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Studies on Reactions of Polypropyrene. VI. The Thermal Degradation of Polypropylene Accelerated by the Fine Powdery Polymer with Closslinkage

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The thermal degradation of polypropylene was investigated in the presence of the fine powdery polymer with crosslinkage by the use of an extruder under a nitrogen atmosphere. The fine powdery polymer was thus found to be effective as an accelerator for the thermal degradation of polypropylene. The fine powdery polymer used was prepared by the emulsion polymerization of some vinyl monomers and divinyl benzene or by the polymerization of glycidyl methacrylate and divinyl benzene in *n*-heptane. The fine powdery polymer consisting of glycidyl methacrylate and divinyl benzene was preferable to that with no reactive functional group, because of the reactivity of the glycidyl group. The polypropylene was modified and made dyeable by the thermal degradation accelerated by the fine powdery polymer.

It is well known that there are a few drawbacks to the practical uses of polypropylene; such as the poor flow properties resulting from its very high molecular weight, and the poor dyeability resulting from its nonpolarity and its high crystallinity. Therefore, many processes have been proposed to overcome these drawbacks.[1-10] In the thermal degradative process accelerated by such vinyl polymers as polystyrene and polymethyl methacrylate, graft or block copolymers were formed, and the poor dyeability of polypropylene could be modified.[11] However, some of the vinyl polymers used in this process were extractable by acetone, and it was considered to be undesirable for practical use.

In this paper, the fine powdery polymer with crosslinkage (FPC) was used as an accelerator for the thermal degradation of polypropylene. The thermal degradation was carried out by the use of an extruder, so this simple process should be practically useful.

Experimental

Materials.—The polypropylene (PP) powder used was under 30 mesh and contained no stabilizer. The properties of the polypropylene samples were as follows:

PP(A) melt index (at 230°C, load: 2.16 kg./cm.^{2}): 0.25 g./10 min., specific gravity: 0.912, and grain size: under 30 mesh.

PP(B) melt index (at 230°C, load: 2.16 kg./cm.^{2}): less than 0.01 g./10 min., specific gravity: 0.913, and grain size: under 30 mesh.

All the reagents, such as vinyl monomers, divinyl benzene (DVB), and solvents, were of chemical grade. The DVB content in commercial DVB was 50% by weight.

The Preparation of the Fine Powdery Polymer by the Emulsion Polymerization (EPC·E).—The vinyl monomers and DVB were polymerized by stirring at 80°C for 2—3 hr. under a nitrogen atomsphere. Then, the polymer was salted out, washed with water,

TABLE I. THE EXAMPLES OE THE PREPARATION OF FPC·E

Sample	Vinyl monomer, g.			DVB g.	Yield %
	Styrene	2-Methyl 5-vinyl pyridine	Methyl acrylate		
FPC·E-1	24	—	—	1	84
FPC·E-2	—	12	12	1	80
FPC·E-3	—	24	—	1	80
FPC·E-4	—	—	24	1	82

The quantities of water and Monogen-W were 300 cc. and 2 g. respectively.

Monogen-W was the emulsifier from Daiichi Kogyo Seiyaku Co., Ltd.

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11) Y. Mizutani, S. Matsuoka and K. Yamamoto, This Bulletin, **38**, 2054 (1965).

and dried at 70°C under a vacuum. An example of the polymerization is shown in Table I. Potassium persulfate was used as an initiator of the polymerization.

The Preparation of the Fine Powdery Polymer by the Polymerization of Glycidyl Methacrylate and DVB in *n*-Heptane (FPC·H).—Glycidyl methacrylate (GMA) and DVB were polymerized in *n*-heptane by stirring at 70°C for 5—6 hr. under a nitrogen atmosphere. Benzoyl peroxide was used as an initiator of the polymerization. The polymer prepared was filtered, washed with petroleum ether and dried under a vacuum. An example of the polymerization is shown in Table II.

Table II. The examples of the preparation of FPC·H

Sample	GMA g.	DVB g.	DVB*/(GMA+DVB)	*n*-Heptane cc.	BPO** g.	Yield %
FPC·H-1	190	10	0.025	2800	10	83
FPC·H-2	180	20	0.050	2800	10	82
FPC·H-3	170	30	0.075	2800	10	84

* Pure DVB

** Benzoyl peroxide

Blending.—FPC was dispersed in a solvent beforehand by the use of a mixer; then the polypropylene powder was added to the mixer, and the slurry was well mixed. The polymers were then filtered out and dried under a vacuum. The solvents used were methanol for FPC·E and *n*-heptane for FPC·H.

