

Studies on Composites from Wood and Polypropylenes. II

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Synopsis

Composites of polypropylene (PP) or maleic-anhydride-modified polypropylene (MPP) with refiner ground pulp (RGP) were prepared under various kneading conditions (mixing temperature, rate of rotation, and mixing time) and evaluated for their tensile strength (σ_{\max}), break elongation (ϵ_{\max}), and Young's modulus (E). Particularly, for the rate of rotation, fiber length distribution and its fibrillation were investigated in connection with mechanical properties of the composites. Also evaluated in this study was the effect of modifiers of PP on the properties. Modified PP that can be grafted or can have affinity to RGP was proved to improve the tensile strength of the molded composites as the RGP content increases, while the strength was decreased for PP-RGP composite without a modifier. MPP was also evaluated as a compatibilizer for the PP-RGP composites, and a tremendous improvement of tensile strength was achieved with MPP addition of only 2.5%, indicating that MPP can act as a compatibilizer in its system. These lines of evidence is interpreted to be caused from the improvement of the adhesion between RGP and PP through localizing MPP at the interface of these two components.

INTRODUCTION

In the previous report (Part I),¹ an adhesion between the polyolefin matrix and the filler [refiner ground pulp (RGP)] was found to improve its mechanical properties, when maleic-anhydride-modified polypropylene (MPP) was used as the matrix for the processing of RGP-polypropylene (PP) composites. Such betterment is achieved through the formation of grafting between RGP and MPP by esterification. The MPP sample used in the previous study, however, was commercially available polymers containing elastomeric additives. To investigate the essence of its polymer, chemically pure modified PP samples should be desirable. Therefore, in this study, chemically modified pure polyolefins were prepared and used. On the other hand, concerning these moldable wood-plastic composites, several studies have already been published.²⁻⁶

In the present study, kneading conditions for processing (mixing temperature, rate of rotation, and mixing time), which are considered to have a large effect on the physical properties of composites, were investigated through the tensile test of composite films, the measurements of fiber length distribution, and so forth. Effects of various modified PP used as matrix polymers were then studied in detail on the adhesion between the filler and the matrix as well as on the physical properties of composites. Further study was also performed on the action of one of the modified PP, that is MPP, as a so-called "compatibilizer."

TABLE I
Preparation of Modified PP

Samples ^a	Modifier	Modifier content (%)	Initiator content (%)
MPP(1)	MAH	0.2	0.2
MPP(2)	MAH	1.0	0.2
GMA-PP	GMA	1.0	0.25
HEMA-PP	HEMA	0.5	0.25

^aMPP, MAH, GMA, HEMA: refer to the text.

EXPERIMENTAL

Samples

Refiner ground pulp (RGP) of Radiata pine from New Zealand was used as a wood sample as described in the previous report.¹

Isotactic PP (purified) samples were supplied from Ube Industries, Ltd., which have the melt index (MI) of 1.0 or 35. Then, PP with MI of 1.0, an initiator (*tert*-butyl peroxy benzoate), and one of these modifiers were added together to an extruder (Nihon Seiko Co., Ltd.) with an appropriate proportion (Table I), and kneaded at about 200°C and a rate of rotation of 60 rpm to obtain modified polypropylenes. To obtain modified PP, maleic anhydride (MAH), glycidylmethacrylate (GMA), and hydroxyethylmethacrylate (HEMA) were selected.

Kneading of RGP with Polyolefin

A prescribed amount of dried RGP, polyolefin, and oxidation inhibitor (0.1 wt % based on a total weight) were mixed within a polyethylene bag, and then the mixture was added into a kneader (Toyo Seiki Labo-Plastmill LPM 18-125) preheated to 170°C, under a rotation rate of 10 rpm for 10 min. Subsequently, kneading was accomplished at a definite temperature and rate of rotation.

Preparation of Molded Films

The kneaded samples obtained were molded into the films by hot-pressing with Toyo-Seiki 10T bench hot-press for testing. The samples were placed between a pair of Mylar sheet in hot press of 190°C in its temperature. After heating at this temperature for 5–6 min, the samples were pressed under 150 kgf/cm² for 30 s to form a sheet with 0.4 mm in thickness. The samples were then cooled to room temperature through cold-pressing at the same pressure for 30 s.

Tensile Test

Strip samples with a dimension of 80 × 5 × 0.4 (mm) were prepared from the molded film. Average values of tensile strength (σ_{\max}), break elongation (ϵ_{\max}), and Young's modulus (E) were obtained as shown in the previous report.¹

Solvent Extraction of Kneaded Samples

Solvent extraction of kneaded samples was carried out as described in the previous report.¹

Measurements of Fiber Length and Observation of Its Structure

The kneaded samples were extracted with hot xylene by a Soxhlet extractor for 48 h. After dispersion of the extracted residues within 100% ethanol, they were strained with 1% Safranin ethanol solution and mounted on glass slides for observations of fiber structure by light microscopy. Subsequently, the length of 300 fibers was measured carefully through a projector. Since longitudinal tracheids consisting of about 90% of the total wood cell volume contribute in a major way to the physical and mechanical properties of RGP, short cells of parenchyma were ignored for its measurements.

Measurement of Melt Index (MI)

Melt index was measured by a melt indexer (Toyo Seiki Co. Ltd.) in accordance with ASTM D1238.

