Studies on Polymer Blend of Nylon 6 and Polypropylene or Nylon 6 and Polystyrene Using the Reaction of Polymer

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Synopsis

In the presence of maleic anhydride-grafted polypropylene, marked dispersibility of the polymer blend of isotactic polypropylene and nylon 6 was obtained. This appeared to be caused by the formation of a certain graft polymer between maleic anhydride in polypropylene and terminal amino groups of nylon 6. The same phenomenon was observed when polystyrene and nylon 6 were blended with styrene–methacrylic acid copolymer as the interpolymer. The existence of such a graft polymer was confirmed by solvent extraction, estimation of the amino group of nylon 6, and identification by differential scanning calorimetry. The physical properties, especially mechanical properties of nylon 6–polypropylene polymer blends, were remarkably improved with increase of maleic anhydride added to the polymer blend. On the other hand, the physical properties those of nylon 6–polystyrene polymer blends were very little improved even in the presence of good dispersibility.

INTRODUCTION

It is very difficult to obtain good dispersibility in polymer blends which dissolve within each other with difficulty, such as the combination of nylon 6 (N6) and polypropylene (PP) or N6 and polystyrene (PSt), if only mechanically blended.

However, it may be possible to obtain good solubility in the blend of these undissolved polymers by introducing a certain suitable interpolymer that has good solubility with each polymer to be blended.

We therefore tried to blend N6 and PP using maleic anhydride-grafted PP (MAH–PP) as the interpolymer, and also tried to blend N6 and PSt using styrene–methacrylic acid copolymer (St–MAA copolymer) as the interpolymer. In both cases, we were able to scheme good dispersibility. In this paper, the fundamental relation of the reaction among these polymers will be considered.

EXPERIMENTAL

Materials

Maleic Anhydride-Grafted Polypropylene (MAH–PP).[1] PP powder, MAH, and xylene were put into a vessel and heated with stirring under

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nitrogen atmosphere. When the temperature reached to 120°C, benzoyl peroxide (BPO) dissolved in acetone was put into the vessel and reacted for about 6 hr at 120°C. The $[\eta]$ of this reaction product was 1.29 at 135°C in tetrahydronaphthalene, and the amount of reacted MAH was 1.15 wt-%.

St–Methacrylic Acid Copolymer (St–MAA copolymer).[2] St and MAA were copolymerized by suspension polymerization by the usual method. Acid content was 10 wt-%, and the intrinsic viscosity was 0.50 at 25°C in methyl ethyl ketone.

PP, N6, and PSt. PP, N6, and PSt used in this research were industrial products. PP, whose intrinsic viscosity was 2.19 at 135°C in tetrahydronaphthalene, was from Mitsubishi Yuka Co., N6, where η_{rel} was 1.98 at 25°C in m-cresol, was from Tore Co., and the amount of amino groups of N6 was 0.42×10^{-4} equiv/g. PSt, whose intrinsic viscosity was 0.51 at 25°C in methyl ethyl ketone, was from Yahata Kagaku Co.

Reaction Conditions

The master pellet was made from MAH-PP powder by extrusion molding. After this, the master pellet was mixed with N6, and PP in a suitable ratio in pellet state and then molded by the extruder at 230°C under nitrogen (N_2) conditions.

In the same manner, St–MAA copolymer was mixed with N6 and PSt in the pellet state, and then molded by the extruder at 230°C.

Measurements

Crystallinity. Thermograms of fusion were measured by differential scanning calorimetry, Perkin Elmer DSC Type I; the rate of temperature increase was 10°C/min under N_2.

Christallinity was calculated by the heat of fusion of the N6 peak and the PP peak of the polymer blend, on the assumption that ΔH of PP[3] was 45 cal/g and ΔH of N6 was 45.6 cal/g when they were all in the crystalline state.

Dynamic Mechanical Testing. The speciman dimensions were 2 × 0.1 × 0.02 cm. They were measured by a Vibron DDV Type I, with 110 c/s frequency.

Melt Index. The weight of the polymer flow for 10 min was measured by a Melt Indexer under a 2160-g load at 230°C (ASTM D 1238-57T).

