

Polypropylene Composites. I. Studies of the Effect of Grafting of Acrylic Acid and Silane Coupling Agent on the Performance of Polypropylene Mica Composites

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Synopsis

To improve adhesion between polypropylene (PP) and mica in PP composites, acrylic acid (AA) is graft-copolymerized onto PP by a melt-mixing method. At the same time, applying a silane coupling agent to treat the surface of inorganic filler enhances the mechanical, thermal, and electrical properties, as well as decreases mold shrinkage and color difference of the composites.

INTRODUCTION

Factors affecting mechanical, thermal, electrical, and physical properties of polymer composite materials include the matrix structure and molecular weight, fillers and reinforcements, and experimental conditions such as matrix modification, coupling-agent treatment, and hardeners added. The filler contents, surface treatment, and adhesion between filler and polymer matrix that forms a good interface may significantly affect the macroscopic characteristics of composite materials.

Mica is an abundant, naturally occurring mineral with high strength, good thermal stability, and good corrosion resistance. Therefore, mica-reinforced polypropylene (PP) composites possess several excellent properties, among them being high stiffness, good dimensional stability, adequate temperature performance, and reduced cost.^{1,2}

When fillers are blended into plastics to form composites, the adhesion between polymer and filler will influence the performance of the plastic composite. The filler with hydrophilicity or polarity and the polymer with polar groups will facilitate surface bonding because the surface of a filler can be easily wetted by a polymer. Therefore, whether or not the polymer molecule bears polarity is also a major factor in determining the reinforcement effect of plastics composites. In fact, chemical bonding between polymer matrix and filler will offer a best bonding of composites. To have a good interface adhesion between polyolefins and filler, it is necessary for this kind of plastic to bear the polarity before a good affinity with fillers can be brought about. Generally, by graft copolymerization of a polar monomer such as acrylic acid (AA) onto PP, the surface adhesion between polymer and inorganic mineral will be improved significantly.³⁻⁵ Improvement can also be made by using coupling agents for molecular bonding between the interface of a polymer matrix and an inorganic fillers or a reinforcement material.⁶⁻⁹

Because PP is a nonpolar, hydrophobic substance, only a limited amount of hydrophilic filler can be added to it. If a substantial quantity of hydrophilic filler is applied, hardness and stiffness will increase but strength would decrease. To avoid the reduction in strength, the adhesion between PP matrix and filler will have to be enhanced. Two options are possible: one is to chemically modify the PP, and the other is to provide surface treatment to the inorganic filler. By adopting both options, we can expect to heighten the synergistic effect.

This paper reports the properties of a composite made up of acrylic acid-graft-polypropylene (PP-*g*-AA) and mica powder treated with a silane-coupling agent. The effects of the percentage of AA grafted onto PP, the filler contents, and the surface modification of the filler on the mechanical, thermal, electrical, and physical properties, which include mold shrinkage, hardness, density, together with color differences of filler-filled PP composite materials, are investigated.

EXPERIMENTAL

Materials

The polypropylene used was Pro-fax PC-366 made by Taiwan Polypropylene Co. Its melt index (MI) = 4 (g/10 min), and its density was 0.902, and heat distortion temperature (HDT) = 102°C at 4.6 kg/cm². The mica used was of particle size larger than 250 mesh. The acrylic acid used was of reagent grade without further purification. The coupling-agent used was *N*-(2-aminoethyl)- γ -aminopropyltrimethoxysilane made by Tokyo Kasei Chemical Industries, trade name Z-6020.

Graft Copolymerization and Blending

Acrylic acid (AA) and benzoyl peroxide (BPO) were dissolved in acetone to form a homogeneous solution, which were then sufficiently mixed with PP powder before the acetone was completely volatilized. The treated PP was poured into an extruder for the graft copolymerization by a melt-mixing method, then acrylic acid-graft-polypropylene (PP-*g*-AA) extrude was obtained when the temperature was controlled at 130, 200, and 200°C and the extrusion speed was 15 rpm. A certain amount of coupling agent of Z-6020 was dissolved in distilled water and was mixed with a filler at ratios of 4 : 5. The mixture was allowed to stand overnight. The treated filler was then dried in an oven at 100°C and was ground into powder.

The PP-*g*-AA was first blended in the Brabender Plasti-Corder Model PLE 330 at 180°C for 3 min before the coupling-agent-treated filler was added. A rotating speed was maintained at 70 rpm for 9 min for a well-blended composite. The sample was preheated at 180°C for 7 min before each compounding was compressed at 150 kg/cm² for 5 min. It was then cooled and kept at room temperature for 2 days.

