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Studies on Reactions of Polypropylene. VIII. The Thermal Degradation of Polypropylene Accelerated by Polyglycidyl Methacrylate

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The thermal degradation of polypropylene was investigated in the presence of polyglycidyl methacrylate (PGMA) by the use of an extruder under a nitrogen atmosphere. PGMA was found to be effective as an accelerator for the thermal degradation of polypropylene. The accelerating effect of PGMA was attributed to the facts that PGMA was degraded thermally by the zipper-scission mechanism and that the active radical thus generated was effective in accelerating the thermal degradation of polypropylene by the random-scission mechanism. The surviving ratio of the epoxy group throughout the thermal degradation was not as large as had been expected.

A great number of studies attempting to improve the qualities of polypropylene in practical uses have been already published. It has been established that such vinyl polymers as polystyrene, polymethyl methacrylate, the 2-methyl-5-vinyl pyridine-styrene copolymer, and the acrylonitrile-styrene copolymer were effective in accelerating the thermal degradation of polypropylene and in giving graft or block copolymers.(1) On the other hand, the utility of a reactive polymer has also been well-established.(2-5) For example, glycidyl methacrylate (GMA) has been grafted onto the polypropylene fiber by Iwakura *et al.*(6)

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(1) Y. Mizutani, S. Matsuoka and K. Yamamoto, This Bulletin, **38**, 2045 (1965).

(2) W. Kern and R. C. Schulz, *Angew. Chem.*, **69**, 153 (1957).

(3) M. Imoto, *Yuki Gosei Kagaku Kyokaishi (J. Soc. Org. Synth. Chem., Japan)*, **15**, 325 (1957).

(4) Y. Iwakura, *ibid.*, **20**, 813 (1959).

(5) M. Okawara, *Kobunshi (High Polymers, Japan)*, **14**, 850 (1965).

(6) Y. Iwakura, T. Kurosaki, K. Nagakubo, K. Takeda and M. Miura, This Bulletin, **38**, 1349 (1965).

and the copolymer of GMA has been blended into polypropylene by Kubota *et al.*7) In this paper, polyglycidyl methacrylate (PGMA) was used as an accelerator for thermal degradation of polypropylene, and its behavior was studied.

Experimental

Polypropylene. The polypropylene sample used (PP) was a powder under 30 mesh and contained no stabilizer. Its properties were as follows: melt index (at 230°C, applied load: 2.16 kg/cm^2): less than 0.01 g/10 min, and specific gravity (at 23°C): 0.909.

The Preparation of PGMA. GMA was polymerized in benzene with stirring at about 60°C for several hours, using benzoyl peroxide as an initiator of the polymerization. The transparent and viscous polymer solution thus obtained was stirred into excess methanol by the use of a mixer. The PGMA precipitated was filtered, purified by reprecipitation by the alternate use of acetone and methanol, and dried under a vacuum. The epoxy-group content of the PGMA prepared was 6.810 mmol/g, which corresponds to 97% of the theoretical value (7.034 mmol/g). This percentage was very consistent with the values reported by Otsu *et al.*8)

The Preparation of Sample for the Thermal Degradation. The polypropylene powder was stirred into an acetone solution of PGMA; then the dense slurry obtained was stirred into excess methanol by the use of a mixer. The polymer mixture was filtered and dried under a vacuum. The properties of the samples thus prepared are shown in Table 1.

TABLE 1. THE PROPERTIES OF THE SAMPLES

Sample	Epoxy-group content mmol/g	$D_{5.8\mu}/D_{2.3\mu}$	PGMA added %
PP-PGMA·1	0.575	5.72	8.42
PP-PGMA·2	0.397	3.70	5.82
PP-PGMA·3	0.232	2.30	3.40

The Thermal Degradation. The thermal degradation was carried out under a nitrogen atmosphere by the use of the extruder, which was a modification of the MK-1 type from the Modern Machinery Co., Ltd. The heating zone of the extruder was divided into three parts; T_1, T_2, and T_3, showing the temperature of three parts, the part near the sample inlet, the middle part, and the part near the sample outlet respectively, as has been shown in a preceding paper.1)