RESULTS AND DISCUSSION

Effect of Kneading Conditions on Mechanical Properties of Composites

The mechanical properties of kneaded samples are considered to be affected by kneading conditions such as mixing temperature, rate of rotation, and mixing time. Therefore, MPP-RGP samples prepared under various kneading conditions were evaluated for their tensile strength (σ_{\max}), break elongation (ϵ_{\max}), and Young's modulus (E) to study the effect of kneading conditions on mechanical properties of the composites.

Mixing Temperature. The effects of the mixing temperature on tensile parameters of the composite were studied by changing the temperature in the range of 170–200°C, where the rate of rotation and the mixing time during the kneading were fixed to 50 rpm and 10 min, respectively.

The obtained results are shown in Figure 1, in which maximum values of both σ_{\max} and E can be found at 180°C. At a lower temperature, the melt viscosity of the polymers is rather high so that a poor dispersion of RGP resulted in its composites. Concerning the degrading of the film quality at temperatures higher than 180°C, thermal degradation of the matrix polymer and RGP can be considered. Therefore, the degradation of MPP was studied by measuring MI values of the polymer after treatments at high temperatures ranging from 170 to 200°C. The obtained results shown in Table II reveal no difference in the MI values, which further indicates that the degradation takes place in RGP rather than MPP during kneading at a temperature higher than 180°C.

Rate of Rotation. To study the effects of rotation rate on mechanical properties, the kneading was conducted by changing the rotation rate in the range of 30–90 rpm, keeping conditions of mixing temperature at 180°C and mixing time at 10 min. The increase in the rate of rotation during kneading is

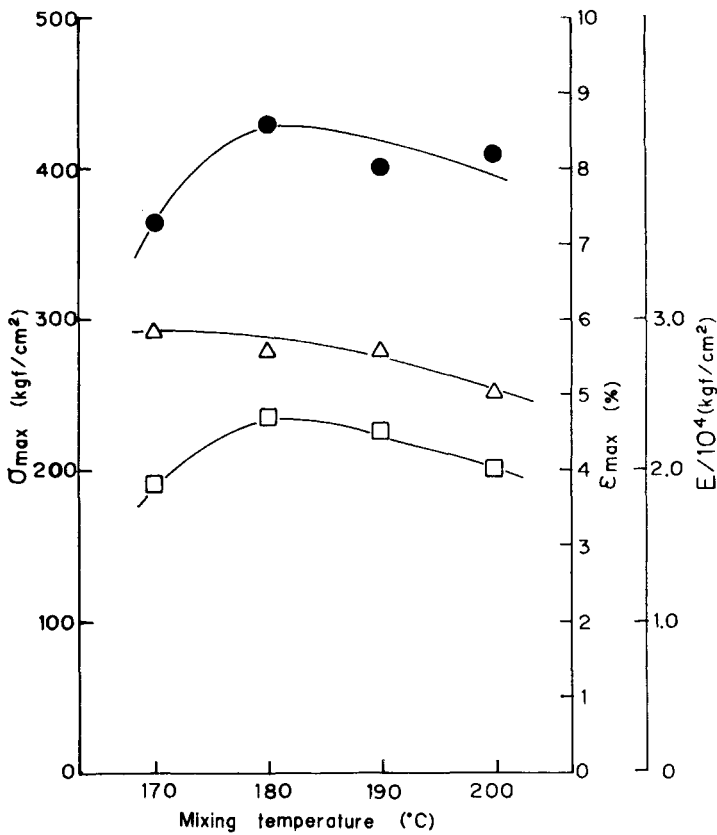


Fig. 1. Effect of mixing temperature on tensile properties of composites. Rate of rotation 50 rpm; mixing time 10 min. (●) σ_{\max} ; (Δ) ϵ_{\max} ; (□) $E/10^4$.

considered to result in the breaking of wood fibers, which decreases the mechanical parameters. Thus, extraction of the composites was tried with xylene by a Soxhlet extractor, the distribution of fiber length of the unextracted residues were measured, and a relationship between the distribution and the mechanical parameters was then evaluated.

The dependencies of σ_{\max} , ϵ_{\max} , and E on the rate of rotation are shown in Figure 2. A maximum for both σ_{\max} and E values was found to be at 50 rpm. The ϵ_{\max} value shows a steady increase with the rate of rotation.

TABLE II
Change in MI of MPP during Kneading at Different Temperature

Mixing temperature (°C)	MI (g/10 min)
170	32
180	33
190	33
200	33
Before kneading	31