The Thermal Degradation.—The thermal degradation was carried out by the use of the extruder, which was a modification¹¹⁾ of Type MK-1 from Modern Machinery Co., Ltd. The heating zone of the extruder was divided into three parts: T_1, T_2, and T_3, which show the temperatures of the 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.[11)]

The Determination of the Glycidyl Group Content.—The polymer extruded was powdered by reprecipitation; the polymer was then dissolved in hot *p*-xylene, and the hot solution was cooled slowly. Then the slurry obtained was stirred into methanol in a mixer. The powdered polymer was filtered, washed with methanol, and dried under a vacuum. The content of the glycidyl group was determined by the method used by Iwakura et al.[4)] The powdered polymer (2 g.) was immersed in a solution of 25 ml. of dioxane and 20 ml. of a 0.1 N dioxane solution of hydrochloric acid. The mixture was then allowed to stand overnight, and the excess hydrochloric acid was titrated with a 0.1 N aqueous solution of sodium hydroxide, using phenolphthalein as an indicator.

Results and Discussion

The Thermal Degradation Accelerated by FPC·E.—It is beyond question that the change in intrinsic viscosity is the most preferable measure of the degree of the degradation, but the melt index was used in this study because FPC used was insoluble in any solvent.

Table III. The results of the thermal degradation of PP(A) accelerated by EPC·E

Sample	Reaction temp., °C			Melt index g./10 min.
	T_1	T_2	T_3	
PP(A)	220	300	270	0.6
PP(A)	220	320	290	0.8
PP(A)-FPC·E-1	220	320	290	4.2
PP(A)-FPC·E-2	220	300	270	3.2
PP(A)-FPC·E-3	220	320	290	3.2
PP(A)-FPC·E-4	220	320	290	3.4

The quantity of FPC added was 5% by weight

The rotating speed of the screw shaft was 20 r.p.m.

Table III shows the results of the thermal degradation. It was established that FPC·E was effective as an accelerator for the thermal degradation of polypropylene. No vinyl polymer was extracted by acetone from the extruded polymer. This was considered to be reasonable, because FPC·E was crosslinked by DVB. However, although FPC·E was effective as an accelerator, FPC·E is practically inferior to FPC·H for the following reasons:

1) FPC·E is contaminated by the emulsifier, so the surface of FPC·E is hydrophilic and is therefore poor in affinity with polypropylene.

2) FPC·E is separated by salting-out from the emulsion and is strongly agglomerated; therefore, it is inferior to FPC·H because the blend of FPC·E to polypropylene is not easier than that of FPC·H.

3) FPC·E is prepared in water, so monomers with a reactive functional group can not be polymerized often.

The Thermal Degradation Accelerated by FPC·H.—In Table IV, it is shown that FPC·H was effective as an accelerator for the thermal degradation of polypropylene and that the degree of degradation increased with the elevating of the reaction temperature.

Table IV. The temperature effect on the thermal degradation of PP(B) accelerated by FPC·H-2

The quantity of FPC·H-2 added, %	Reaction temp., °C			Melt index g./10 min.
	T_1	T_2	T_3	
0	220	325	280	0.01
6.5	220	280	280	0.12
6.5	220	310	280	0.6
6.5	220	325	280	2.6

The rotating speed of the screw shaft was 20 r.p.m.

Figure 1 shows the effect of the rotating speed of the screw shaft, which was related to the retention time of the polymer in the extruder. With the increase in the rotating speed, namely, with the decrease in the retention time of the polymer, the degree of degradation decreased. The shearing

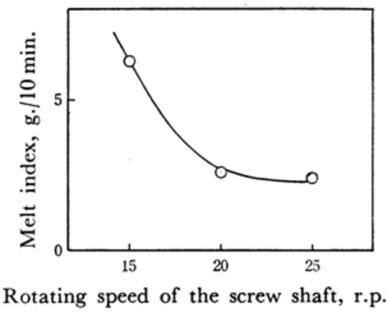

Fig. 1. The effect of the rotating speed of the screw shaft of the extruder on the thermal degradation of PP(B).
The content of FPC·H-2 added: 6.5%
Reaction temperature: T_1=230°C, T_2=325°C, and T_3=280°C
Retention time: about 5 min. for 15 r.p.m.
about 4 min. for 20 r.p.m.
and about 3 min. for 25 r.p.m.

effect of the screw shaft is negligible, because the shearing effect has a negative temperature coefficient;[12] 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: 240°C, T_3: 200°C, and the rotating speed of the screw shaft: 30 r. p. m.[11] The mixing effect of the screw shaft and the trace of oxygen due to the imperfect air-tightness of the extruder are questionable; however, they can not be explained in detail now.

Fig. 2 shows that with the increase in the FPC·H content, the melt index increased.