Tensile Measurements. Type II specimens (dumbbell shaped) were formed as test pieces for testing of stress–strain properties, and were measured in accordance with ASTM D 638-58T (1959).

Impact Strength. The falling weight method was in accordance with JIS K 6718-1959. Injection plates molded by injection molding, 10 × 10 × 0.2 cm in size, were used as test pieces. Izod impact strength was measured according to ASTM D 256-54T (V-notched, $r = 0.254$ mm, $\theta = 45°$).

RESULTS AND DISCUSSION

Blend of N6 and PP

Characterization of the Reaction

In the appearance of the pellets, great differences were observed between the N6–PP polymer blend containing MAH–PP graft polymer and only mechanically blended polymer of N6 and PP without MAH–PP graft polymer.

Dispersibility of these polymer blends was well illustrated by Figures 1 and 2, where the blend ratio of N6/PP was 2/8; therefore, N6 was the dispersed phase and PP was the dispersing medium.

The N6 phase of only mechanically blended polymers was easily observed, having a diameter of about 10 μ. On the other hand, that of the N6–PP polymer blend in the presence of MAH–PP graft polymer was hardly distinguishable from PP, as the result of improvement in dispersibility. This clear difference of dispersibility was attributed to a certain chemical reaction concerned with MAH–PP graft polymer.

To confirm this reaction, solvent extractions were tried in regard to the polymer blend under various blending ratios. Figure 3 shows the result of Soxhlet extraction of the polymer blend with xylene, where the blending ratio of N6/PP was 2/8 by weight. The symbol [N] in Figure 3 means the equivalent ratio of MAH in PP to terminal amino groups of N6; and the residue of Soxhlet extraction of only mechanically blended polymer ([N] = 0) was about 20%, indicating that the entire PP phase was extracted. On the other hand, the residue of the N6–PP polymer blends in the presence of MAH–PP graft polymer increased in proportion to [N], that is to say, the
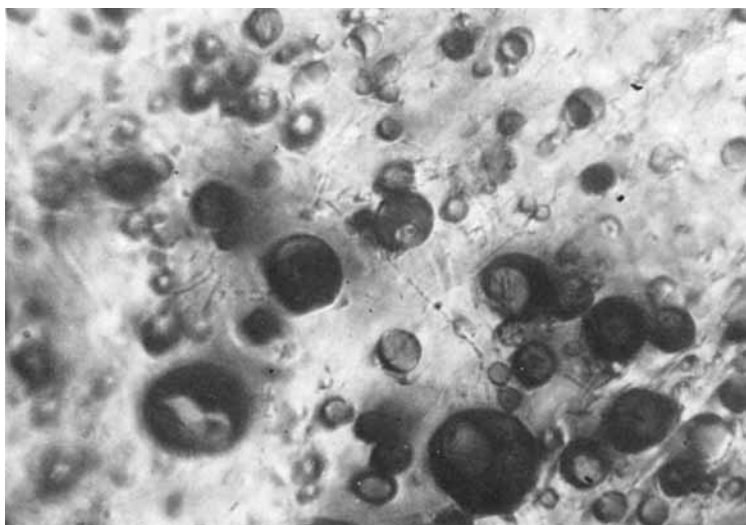

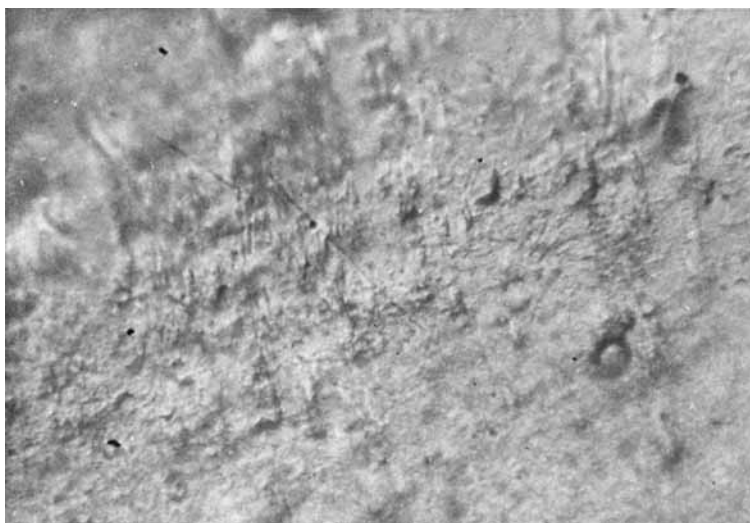Fig. 1. Dispersibility of mechanically blended polymer of N6 and PP.