The Determination of the Epoxy-group Content. The extruded polymer was powdered by reprecipitation: the polymer (3 g) was dissolved in hot *p*-xylene (150 m*l*) under a nitrogen atmosphere; this hot solution was then slowly cooled overnight. Then the resultant slurry was stirred into methanol (1.5 *l*) by the use of a mixer. The powdered polymer was filtered, washed with methanol, and dried under a vacuum. This powdery polymer was extracted by dry acetone for about 20 hr by the use of a Soxhlet extractor under a nitrogen atmosphere and then dried under a vacuum. The epoxy-group content was determined by the method used by Iwakura *et al.*6) The powdery polymer (2.5 g) was immersed in a solution of 25 m*l* of dioxane and 20 m*l* of a 0.1 N dioxane solution of hydrochloric acid. The mixture was then allowed to stand overnight, after which the excess hydrochloric acid was titrated with a 0.1 N aqueous solution of sodium hydroxide, using phenolphthalein as an indicator.

The Determination of the Carbonyl-group Content. The sample was molded to a thin film and the ratio of the optical densities ($D_{5.8\mu}/D_{2.3\mu}$) was used as a measure of the content of the carbonyl group due to the glycidyl ester group. The spectrophotometer used was Hitachi-Perkin Elmer 125, Grating Infrared Spectrophotometer from the Hitachi Ltd. As is shown in Fig. 1, the calibration line was determined expediently by using atactic polypropylene and the polymeric fine powder with crosslinkage of the GMA-divinyl benzene system (PFPC)9,10) in place of the polypropylene sample and PGMA respectively, since both the polypropylene sample and PGMA were immiscible and good experimental reproducibility could hardly be expected. On the other hand, atactic polypropylene and PFPC could be easily blended at room temperature by the use of a mixing roller.

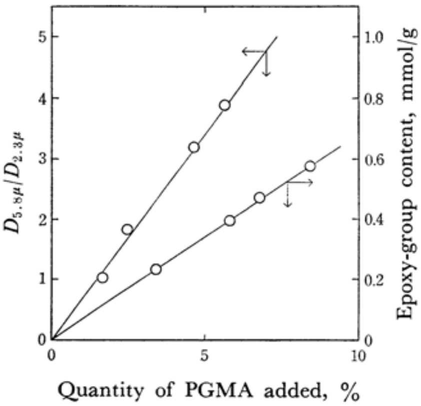

Fig. 1. The relation between the quantity of PGMA added and the carbonyl-group content or the epoxy-group content.

The carbonyl-group content in PFPC was determined by elementary analysis, assuming that all the oxygen present in PFPC was to be attributed to the glycidyl ester group. The carbonyl-group content in PFPC was calculated to be 6.21 mmol/g from the results of the elementary analysis of PFPC; C: 63.20%, H: 6.98%, and O: 29.82%.

The Determination of the Degree of Degradation. Beyond question, the change in intrinsic viscosity is the most reliable measure of the degree of degradation, but the melt index was inevitably used in this study because it was observed that the PGMA in the degraded

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7) M. Kubota, M. Katayama and S. Ishizuka, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **66**, 725 (1963).

8) T. Otsu, K. Goto and M. Imoto, *Kobunshi Kagaku (Chem. High Polymers, Japan)*, **21**, 703 (1964).

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

10) Y. Mizutani, *ibid.*, **39**, 1088 (1966).

polymer became insoluble, as will be discussed below, thus making viscosity measurements unreliable. The melt index was determined at 230°C by applying the load of 2.16 kg/cm^2 by the use of a melt indexer from the Shimadzu Seisakusho Co., Ltd.