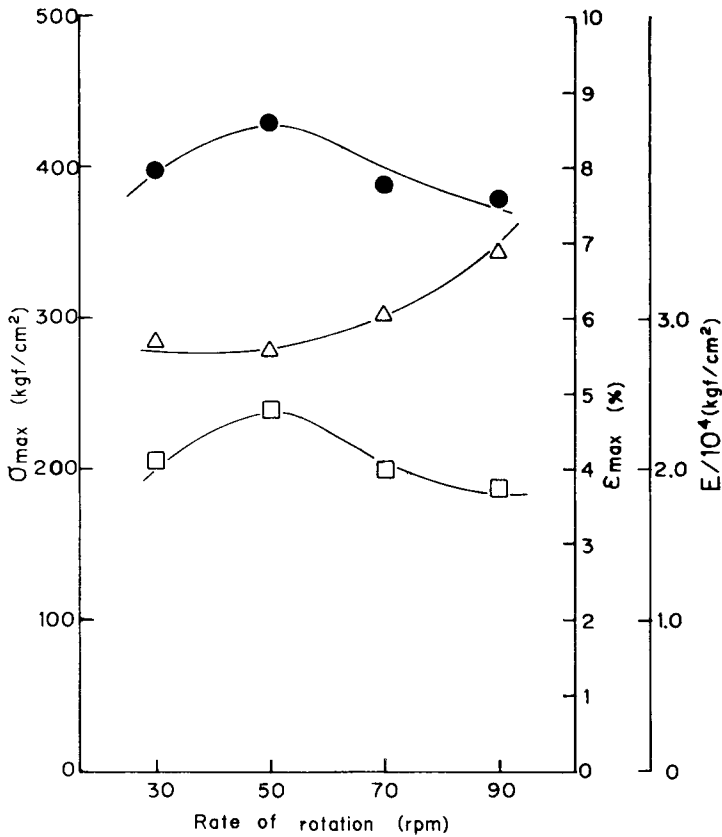


Fig. 2. Effect of rate of rotation on tensile properties of composites. Mixing temperature 180°C; mixing time 10 min. (●) σ_{\max} ; (Δ) ϵ_{\max} ; (□) $E/10^4$.

Figures 3–5 reveal the distribution of fiber length in the composites prepared with three different rates of rotation, whereas, in Figure 6, the corresponding three photomicrographs are shown. It is quite apparent from these figures and Figure 6 that the fibers decreased in their length and their structure of fibers starts diminished and were finely pulverized as the rate of rotation increased from 30 to 90 rpm. At the same time, dispersion of RGP within composites can be enhanced by a higher rate of rotation. Thus, it can be said that the maximum of the mechanical parameters appears as a balance of the increase in homogeneity of the film and the retention of the fiber length of the filler. In connection with the latter, it is known that, because the fiber ends do not carry load, the relatively effective portions of the fiber decrease as the fiber length decreases.⁷ Actually, the term “critical fiber length” is often used.

From Figure 6(b), it is also recognized that the RGP fiber kneaded at 50 rpm shows fibrillation. This fibrillation perhaps leads to an enlargement of the surface area of the fiber and an enhancement of the adhesion between the matrix polymers and fillers. This would further participate in the preparation of the composites with better mechanical properties.

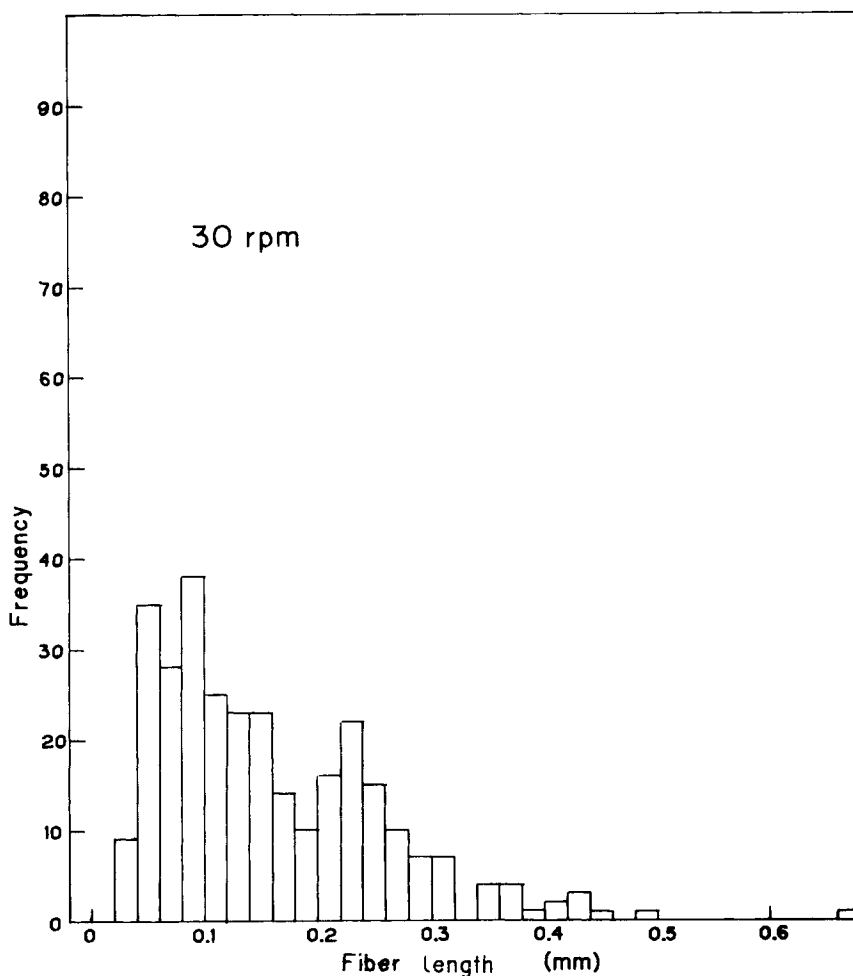


Fig. 3. Fiber length distribution of the composite prepared after kneading at 30 rpm.

Concerning ϵ_{\max} , its value steadily increases in Figure 2 with an increase in the rate of rotation. This tendency is different from that of σ_{\max} and E and would be due to the effects of pulverization of the RGP fiber and high degree of homogeneity of the fillers with matrix polymers.

As a result, overall mechanical properties of the composites are the results of homogeneity of the film, fiber length of the fillers, and its fibrillation, all of which can be affected by rate of rotation.