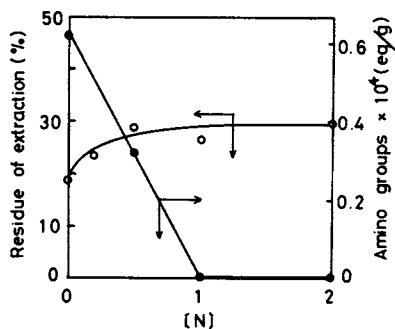Fig. 2. Dispersibility of N6–PP polymer blend in the presence of maleic anhydride-grafted PP ([N] = 0.5).

Fig. 3. Plot showing tendency of the residue after Soxhlet extraction to increase and of the amino groups to decrease with [N] for N6–PP polymer blends: blending ratio N6/PP = 2/8 (by wt); Soxhlet extraction with xylene for 48 hr; [N] = equivalent ratio of MAH in PP to amino groups in N6.

amount of MAH added to the polymer, and it seemed to be constant after [N] was more than 0.5–1.

The amount of amino groups in the residue after Soxhlet extraction decreased with increase in [N], and there were no amino groups in the residue after [N] reached more than 1. That is to say, increasing the amount of MAH added to the polymer results in a decrease in the amino groups of N6. As a matter of fact, it became difficult to dye the N6 phase by acid dye in proportion to the amount of MAH–PP graft polymer, and this suggested that the terminal amino groups in N6 were certainly involved in the reaction.
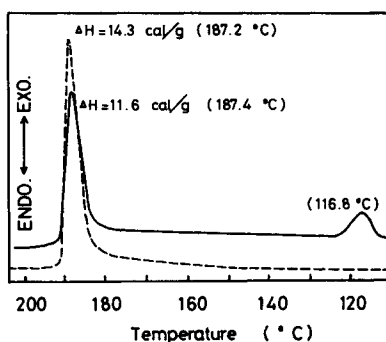
Fig. 4. Thermograms of fusion of the residue after Soxhlet extraction for N6–PP polymer blends: Blending ratio N6/PP = 2/8 (by wt); extracted with xylene for 48 hr; (———) [N] = 0.5; (– – – –) [N] = 0; [N] = equivalent ratio of MAH in PP to amino groups in N6.

Thermograms of fusion of the residue after Soxhlet extraction for N6–PP polymer blends were also characterized by differential scanning calorimetry, as shown in Figure 4. In the thermogram of the residue of only mechanically blended polymer of N6 and PP, there appeared only one peak of fusion belonging to N6 at nearly 187°C. On the other hand, the residue of the N6–PP polymer blend with MAH–PP graft polymer had two peaks; one peak at nearly 187°C belonged to N6, and the other peak at nearly 116°C belonged to PP.

All results mentioned above suggested that some chemical reaction occurred in the blend of N6 and PP in the presence of MAH–PP graft polymer, and that a certain graft polymer formed between MAH in PP and the terminal amino groups of N6, as shown below, for example:
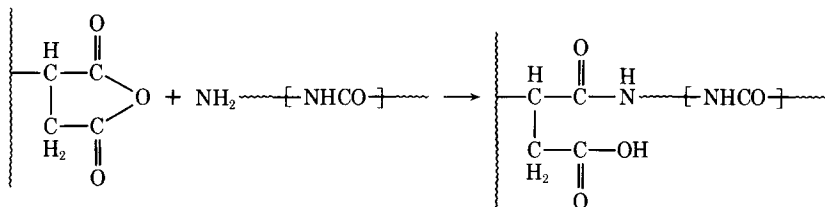
Physical Properties of the Polymer Blend

Crystalline Property. Heat of fusion and crystallinity of N6–PP polymer blends are shown in Table I. Crystallinity tend to decrease in proportion to increasing [N]. The decrease in crystallinity was caused by a difficulty in polymer chain arrangement, whereby movement of segments was presented by the branched chain.

