

Preparation of Fine Powdery Copolymer with Crosslinkage and Monoalkyl Maleate Unit

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Synopsis

In order to prepare fine powdery and crosslinked copolymer as a foaming agent and a modifier for polypropylene, the following processes were investigated: (1) polymerization of monoalkyl maleate-styrene-divinylbenzene; (2) polymerization of monoalkyl maleate-maleic anhydride-styrene-divinylbenzene; (3) polymerization of maleic anhydride-styrene-divinylbenzene and esterification of the copolymer with methanol, and (4) polymerization of maleic anhydride-styrene-divinylbenzene in the presence of methanol. The thermal treatment of copolymer thus obtained and the foaming ability for polypropylene were then investigated.

INTRODUCTION

It is well known that maleic anhydride (MAN) and/or monoalkyl maleate (MAM) are copolymerizable with styrene (St),¹⁻⁴ that the MAN unit of the copolymer of St-MAN is easily mono-esterified with aliphatic alcohols,⁵⁻⁷ and that the MAM unit is convertible to the MAN unit by thermal treatment with liberation of the alcohol.⁵

On the other hand, fine powdery copolymer is prepared by polymerizing glycidyl methacrylate-divinylbenzene (DVB) or St-MAN-DVB in an aliphatic hydrocarbon,⁸ and blending the powdery copolymer into polypropylene (PP) modifies the luster and the waxy touch of PP.⁹

Accordingly, provided that the fine powdery copolymer with the MAM unit (FPC) is blended into PP and the composite is thermally treated to liberate the aliphatic alcohol. FPC could presumably be useful either as a foaming agent or as a modifier for PP as described above. The preparation of FPC and its thermal reaction and foaming ability are investigated in this paper.

EXPERIMENTAL

Materials

All the reagents, the alcohols, St, DVB, MAN, benzene, and benzoyl peroxide (BPO), were of commercial grade. St and DVB were dried with calcium chloride after excluding the stabilizer and distilled under a reduced

nitrogen atmosphere just before use. Benzene was treated with molecular sieve 3 Å after distillation. Pure DVB content in the commercial DVB was 57%, and the other components were mainly ethylstyrenes. The commercial DVB is shown as DVB for brevity in this paper. Monomethyl maleate (MMM), monoethyl maleate (MEM), mono-*n*-propyl maleate (MPM), and mono-*n*-butyl maleate (MBM) were prepared by the reaction of MAn with the alcohols in a glass autoclave at 100–130°C for 4 hr under nitrogen atmosphere. The alcohol equivalent to the quantity of MAn was used, and thus MAM was prepared quantitatively.¹⁰

Polymerization of MAn–St–DVB

The monomers were polymerized in benzene at 75°C under nitrogen atmosphere with stirring. BPO was used as initiator. After a definite time, a small amount of benzene solution of *p*-benzoquinone was added and the product was filtered, washed with benzene, and dried at 60°C under vacuum. On the other hand, samples A, B, and C were prepared under the conditions shown in Table I.

Esterification of MAn–St–DVB Polymer and Determination of Ester Value

The polymer (2 g, samples A, B, and C shown in Table I) were esterified with methanol (50 ml) at 50°C in a glass ampoule. The product was then filtered, washed with benzene several times to remove methanol, and dried at 40°C under vacuum. The ester value was determined from the ratio of the optical densities ($D_{1730\text{ cm}^{-1}}/D_{1700\text{ cm}^{-1}}$), measured by the aid of a grating infrared spectrophotometer, type EPI-G3 from Hitachi Ltd.

Polymerization of MAM–St–DVB and MAM–MAn–St–DVB

The monomers were polymerized under nitrogen atmosphere in a glass ampoule. The molar ratios of MAM:St:DVB and MAM:MAn:St:DVB were 5:4:1 and 2.5:2.5:4:1, respectively. The treatment after polymerization was the same as that shown in the polymerization of MAn–St–DVB.