Mixing Time. Evaluation of the effect of the mixing time on mechanical properties was performed by changing its time from 5 to 20 min with fixed conditions of the mixing temperature being 180°C and the rate of rotation, 50 rpm. Obtained results are shown in Figure 7, indicating that the maximum value of σ_{\max} appears at the mixing time of 10 min, while the ϵ_{\max} value increases with an increase in the mixing time. These observations are attributable to the phenomenon that the degree of the homogeneity of the fiber

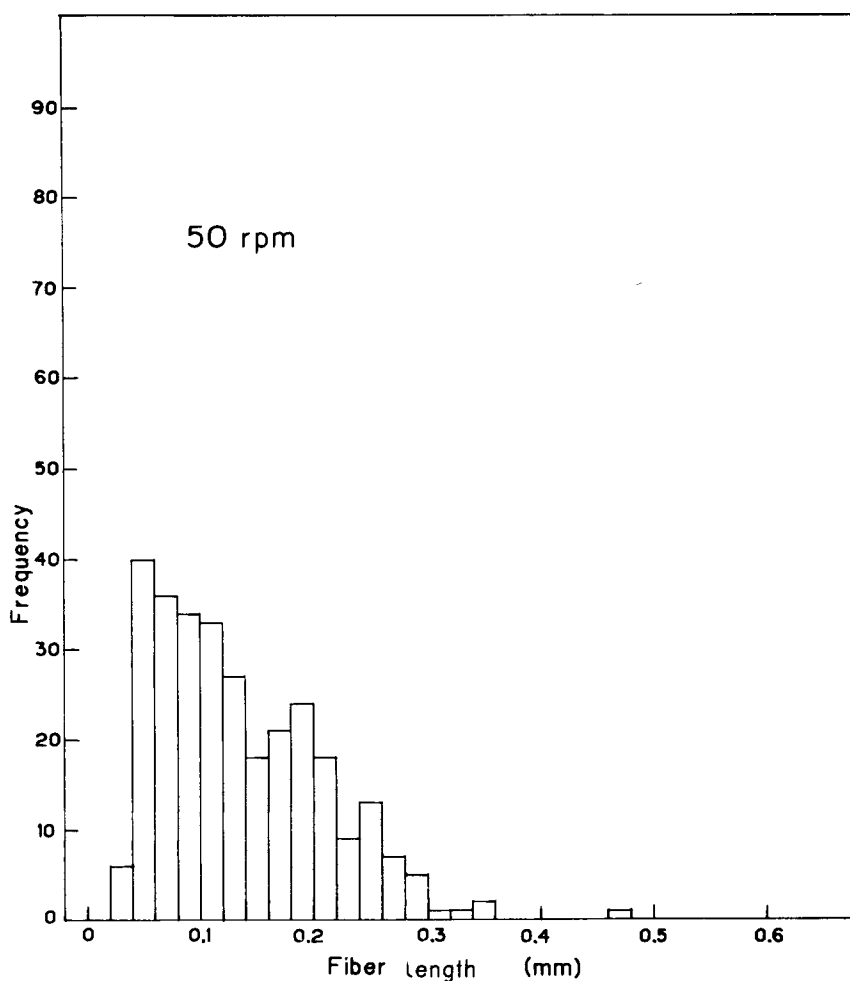


Fig. 4. Fiber length distribution of the composite prepared after kneading at 50 rpm.

distribution becomes greater as the mixing time is prolonged, and, at the same time, the fibers are more finely pulverized.

Effect of the Modifiers on the Mechanical Properties of Composites

To obtain PP-filler composites with high strength and quality by improving the adhesion between the filler and the matrix PP, the methods of utilizing the modified PP, which is partly grafted with a small amount of monomers, has often been used. Especially maleic anhydride is considerably well utilized as a modifier. In this study, MAH, GMA, and HEMA were used as the modifiers. And the effect of using these modifiers on the mutual interaction between RGP and the modified PP and its mechanism were studied through mechanical testing of the composites.