Dynamic Viscoelasticity. Temperature dependence of dynamic modulus (E') and loss modulus (E'') for N6–PP polymer blends is shown in Figure 5, and that of the dissipation factor (tan δ) is shown in Figure 6. As shown in Figure 5, the dynamic modulus (E') of N6–PP polymer blend ([N] = 1) was higher than that of only the mechanically blended polymer ([N] = 0).

TABLE I
Heat of Fusion and Crystallinity for N6–PP Polymer Blends[a]

N6/PP (by wt)	[N]	ΔH_p, cal/g	ΔH_N, cal/g	D.C., %
2/8	0	13.2	3.3	36.2
	0.5	12.4	2.9	32.1
	1.0	13.2	2.8	32.3
	2.0	12.0	2.7	30.2
	6.0	11.2	2.9	32.4
7/3	0	4.7	12.5	36.0
	0.25	4.6	11.3	34.5

[a] [N] = Equivalent ratio of MAH in PP to amino groups in N6; ΔH_p = heat of fusion from PP; ΔH_N = heat of fusion from N6; D.C. = average crystallinity.
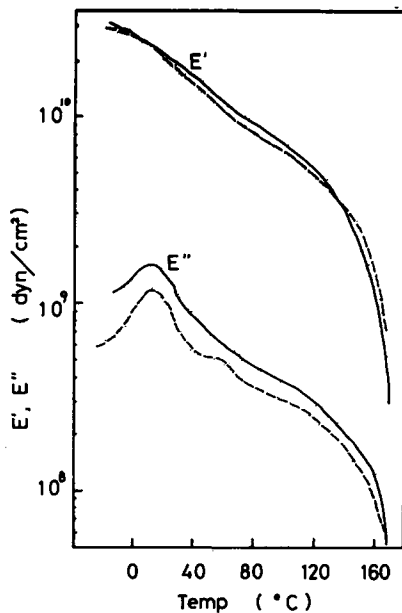

Fig. 5. Temperature dependence of dynamic modulus E' and loss modulus E'' for N6–PP polymer blends: blending ratio N6/PP = 2/8 (by wt); [N] = equivalent ratio of MAH in PP to amino groups in N6; (———) [N] = 1; (– – –) [N] = 0.

On the other hand, loss modulus (E'') of the N6–PP polymer blend ([N] = 1) was higher than that of only mechanically blended polymer [[N] = 0).

This result was, as already discussed under crystalline properties, due to a decrease of crystallinity of N6–PP polymer blends caused by the interference of the polymer chains.

In the same manner, the dissipation factor (tan δ) of N6–PP polymer blend ([N] = 1) was higher than that of only mechanically blended polymer ([N] = 0), as shown in Figure 6, where the peak of fusion of the crystal area for N6–PP polymer blend ([N] = 1) appeared at a lower temperature than
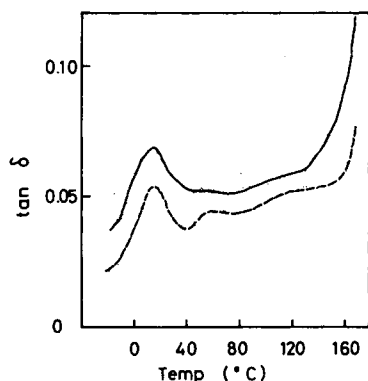
Fig. 6. Temperature dependence of dissipation factor tan δ for N6–PP polymer blends: blending ratio N6/PP = 2/8 (by wt); [N] = equivalent ratio of MAH in PP to amino groups in N6; (————) [N] = 1; (– – – –) [N] = 0.
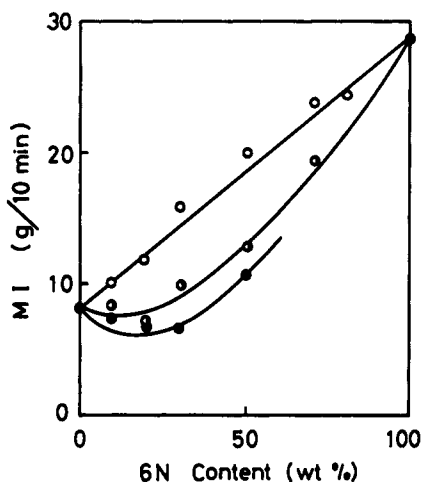