Results and Discussion

It became clear that PGMA was effective in accelerating the thermal degradation of polypropylene, as is shown in Table 2. With the elevation of the reaction temperature, the degree of degradation increased. The degradation under air was found to be more violent than that under a nitrogen atmosphere; this was attributed to the participation of oxygen in air. Figure 2 shows the effect of the rotating speed of the screw shaft on the thermal degradation of polypropylene. With the increase in the rotating speed of the screw shaft, namely, with the decrease in the retention time of the polymer in the extruder, the degree of degradation decreased. The shearing effect of the screw shaft is negligible, because the shearing effect has a negative temperature coefficient:[11] no degradation of polypropylene ([η]: 4.3 dl/g at 135°C in tetraline) was observed under the following conditions: T_1: 190°C, T_2: 140°C, T_3: 200°C, and the rotating speed of the screw shaft: 30 rpm.[1]

TABLE 2. THE EFFECTS OF REACTION TEMPERATURE AND ATMOSPHERE ON THE THERMAL DEGRADATION OF PP AND PP-PGMA·2

Sample	Reaction temp. °C T_1	T_2	T_3	Atmosphere	Melt index g/10 min
PP	220	330	250	N_2	0.2
PP	220	330	250	air	0.4
PP-PGMA·2	220	320	250	N_2	1.2
PP-PGMA·2	220	330	250	N_2	3.5
PP-PGMA·2	220	340	250	N_2	7.3
PP-PGMA·2	220	330	250	air	5.5

Rotating speed of the screw shaft: 20 rpm.

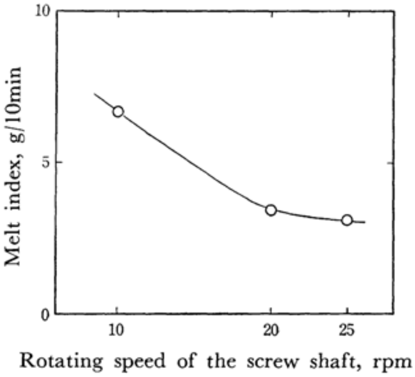

Fig. 2. The effect of the rotating speed of the screw shaft on the thermal degradation of PP-PGMA·2.
Reaction temperature; T_1: 220°C, T_2: 330°C and T_3: 250°C

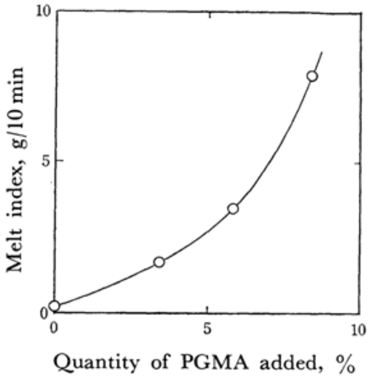

Fig. 3. The effect of the quantity of PGMA added on the thermal degradation of PP.
Reaction temperature; T_1: 220°C, T_2: 330°C, T_3: 250°C
Rotating speed of the screw shaft: 20 rpm

Although the mixing effect of the screw shaft and the trace of oxygen due to the imperfect air-tightness of the extruder are questionable, strictly speaking, the degradation in this study may be understood to be thermal. As is shown in Fig. 3, the degree of degradation increased with the increase in the PGMA content. This was reasonable, since the increase in the PGMA content means an increase in the accelerator content. It was established that the addition of 2—5% of PGMA (by weight) was sufficient to modify, by extrusion, the very high molecular weight of polypropylene to a practically useful molecular weight. The results shown in Figs. 2 and 3 show a tendency producing results very similar to those shown in a preceding paper,[9] in which PFPC was used as an accelerator. However, the direct comparison of both results was impossible, because the polypropylene samples used were different. The degraded polymer in this study was transparent. On the other hand, when such vinyl polymers as polystyrene, the 2-methyl-5-vinylpyridine-styrene copolymer, and the acrylonitrile-styrene copolymer were used as accelerators, the thermally-degraded polymer was opaque.

PGMA was degraded to the monomer by the zipper-scission mechanism, and the active radical thus generated was effective in accelerating the degradation of polypropylene by the random-scission mechanism. In order to investigate the behavior of PGMA, the PGMA content was determined after the degradation and acetone-extraction, using the carbonyl-group content

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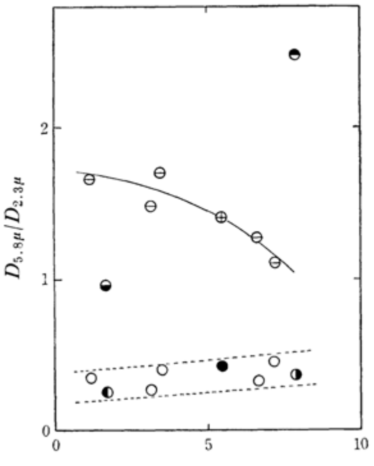
[11] R. J. Ceresa, "Block and Graft Copolymers," Butterworths, London (1962), p. 69.