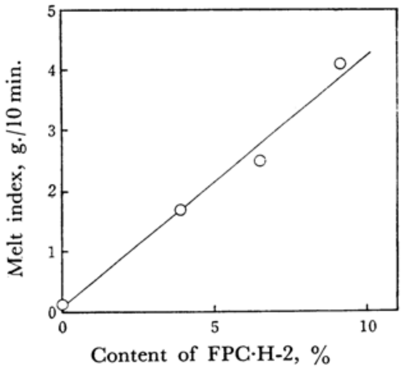

Fig. 2. The effect of the content of FPC·H-2 on the thermal degradation of PP(B).
Reaction temperature: T_1=220°C, T_2=325°C, and T_3=280°C
The rotating speed of the screw shaft: 20 r.p.m.

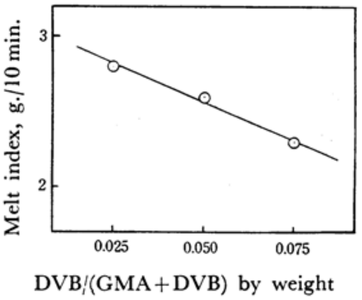

Fig. 3. The effect of the DVB content of EPC·H on the thermal degradation of PP(B).
The content of FPC·H: 6.5%
Reaction temperature: T_1=220°C, T_2=325°C, and T_3=280°C
The rotating speed of the screw shaft: 20 r.p.m.

Figure 3 shows the effect of the DVB content of FPC·H. With the increase in the DVB content, the melt index decreased; namely, the accelerating effect of FPC·H decreased. This can be explained in term of the fact that the rate of the degradation of polystyrene crosslinked by DVB decreases with the increase in the DVB content.[13]

As has been described above, FPC·H containing the glycidyl group was effective in accelerating the thermal degradation of polypropylene. Furthermore, the glycidyl group must survive after the degradation of polypropylene in order to hold its reactivity. Therefore, the change in the content of the glycidyl group was determined by measuring the contents before and after extruding. Table V shows that the greater part of the glycidyl group survived after extruding. This could be explained in terms of the fact that the glycidyl group generally reacts under ionic conditions and is not changed by the radical polymerization for the preparation of FPC·H or by the thermal degradation of polypropylene, which is also a radical reaction.[14]

Table V. The glycidyl group contents before and after extruding

Sample	Reaction temp. °C			Glycidyl group content mmol./g	Ratio of glycidyl group content S-2/S-1 or S-3/S-1
	T_1	T_2	T_3		
S-1	—	—	—	0.33	—
S-2	220	240	220	0.31	0.91
S-3	220	325	280	0.25	0.76

The rotating speed of the screw shaft was 20-r.p.m.
PP(B) and FPC·H-2 were used.

Because the smell of glycidyl methacrylate was perceived during the extrusion, the degradation of FPC·H to the monomer seems to have occurred, although the quantity of the monomer liberated was probably not much. The active radical generated in the degradation of FPC to the monomer

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

[13] H. H. G. Jellinek, "Degradation of Vinyl Polymers," Academic Press Inc., Publishers, New York (1955), p. 123.

[14] F. Hamada, *Chem. High Polymers Japan* (*Kobunshi Kagaku*), **19**, 402 (1962).

may be effective in accelerating the thermal degradation of polypropylene, but the accelerating effect of FPC should be inferior to that of a linear vinyl polymer, as FPC was crosslinked by DVB, and the degradation rate of FPC should be slower than that of a linear vinyl polymer. Furthermore, interactions among the vinyl monomer liberated, FPC radicals, polypropylene radicals, and polypropylene molecules may be presumed to have occurred. This presumption is supported by the fact that, when a linear vinyl polymer was used in place of FPC, graft or block copolymer were detected.[11)]

Dyeability.—The utility of a reactive polymer is well known.[15-17)] The modification of polypropylene by glycidyl methacrylate has been reported already: the graft copolymer has been prepared[4)] and the glycidyl methacrylate copolymer has been blended to polypropylene.[7)] When the fiber of the modified polypropylene was dyed by a dye which has a functional group reactive with the glycidyl group, the dye could be perfectly fixed in the fiber, as determined by extraction with acetone.[7)] The thin film (0.15 mm. in thickness) 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.[7)] The film containg FPC·E was well dyed, but the dyed film was decolored by the extraction with acetone. On the other hand, the film containing the glycidyl group (FPC·H) was well dyed and the dyed film was not decolored with acetone. This fact was an evidence showing the utility of FPC·H as a reactive polymer. Also, it was elucidated by microscopic observation that FPC dispersed in polypropylene was well dyed, while polypropylene itself was not dyed.

Conclusion

The fine powdery polymer with crosslinkage was effective as an accelerator in the thermal degradation of polypropylene and also as a mordant in the dyeing of polypropylene. Among several polymeric systems, the fine powder of the glycidyl methacrylate - divinyl benzene polymer was preferable because of the reactivity of the glycidyl group.

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