Fig. 7. Effect of N6 content on *MI* for N6–PP polymer blends. *MI* measured at 230°C under 2160-g load: (○) [N] = 0; (◑) [N] = 0.5; (●) [N] = 1.

that of only mechanically blended polymer ([N] = 0). These results were much the same as those of the crystal properties.

On the other hand, besides the peak of PP at 15°C, only the mechanically blended polymer had the broad peaks around 60–80°C which belong to the amorphous area. In case of the N6–PP polymer blend ([N] = 1), the peaks around 60–80°C were much weaker than that of only mechanically blended polymer ([N] = 0). This suggested that the N6–PP polymer blend ([N] = 1) had good dispersibility in the amorphous area, while the mechanically blended polymer had poor dispersibility, and each amorphous phase was almost separated.

Fluidity. Plots of melt index (*MI*) versus N6 content are shown in Figure 7. The *MI* of mechanically blended polymer increased in proportion to

TABLE II
Relation Between Impact Strength and Polymer Composition for
N6–PP Polymer Blends

| Polymer composition | | Impact Strength | |
| | | | |
N6/PP (by wt)	[N]	Izod impact, kg·cm/cm²	Falling weight method, 533.3 g·cm
6Nᵃ	—		>220
6Nᵇ	—		150
7/3	1/8	6.3	60
	1/4	9.8	210
	1/2	11.4	>220
5/5	1/2	5.9	0
3/7	1/2	• 7	
2/8	0	2.9	65
	1/2	5.5	162
	1	6.5	>220
PPᶜ	—	1.7	130

ᵃ η_{rel} = 1.98.
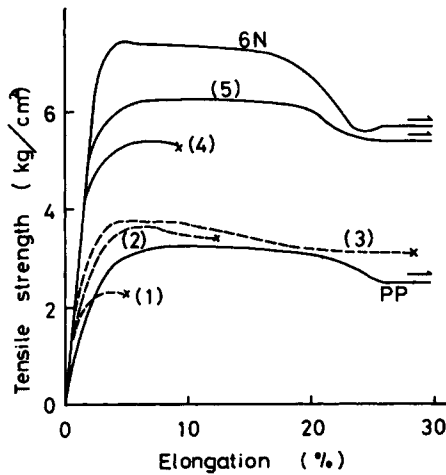ᵇ η_{rel} = 1.60.
ᶜ $[\eta]$ = 2.19.

Fig. 8. Stress–strain behavior for N6, PP, and N6–PP polymer blends: (1) N6/PP = 2/8, [N] = 0; (2) N6/PP = 2/8, [N] = 0.5; (3) N6/PP = 2/8, [N] = 1; (4) N6/PP = 5/5, [N] = 0.5; (5) N6/PP = 7/3, [N] = 0.5.

N6 content; on the contrary, that of the N6–PP polymer blend with MAH–PP graft polymer showed a minimum on the plots.   That is to say, in case of the mechanical blend, there was only a little interaction between N6 and PP.   On the contrary, in N6–PP polymer blend with MAH–PP graft polymer, there was a strong interaction among these different polymer chains.   This behavior of the *MI* was also indicated by Dr. Minoura et al.[5] in SBR polymer blend.

Mechanical Properties. Stress–strain behavior.for N6, PP and N6–PP polymer blends is shown in Figure 8. Tensile strength and elongation of the polymer blend were remarkably improved with increase in MAH added to the polymer blend.

Table II shows the relation between impact strength and polymer compositions for N6–PP polymer blends. Impact strength improved strongly with increase in [N].