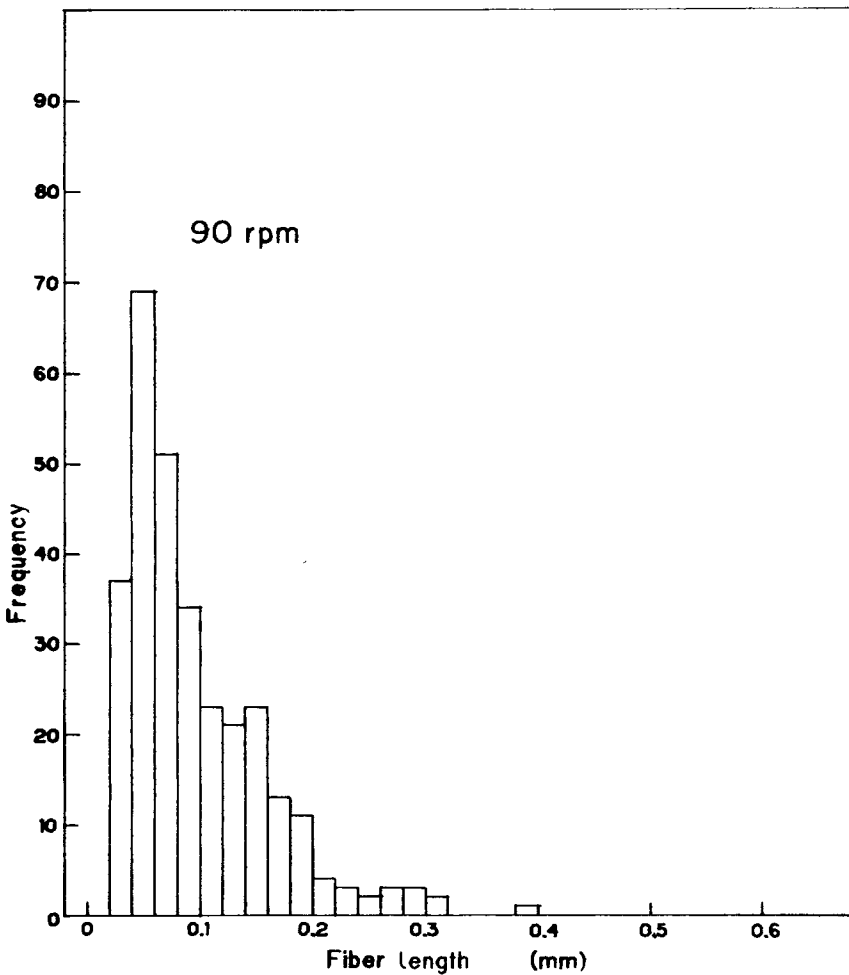


Fig. 5. Fiber length distribution of the composite prepared after kneading at 90 rpm.

Figure 8 exhibits the results of tensile tests. The σ_{\max} value of the MPP and GMA-modified PP (GMA-PP) composites increases with increasing the RGP content, whereas that of HEMA-modified PP (HEMA-PP) composites remain unchanged. However, the unmodified PP composite decreases in its σ_{\max} value. For E value, all of the composites increase to some extent as seen in Figure 9. Such a trend is basically the same with the result of σ_{\max} value in Figure 8.

Based on these findings, the following equations⁸ can be referred to:

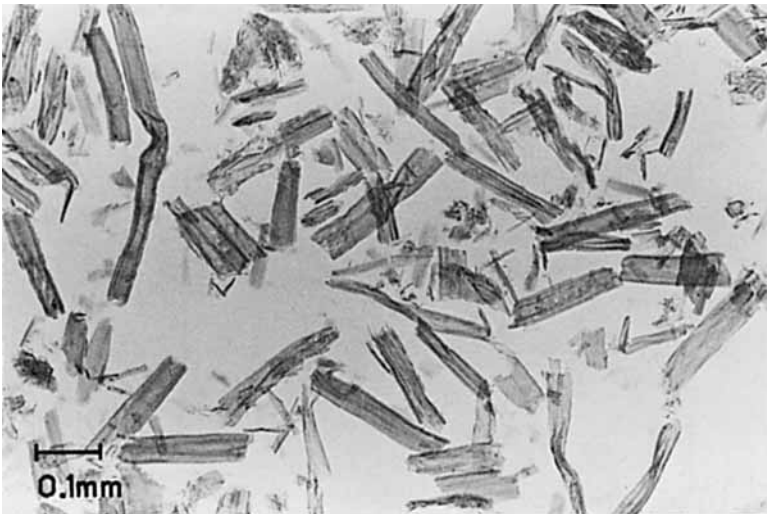
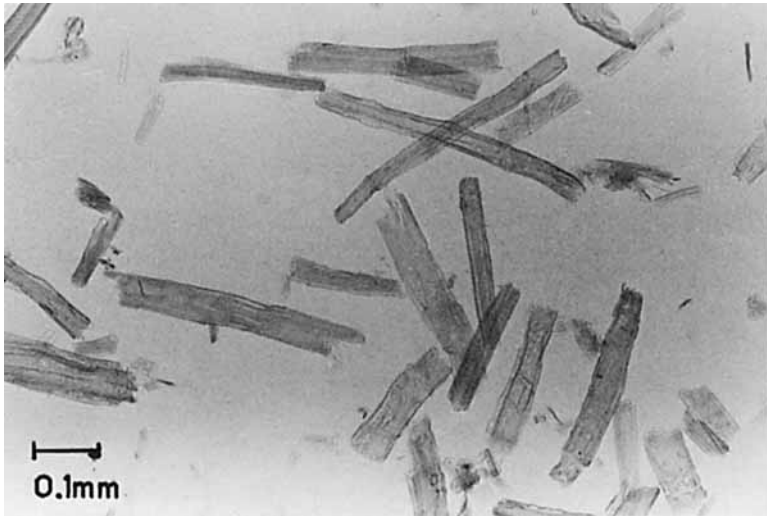
$$\sigma_{\max} = KV_f\sigma_f(1 - L_c/2L) + (1 - V_f)\sigma_m$$

$$L_c = D\sigma_f/2\tau$$

where σ_{\max} = tensile strength of the composite, K = empirical fiber efficiency parameter, V_f = volume fraction of fiber, σ_f = tensile strength of the fiber,

σ_m = tensile strength of the matrix, L = fiber length, L_c = critical fiber length, D = diameter of the fiber, τ = interface shear strength. From these equations, it is apparent that the value of σ_{max} increases with an increase in τ . This implies that the improvement of adhesion between RGP and the matrix polymers by the modification of its matrix substances can directly reflect an enlargement of the tensile strength of the composite.

In connection with the adhesion between RGP and the matrix polymers, the previous report¹ has proved the occurrence of grafting between MPP and RGP during kneading. Grafting of MPP onto RGP can result in high interfa-



(b)

Fig. 6. Light microphotographs of fibrous residues obtained after extraction with hot xylene: (a) 30 rpm; (b) 50 rpm; (c) 90 rpm.