Polymerization of MAn–St–DVB in the Presence of Methanol

The monomers were polymerized at 100°C for 4 hr under nitrogen atmosphere in benzene containing a definite quantity of methanol, using BPO as initiator. After a definite time, a small amount of benzene solution of *p*-benzoquinone was added, and the product was filtered, washed with benzene, and dried at 60°C under vacuum.

Thermal Treatment of FPC and Preparation of PP Foam

FPC was treated at 170–200°C for 6 min under vacuum, and the change of the ester value was measured. Powdery PP (100 parts, specific gravity at 23°C, 0.91; melt index at 230°C, 5.1; determined by applying a load

TABLE I
Polymerization Conditions

Sample	Total weight, g	Monomer molar ratio				Benzene, ml	BPO, g	Temp., °C	Time, hr.
		MAM	MAn	St	DVB				
A	100	—	5.0	4.5	0.5	1000	2	80	4
B	100	—	5.0	4.0	1.0	1000	2	80	4
C	100	—	5.0	3.5	1.5	1000	2	80	4
D	40	2.5	2.5	4.0	1.0	200 (+2 ml CH ₃ OH)	0.8	100	4

of 2.16 kg/cm²), FPC (2 parts), dilauryl thiodipropionate (0.2 part), and 2,6-di-*t*-butyl-*p*-cresol (0.2 part) were blended by the aid of a V-blender. The mixture was then extruded at 165–175°C to prepare a midair pipe. The extruded polymer was drawn with a definite speed (160 m/min) and rapidly cooled by water. The extruder was devised to make it possible to introduce air with a definite pressure (20–30 mm Hg larger than that of the molten polymer) into the center of the extruded polymer. The heating zone of the extruder was divided into three parts: T_1 , T_2 , and T_3 , which represent the temperatures of the parts near the sample outlet, the middle part, and the part near the sample inlet, respectively.

RESULTS AND DISCUSSION

All the polymerizations in this study were heterogeneous: the resulting polymer precipitated from the medium in which the monomers were soluble. The polymer obtained was fine powdery and its size was about 0.1 μ or less. Some heterogeneous polymerizations so far are known,^{11,12} but polymerization containing a crosslinking agent is rarely known and its detail is still obscure. The polymerization in this paper was too complicated to investigate its detailed kinetics.

Polymerization of MAN–St–DVB and Esterification of the Polymer

Figure 1 shows a time–conversion curve. Polymerization rapidly proceeded up to the maximum value in about 2 hr and then leveled off. The abrupt increase in the polymerization rate at the earlier stage shows an auto-accelerating effect,^{13,14} which is characteristic of heterogeneous polymerization. Figure 2 shows the effect of BPO on conversion. The conversion did not change with use of BPO between 0.5 and 2.0 g/l, and it was confirmed that the use of the BPO concentration larger than 0.5 g/l was sufficient to reach maximum conversion. This result is probably due to a decrease in the efficiency of the radicals from BPO, since no BPO was detected in the solution (with the aid of potassium iodide) after polymerization.¹⁵ Figure 3 shows the effect of the weight ratio of MAN/St on

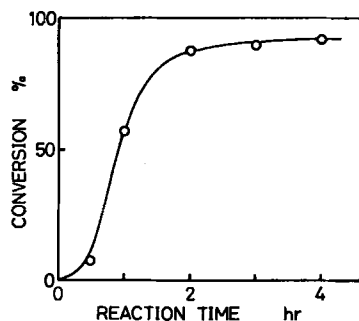


Fig. 1. Time–conversion curve of MAN–St–DVB system at 75°C: monomers/benzene, 100g/l.; BPO/benzene, 0.5g/l.; MAN:St:DVB = 4.5:4.5:1 by weight.

