figure 5 shows that

TABLE 6. NUMBERS OF PHENOLIC HYDROXYL GROUPS AND QUANTITIES OF ANTIOXIDANTS ADDED

Sample ^{a)}	Antioxidant	Number of -OH in a molecule	Antioxidant added mmol/g
P-5	DVMP	1	4.0×10^{-3}
P-6	MTVP	2	2.0×10^{-3}
P-7	VHMP	3	1.3×10^{-3}
P-8	MDTP	2	2.0×10^{-3}
P-9	TTBP	2	2.0×10^{-3}
P-10	—	—	—

a) PFPC-GD content: 4.6 wt%.

the induction period increases as the number of hydroxyl group increases. Also, the induction period increased in such an order as: P-8 (MDTP) < P-9 (TTBP) < P-6 (MTVP); this order may be mainly due to the decrease in the steric hindrance to the hydroxyl groups of antioxidants, as can be guessed from the molecular structure. However, it has not yet been explained why the induction period of P-5 (DVMP) (shown in Fig. 5), the one phenolic hydroxyl group of which may be consumed in the reaction with the epoxy groups of PFPC-GD was longer than that of P-10.

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