(c)

Fig. 6. (Continued from the previous page.)

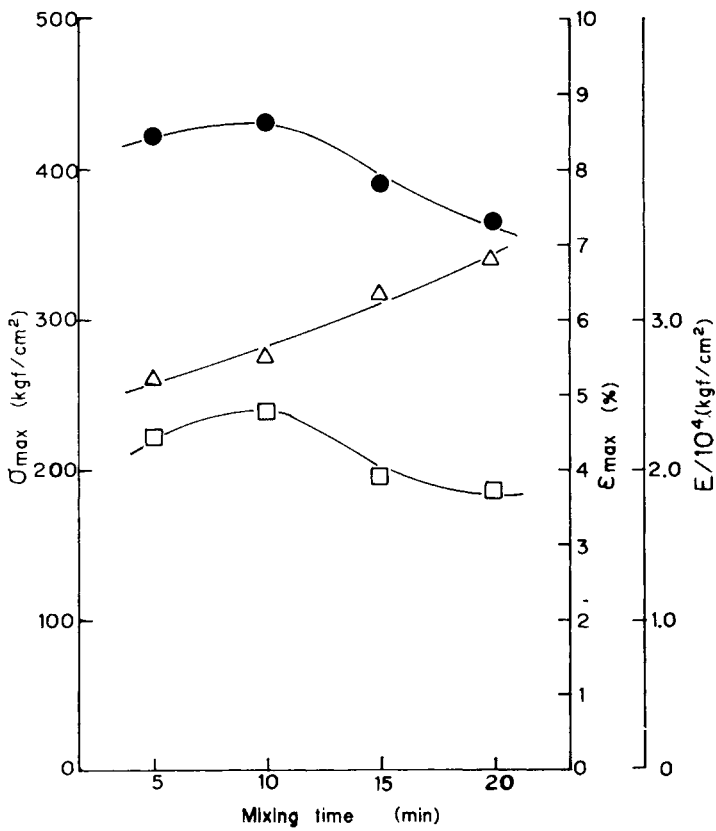


Fig. 7. Effect of mixing time on tensile properties of composites. Mixing temperature 180°C; rate of rotation 50 rpm. (●) σ_{\max} ; (Δ) ϵ_{\max} ; (□) $E/10^4$.

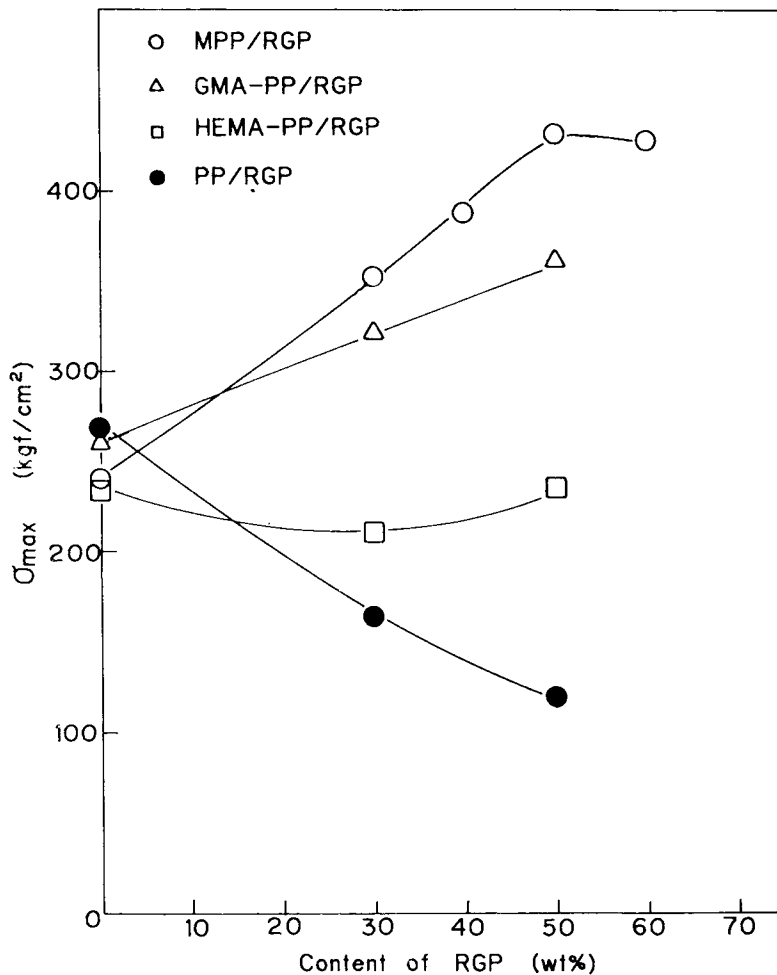


Fig. 8. Effect of modified PP species on tensile strength of composites. (○) MPP/RGP; (△) GMA-PP/RGP; (□) HEMA-PP/RGP; (●) PP/RGP.