Melt index, g/10 min

Fig. 4. The relation between the melt index and the carbonyl-group content.

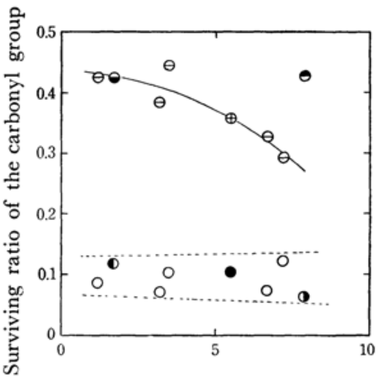
◓ PP-PGMA·1 }
⊖ PP-PGMA·2 } Extruded polymer
◒ PP-PGMA·3 }
◑ PP-PGMA·1 }
○ PP-PGMA·2 } Powdery polymer after acetone-extraction
◐ PP-PGMA·3 }
● PP-PGMA·2, etruded under air, powdered, and extracted with acetone
⊕ PP-PGMA·2, extruded under air

($D_{5.8\mu}/D_{2.3\mu}$) as a measure of the PGMA content. Figure 4 shows that the carbonyl-group content decreased with the increase in the degree of degradation. The smell of the monomer could be clearly perceived during the extrusion, and so PGMA was lost by the volatilization. Furthermore, the carbonyl-group content in the powdered polymer was lowered considerably, and the results obtained were poor in reproducibility. It was presumed that the molecular weight of PGMA must have become smaller by the degradation. Namely, the PGMA in the degraded polymer must have become relatively small fragments and must have become soluble or extractable in a mixed solution of methanol and *p*-xylene. However, there are yet no conclusive evidence. The surviving ratios of the carbonyl group were defined as follows:

$$SR_D=\frac{\text{the carbonyl-group content in the extruded polymer}}{\text{the carbonyl-group content in the polymer sample before degradation}}$$

$$SR_A=\frac{\text{the carbonyl-group content in the powdery polymer after acetone-extraction}}{\text{the carbonyl-group content in the polymer sample before degradation}}$$

Figure 5 shows that about 55—70% of PGMA was lost in the extruding process by volatilization, and that about 10% of PGMA survived the degradation and acetone-extraction.



Melt index, g/10 min

Fig. 5. The surviving ratio of the carbonyl group as a function of the melt index.
The symbols are the same as those shown in Fig. 4.

The reasons why PGMA was detected in the powdery polymer after acetone-extraction were considered to be as follows:

(1) The formation of a graft or block copolymer by the interaction among the polypropylene molecule, the polypropylene radical, the PGMA radical, and the GMA liberated in the thermal degradation, and/or (2) The crosslinking of PGMA by the thermal treatment.

Probably, both processes operate. (1) was supported by the fact that a graft or block copolymer was prepared in the thermal degradation of polypropylene accelerated by such vinyl polymers as polystyrene and polymethyl methacrylate,[1] so a similar situation could easily be considered to hold in this study. (2) was also supported by the fact that when the extruded polymer was dissolved in hot *p*-xylene, some fine, insoluble particles were observed in the hot *p*-xylene solution, although both polypropylene and PGMA are soluble in hot *p*-xylene and give a transparent polymer solution. The mechanism of the insolubilization of PGMA was presumed to be as follows: Gritter *et al.*[12] and Oku *et al.*[13] have shown that the epoxy ring can be opened and the epoxy compounds transformed to the carbonyl compounds containing the hydroxyl group by the radical reaction, when such radical sources as *t*-butyl hydroperoxide or benzoyl peroxide are used. If such a hydroxyl group is once generated, the reaction between the hydroxyl group and the epoxy ring should naturally follow, being promoted by the elevated temperature of the thermal degradation. In fact, PGMA became insoluble in acetone when heated in a sealed glass ampule at 180—190°C for about 3 hr, either in air or in a vacuum (PGMA

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[12] R. J. Gritter and T. J. Wallace, *J. Org. Chem.*, **26**, 282 (1961).