Besides these effects of [N] on mechanical properties, they were considerably influenced by the ratio of N6 and PP. Even in the presence of MAH–PP graft polymer, the mechanical properties were still poor when the ratio of N6/PP was about 50/50, in which neither component could form a matrix.

Blend of N6 and PSt

Characterization of the Reaction

In the same way as N6–PP blend polymer, great differences were observed in the appearance of the pellets between N6–PSt polymer blend in the presence of St–MAA copolymer as the interpolymer and only mechanically blended polymer of N6 and PSt without St–MAA copolymer. These appearances are shown in Figures 9 and 10. As shown in Table III, the

TABLE III
Some Physical Properties of N6–PSt Polymer Blends

Polymer composition		Residue of Soxhlet extraction,[b] %	MI,[c] g/10 min	Strand appearance[d]
N6/PSt (by wt)	[N]			
PSt	—	0	19.8	O
2/8	0	21.9	19.0	X
	1	21.9	13.4	O
	2	22.0	13.4	O
	∞[a]	25.0	2.7	O
3/7	0	28.0	20.0	X
	1	34.0	14.6	O
	2		16.4	O
	∞	45.0	4.4	O
5/5	0		23.9	X
	2		15.0	O
	∞		8.2	O
7/3	0		—	XX
	1		16.7	O
	2		15.8	O
	∞		13.0	O
8/2	0		—	XX
	2		16.8	O

[a] St–MAA copolymer was used instead of PSt.
[b] Extracted with benzene for 48 hr.
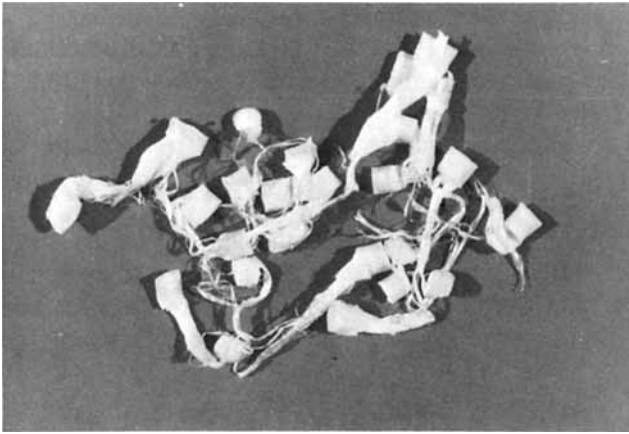[c] Measured at 230°C under 2160-g load.
[d] (O) Good; (X) poor; (XX) bad.

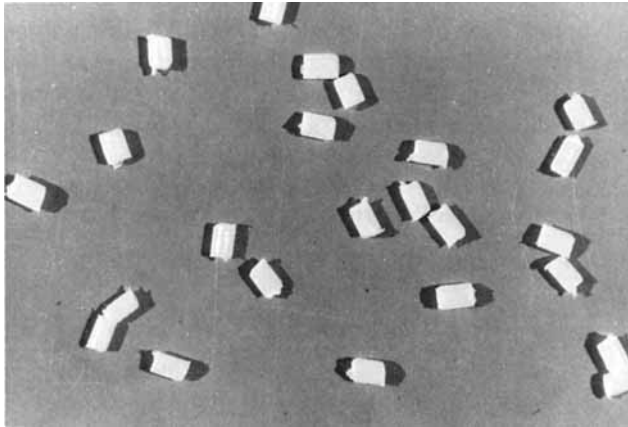Fig. 9. Appearance of pellets of mechanically blended polymer of N6 and PSt ([N] = 0).

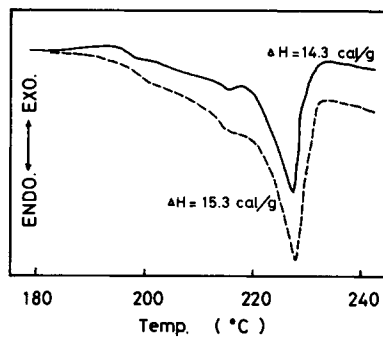Fig. 10. Appearance of pellets of N6–PSt polymer blend in the presence of St–MAA copolymer ([N] = 1).