cial adhesion. In this experiment, the difference in the nature of interaction between modified PP and RGP was examined for the MPP-RGP, HEMA-PP-RGP, and the unmodified PP-RGP composites. These three composites were first extracted with hot xylene with a Soxhlet extractor for 48 h, and unextracted RGP residues were dried, shaken in an excess of ethyl ether-water mixture with an automatic mixer, and then allowed to stand at room temperature overnight. Figure 10(a) shows the results of this experiment. As shown in the photograph, the RGP residue from the PP-RGP composite precipitated completely at the bottom of the lower layer (water layer), while the residue from the MPP-RGP and HEMA-PP-RGP composites gathered together around the interface between water and ethyl ether. These findings imply that the residue from PP-RGP composites is hydrophilic, while MPP-RGP or HEMA-PP-RGP are hydrophobic. Hydrophilic

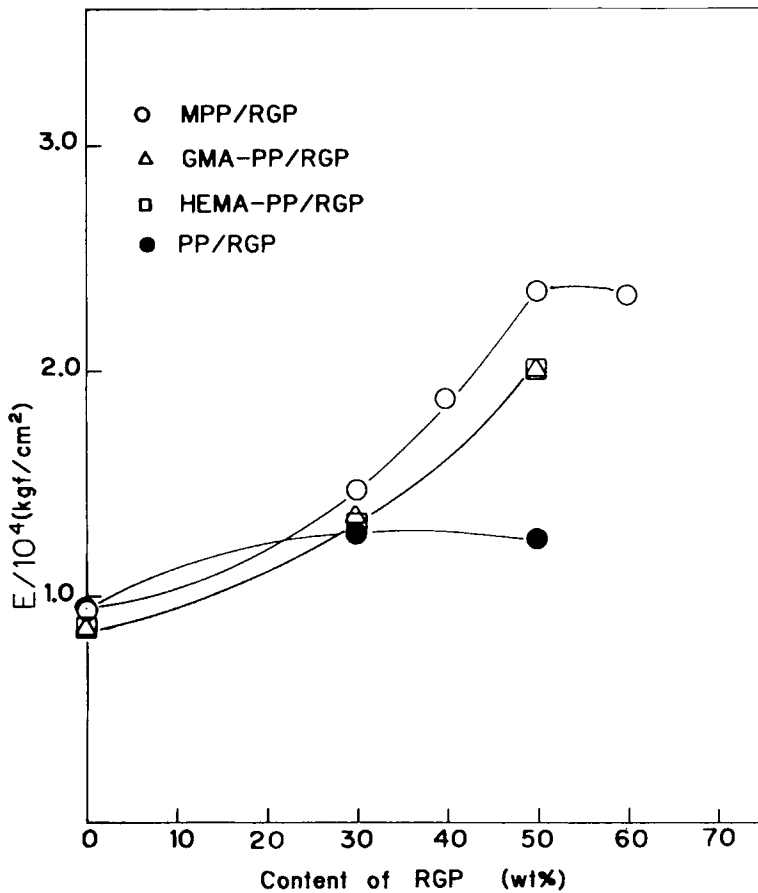
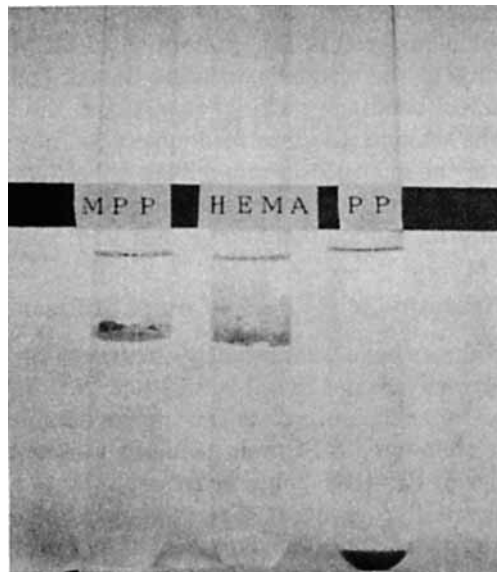


Fig. 9. Effect of modified PP species on Young's modulus (E): (○) MPP/RGP; (△) GMA-PP/RGP; (□) HEMA-PP/RGP; (●) PP/RGP.

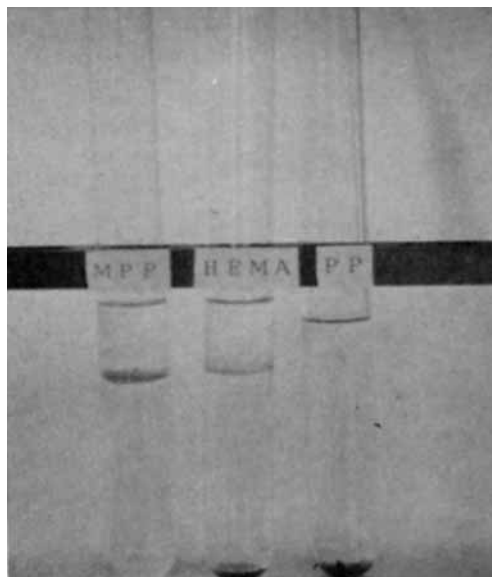
nature suggests that a complete removal of polyolefin remained in the outer and inner surfaces, whereas hydrophobic properties are due presumably to the modified PP still remaining at the surface of the RGP. The interaction between unmodified PP and RGP formed during kneading seems not to be so strong as that between modified PP and RGP, and the former interaction can be easily broken down by contact with hot xylene.