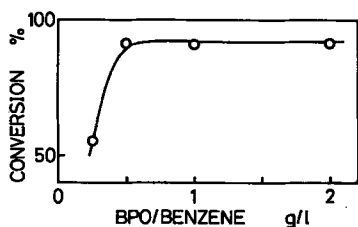


Fig. 2. Effect of BPO quantity on conversion of MAn-St-DVB system at 75°C. Conditions are shown in Fig. 1; reaction time, 4 hr.

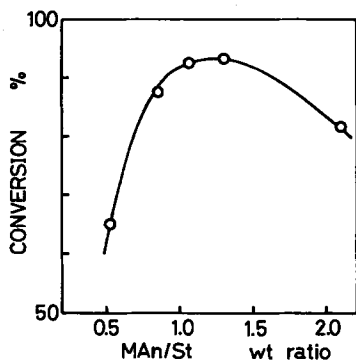


Fig. 3. Effect of ratio of MAn/St on conversion at 75°C: monomers/benzene, 100 g/l.; BPO/benzene, 2g/l.; DVB/(MAn + St + DVB) = 0.1 by weight; reaction time, 4 hr.

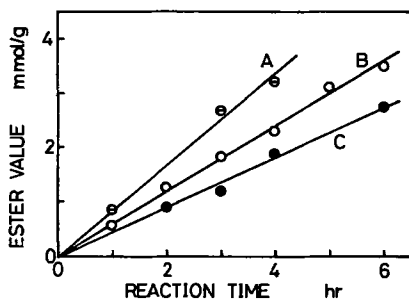


Fig. 4. Relation between the ester value and reaction time: (A), (B), and (C) show samples A, B, and C, respectively, seen in Table I.

the conversion of the monomers, polymerized at 75°C for 4 hr under nitrogen atmosphere. Evidently, the highest conversion was obtained at a weight ratio MAn/St = 1.3, and this value is equivalent to the molar ratio MAn/(St+DVB) \approx 1. The result obtained thus should be due to the good alternate copolymerizability of MAn with St or DVB.

The esterification of the MAn-St-DVB polymer was investigated using samples A, B, and C shown in Table I. Figure 4 shows that the ester value linearly increased with reaction time and that the increase in the DVB content slowed down the esterification. Since the methanol concen-

tration was constant and the reaction of methanol with the MAn unit itself should proceed at the same rate, the diffusion of methanol into the polymer matrix should be rate determining. The more the copolymer is crosslinked, the more difficult the diffusion of methanol through the polymer matrix should be. The method described above was simple but had the drawback that FPC thus obtained is apt to aggregate after the reaction with methanol and washing with petroleum ether or benzene.

Polymerization of MAM-MAn-St-DVB and MAM-St-DVB

The time-conversion curves of the systems were similar to those of the MAn-St-DVB system, but the polymerizations proceeded more slowly than that of the MAn-St-DVB system and hardly at all after 4 hr, as shown in Figure 5. In order to use FPC as a foaming agent, the alcohol liberated from FPC should be gaseous at the molding temperature of PP. MAM was thus prepared by the use of alcohols having lower boiling points, such as methanol, ethanol, *n*-propanol, and *n*-butanol, and FPC was prepared by the polymerization of MAM-MAn-St-DVB and MAM-St-DVB. The conversions shown in Figure 6 were rather less from the practical point of view, and the conversions of the MAM-St-DVB system were less than those of the MAM-MAn-St-DVB system.

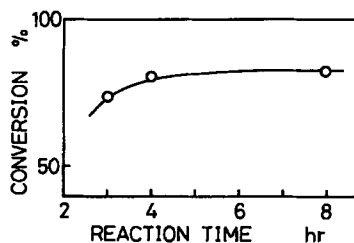


Fig. 5. Time-conversion curve of MMM-MAn-St-DVB system at 75°C: monomers/benzene, 100 g/l.; BPO/benzene, 2 g/l.; MMM:MAn:St:DVB = 2.5:2.5:4:1 (molar ratio).