[13] A. Oku, M. Okano and R. Oda, This Bulletin, **37**, 570 (1964).

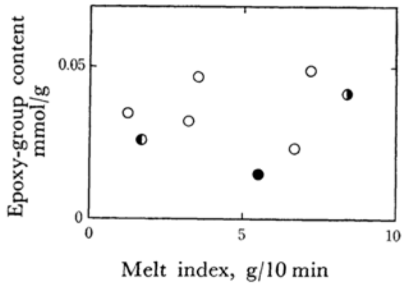

Fig. 6. The relation between the melt index and the epoxy-group content in the powdery polymer after acetone-extraction.

◑ PP-PGMA·1
○ PP-PGMA·2
◐ PP-PGMA·3
● PP-PGMA·2, extruded under air

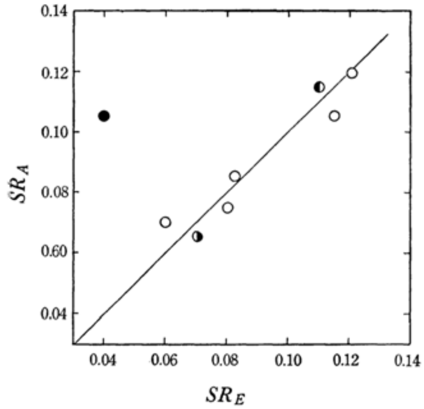

Fig. 7. The relation between SR_E and SR_A. The symbols are the same as those shown in Fig. 6.

became yellowish in the former case). Otsu *et al.*[8] have been reported that PGMA became insoluble on being allowed to stand at room temperature for a month. These facts suggest that the formation of the crosslinkage of PGMA is a reasonable assumption in this study. From these considerations, both (1) and (2) may be said to be responsible for the insolubilization of PGMA. However, the degree of the participation of each process is not known at present.

It was important to know how many epoxy groups could survive the thermal degradation. However, the epoxy-group content of the extruded polymer could not be determined because of the lack of reproducibility. This may be atrributed to the experimental procedure, in which the extruded polymer was once powdered for the determination of the epoxy-group content; the same situation has been described before in connection with the determination of the carbonyl-group content. Furthermore, no definite relationship could be found between the degree of degradation of the polymer and the epoxy-group content of the powdery polymer after acetone-extraction. This result suggests that other factors, such as the reaction temperature, the rotating speed of the screw shaft, and the PGMA content, complicate the matter. The epoxy-group contents were 0.02—0.05 mmol/g and the surviving ratio (SR_E) was 0.06—0.12, which was unexpectedly low.

$$SR_E = \frac{\text{the epoxy-group content in the powdery polymer after acetone-extraction}}{\text{the epoxy-group content in the polymer sample before degradation}}$$

Dyeability. The thin film (0.15 mm thick) was molded from the extruded polymer and was dyed with such dispersion dyes as Estrol Fast Violet B, Estrol Orange 5R, and Celliton Blue Extra by the ordinary method. The dyeability of the film was considerably improved, but it was still considered to be insufficient for practical purposes. The dyed film was not decolored by acetone-extraction. This fact was evidence showing the utility of the glycidyl group surviving the thermal degradation.

Conclusion

Polyglycidyl methacrylate was effective in accelerating the thermal degradation of polypropylene. It was made clear that polyglycidyl methacrylate was degraded thermally by the zipper-scission mechanism and that the active radical thus generated behaved substantially as an accelerator for the thermal degradation of polypropylene by the random-scission mechanism. In the degradative process, about 55—70% of the polyglycidyl methacrylate added was lost by volatilization. The surviving ratios of the epoxy group throughout the thermal degradation and acetone-extraction was 0.06—0.12.

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