To distinguish differences in nature of the interface interaction formed within the composites, RGP residues from MPP-RGP and HEMA-PP-RGP composites were extracted further with an excess of hot 10% dimethylformamide (DMF)-xylene solution, in which DMF is effective to release the hydrogen-bonding present. Dried residues were also shaken within the water-ethyl ether mixture and allowed to stand overnight. The obtained results are shown in Figure 10(b). It is apparent that the residues from HEMA-PP-RGP composite were precipitated to the bottom of the second layer (water layer), showing the complete removal of the polyolefin from the



Xylene extracted

(a)



Xylene-DMF extracted

(b)

Fig. 10. Existence of solvent extracted RGP residues within the ethyl ether-water two layer system: (a) after extraction with hot xylene; (b) after extraction with hot xylene containing DMF.

RGP, while the behavior of those from the MPP-RGP composite was unchanged. These findings imply that the interaction of HEMA-PP with RGP is by hydrogen bonding at the interface, whereas that of MPP and RGP is by something else, chemical bonding (grafting) reported in the previous paper.¹

As a conclusion, the stronger the interface molecular interaction, the larger the tensile strength of the modified or unmodified PP-RGP composite. These arguments also support an importance of gluability between the filler of RGP and the matrix substances unmodified and modified PP polymers.

Utilization of MPP as a Compatibilizer

So-called compatibilizers have been recently developed for the composites in which composite polymers are not miscible together. It is known that the use of the compatibilizer for such composites can improve its mechanical properties. In this study, therefore, MPP was evaluated as a compatibilizer to improve its properties of PP-RGP composites.

With keeping the RGP content at 50%, the ratio of PP to MPP was changed. A mixture of these three polymers was then kneaded together, and molded into the films. MPP used in this study was prepared by the addition of maleic anhydride in 1.0% on weight basis [MPP(2) in Table I]. The result on σ_{\max} is shown in Figure 11, indicating that the tensile strength of the

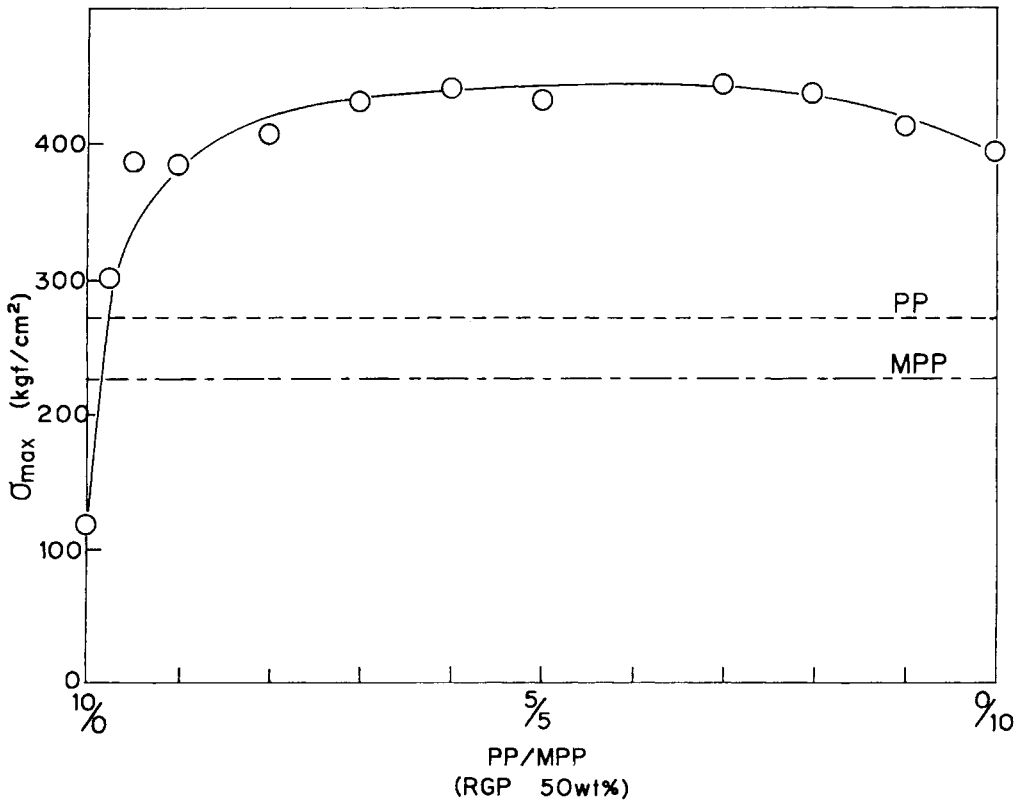


Fig. 11. Effect of MPP amount on tensile strength of composite.

composite increases with an addition of MPP. However, a tremendous increase for its tensile strength was noted up to 2.5% addition of MPP on the whole composite. Surprisingly, such a small addition of MPP could improve tensile strength three times compared with PP-RGP without MPP. An addition of MPP in a quantity between 2.5 and 20% resulted in only a slight improvement of the strength, followed by the plateau region in the range of 20–35%. The addition of more than 35% of MPP to the whole system resulted in a gradual decrease in the tensile strength. The maximum tensile strength obtained was 1.2 times larger than that with the MPP and RGP composite without PP polymers.

These observations imply that MPP can act as a compatibilizer in the system, presumably existing localized at the interface between RGP and the matrix polymer (PP) with improving the adhesion of composite complements each other. Chemical bonding present between MPP and RGP would also play an important role in an improvement of mechanical properties.¹ A substantial addition of MPP is, however, rather harmful for betterment of the composites in mechanical properties, since MPP decreases the strength of matrix portion of the composites.

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