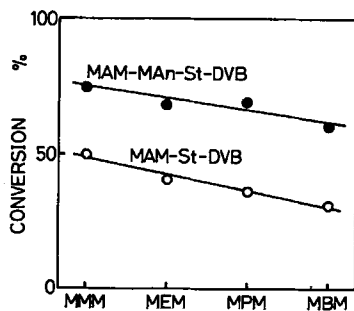


Fig. 6. Conversions of systems containing MAM at 75°C: monomers/benzene, 100 g/l.; BPO/benzene, 2 g/l.; MAM:MAn:St:DVB = 2.5:2.5:4:1 (molar ratio); MAM:St:DVB = 5:4:1 (molar ratio); reaction time, 4 hr.

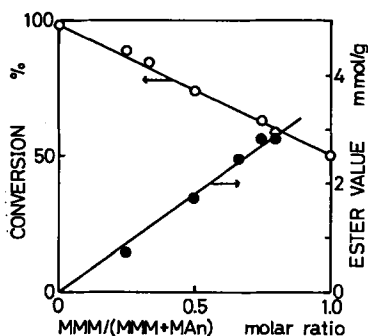


Fig. 7. Effect of $\text{MMM}/(\text{MMM} + \text{MAn})$ ratio on conversion and ester value of resultant polymer at 75°C : monomers/benzene, 100 g/l.; BPO/benzene, 2 g/l.; $(\text{MMM} + \text{MAn})\text{:St:DVB} = 5\text{:4:1}$ (molar ratio); reaction time, 4 hr.

Furthermore, the relations among the molar ratio of $\text{MMM}/(\text{MMM} + \text{MAn})$, the conversion, and the ester value were investigated, as is shown in Figure 7. With increase in the molar ratio, conversion decreased and the ester value of FPC increased. Figures 6 and 7 suggested that MAn was even more copolymerizable than MAM. Since the conversion of the system containing MMM was highest and methanol vapor should be most effective in making foam due to its least compatibility with PP, the use of the MMM unit is evidently most preferable. However, the conversions of the systems containing a relatively high MMM content were not sufficient from a practical point of view.

Polymerization of MAn-St-DVB in the Presence of Methanol

In order to carry out simultaneously both the polymerization of the monomers and the esterification of the resultant polymer, polymerization was investigated in the presence of methanol. Figure 8 shows that the ester value of the resulting FPC increased with increase in the amount of methanol and the conversions ($>95\%$) were higher than those shown in Figures 6 and 7. This result shows that the polymerization proceeded

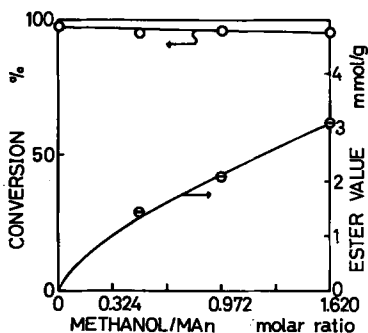


Fig. 8. Polymerization of MAn-St-DVB in the presence of methanol at 100°C : monomers/benzene, 200 g/l.; BPO/benzene, 4 g/l.; $\text{MAn:St:DVB} = 5\text{:4:1}$ (molar ratio); reaction time, 4 hr.

more rapid than the esterification of MAn. The resultant FPC was easily dispersible in PP. Accordingly, this process was preferable in comparison with the other procedures because of its simplicity, though the use of an autoclave was necessary.

Thermal Treatment of FPC

The methanol-liberating ability of the MMM unit introduced into FPC by copolymerizing MMM was compared with that by esterifying the MAn unit with methanol. Figure 9 shows the result of two different samples with about the same ester value, samples D and E. Sample E was prepared by esterifying sample B at 50°C for 4 hr with methanol and sample D shown in Table I. Both samples easily liberated methanol at a temperature higher than about 155°C, presumed by extrapolating the experimental plots. The reason why sample E more easily liberated methanol than sample D was presumably due to the difference in their configurations.