Fig. 11. Thermograms of fusion for N6–PSt polymer blends: Blending ratio N6/PSt = 3/7 (by wt); [N] equivalent ratio of MAA to amino groups in N6; (————) [N] = 1; (— — — —) [N] = 0.

residue after Soxhlet extraction of the polymer blend with benzene increased in proportion to the amount of St–MAA copolymer added to the polymer blend.

These results suggested the same reaction between terminal amino groups of N6 and MAA in St, the same as the reaction between terminal amino groups of N6 and MAH in PP in the N6–PP polymer blends.

Thermograms of fusion of the residue after Soxhlet extraction for N6–PSt polymer blends characterized by differential scanning calorimetry are shown in Figure 11. Heat of fusion (ΔH) of the residue of N6–PSt polymer blends in the presence of St–MAA copolymer ([N] = 1) was lower than that of only mechanically blended polymer of N6 and PSt. These results suggested that some PSt chains were introduced in the N6 polymer chain, as already discussed for the blend of N6 and PP.

Physical Properties

Fluidity. Melt index (*MI*) of N6–PSt polymer blends is shown in Figure 12. The *MI* of N6–PSt polymer blend with St–MAA copolymer as the interpolymer was lower than that of only mechanically blended polymer. These results suggested that the overall molecular weight increased in proportion to the amount of St–MAA copolymer added.

Mechanical Properties. Table IV shows the relation between some mechanical properties and polymer composition. Even if remarkable dispersibility was obtained by the introduction of St–MAA copolymer as the interpolymer, N6–PSt polymer blends could not improve their mechanical properties more than PSt could.

In conclusion, in the presence of a certain interpolymer, marked dispersibility of the polymer blend should be obtained in the blend of polymers which are essentially hard to dissolve within each other. This seems to be caused by the formation of a certain graft polymer between some carboxylic
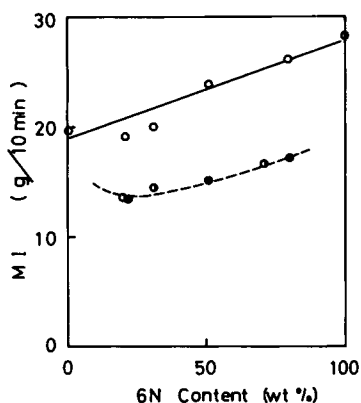

Fig. 12. Effect of N6 content on *MI* for N6–PSt polymer blends. *MI* measured at 230°C under 2160-g load: [N] = Equivalent ratio of MAA to amino groups in N6; (○) [N] = 0; (◑) [N] = 0.5; (●) [N] = 1.

TABLE IV
Relation Between Polymer Composition and Stress–Strain Properties
for N6–PSt Polymer Blends

Polymer composition			T_1		$T_1 + 20°$	
N6/PSt (by wt)	[N]	$T_1, °C^c$	$\sigma_B,$ kg/mm$^{2\,d}$	$\epsilon_B,$ %^{e}	$\sigma_B,$ kg/mm^2	$\epsilon_B,$ %
PSt	—				6.3	2.4
3/7	0^a	—	—	—	—	—
	2	207	5.1	1.5	4.4	1.3
	∞^b	238	7.0	2.0	5.4	1.5
7/3	2	225	8.0	—	8.0	5.3
	∞	250	8.4	—	7.9	—

^{a} Unable to mold by injection molding.

^{b} St–MAA copolymer was used instead of PSt.

^{c} The lowest cylinder temperature where polymer can be sufficiently molded.

^{d} Tensile strength at break.

^{e} Tensile elongation at break.

group such as MAH or MAA and external amino groups of N6. Polymer blends into which such interpolymers are introduced as the third component have better physical properties than only mechanically blended polymers without such interpolymers. The proper combination of polymers to obtain excellent physical properties offers to be very important. That is to say, the physical properties, especially the mechanical properties of N6–PP polymer blends, are remarkably improved with increased MAH added to the polymer blend. On the other hand, polymer blends of N6–PSt cannot have good mechanical properties even if they have good dispersibility. This point of view can be adequately applied to many other combinations of polymer blends.

References

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