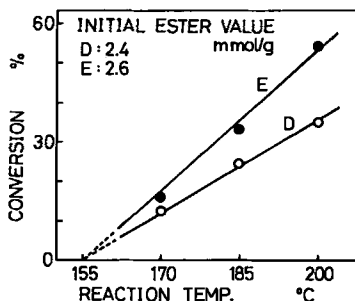


Fig. 9. Relation between reaction temperature and conversion of the MMM unit to the MAn unit.

Sample E was prepared by mono-esterification of the MAn unit of the copolymer prepared by the polymerization of MAn-St-DVB. Thus, the relative configuration of the carboxyl group and the methyl ester group in the MMM unit would be more advantageous to convert to the MAn unit by liberating methanol by heat treatment. On the other hand, sample D was prepared by the polymerization of MMM-MAn-St-DVB; the relative configuration as described above would not be kept because of the free rotation of the carbon-carbon bond in the MMM unit at the propagating step of the polymerization, though the details are not yet clear. Since FPC easily liberated methanol by heat treatment, it was concluded that FPC should be useful as a foaming agent for PP.

Preparation of the Mid-Air Pipe of the PP Form

The mid-air pipe of PP was prepared using FPC prepared by the polymerization of MMM-MAn-St-DVB and by the esterification of the copolymer of MAn-St-DVB with methanol. The appropriate quantity of FPC to be added in PP was preliminarily confirmed to be 2-3%. As is shown in Table II, the apparent specific gravity of the pipe and the micro-

TABLE II
Preparation of Mid-Air Pipe

Sample	Ester value, mmole/g	Quantity added, %	Extrusion temp., °C			Pipe prepared	
			T_1	T_2	T_3	Apparent specific gravity at room temp.	Outer diameter, mm
FPC-1 ^a	0.58	2.0	165	170	175	0.86	1.5
FPC-2 ^a	1.28	2.0	165	170	175	0.84	1.6
FPC-3 ^a	1.82	2.0	165	170	175	0.78	1.6
FPC-4 ^a	2.30	2.0	165	170	175	0.73	1.8
FPC-5 ^b	1.72	3.0	160	170	180	0.71	1.3
FPC-6 ^c	0.70	3.0	170	180	190	0.77	—
FPC-7 ^d	2.11	2.5	160	170	180	0.68	1.7

^a Prepared by esterifying sample B with methanol at 50°C.

^b Prepared by polymerizing the monomers (MMM:MAN:St:DVB = 2.5:2.5:4:1).

^c Prepared by polymerizing the monomers (MMM:MAN:St:DVB = 1.25:3.75:4:1).

^d Prepared by polymerizing the monomers by the method shown in Fig. 8.

scopic observation showed that all FPC was effective as a foaming agent and that the generated foams were rather coarse and not uniform. The inherent metallic luster of PP in sunlight and the waxy touch were considerably modified. Pipes thus prepared were useful as a synthetic substitute for rush, the raw material for Japanese "Tatami-facing." In order to make FPC more useful as a foaming agent, optimum conditions should be studied in the future in relation to the molding process.

CONCLUSIONS

Some procedures were studied to prepare fine powdery copolymer with crosslinkage and a monoalkyl maleate unit. The results were as follows:

1. The polymerization of maleic anhydride-styrene-divinylbenzene and the esterification of the copolymer: This method was simple but had the drawback that FPC obtained was apt to aggregate.

2. The polymerization of monoalkyl maleate-maleic anhydride-styrene-divinylbenzene or monoalkyl maleate-styrene-divinylbenzene: The conversions in these methods were not enough from a practical point of view, and the polymerizations were slower than those of the other two.

3. The polymerization of maleic anhydride-styrene-divinylbenzene in the presence of methanol: This method was preferable because of its simplicity and absence of drawbacks. The copolymer was available as a foaming agent, and a pipe of the foamed polypropylene was produced by applying the reaction of the copolymer to liberate methanol by heat treatment.

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