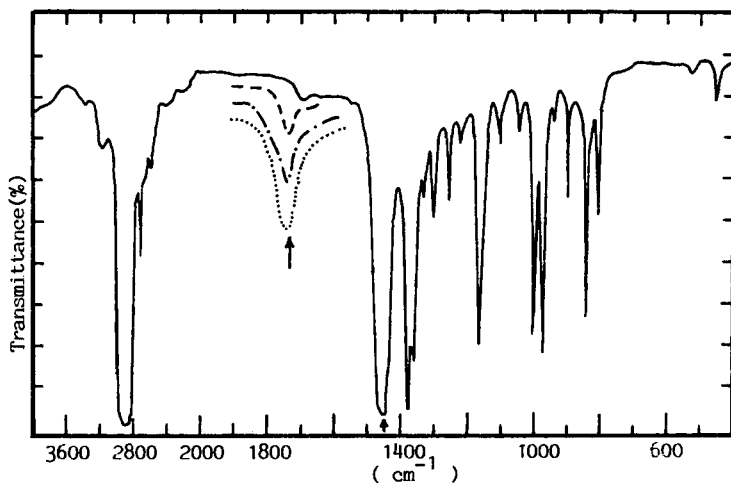


Fig. 1. IR spectra of PP and PP grafted with acrylic acid, sample recovered after extraction with xylene: (—) PP; (---) PP grafted with 1% AA; (-·-) PP grafted with 2% AA; (···) PP grafted with 4% AA.

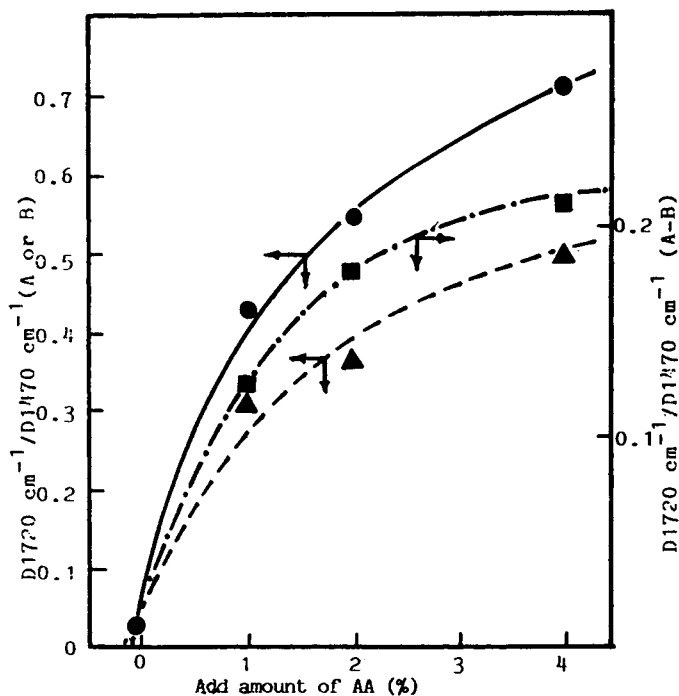


Fig. 2. Effect of AA on the ratio of $D_{1720} \text{ cm}^{-1}/D_{1470} \text{ cm}^{-1}$: (●) nonextracted AA-g-PP, the ratio is A; (▲) AA-g-PP extraction with xylene, the ratio is B; (■) the ratio of $A - B$.

Measurement of Various Properties

Percent of Grafting and Grafting Efficiency

About 12.0 g of PP powder was wrapped with 100-mesh stainless steel net, put into a flask dipped with 450 mL of xylene/methanol 2 : 1 mixed solution, and boiled and refluxed for 8 h. The extracted solution was titrated with 0.1N KOH/methanol solution to obtain the weight (W_1) of grafting acrylic acid (g -AA) and poly(acrylic acid) (PAA). The unreacted acrylic acid is vaporized during the extrusion, because the temperature of the extruder is far beyond the boiling point of acrylic acid (141°C). About 5.0 g of PP- g -AA powder was dissolved in 150 mL of xylene solution, before 150 mL of distilled water was added for extraction. The water layer, obtained using a separatory funnel, was titrated with 0.1N KOH/methanol solution to obtain the weight (W_2) of PAA. Data of grafting copolymerization were calculated as follows^{10,11}:

$$\text{percent of grafting (\%)} = \frac{W_1 - W_2}{\text{wt of original sample}} \times 100$$

$$\text{grafting efficiency (\%)} = \frac{W_1 - W_2}{W_1} \times 100$$

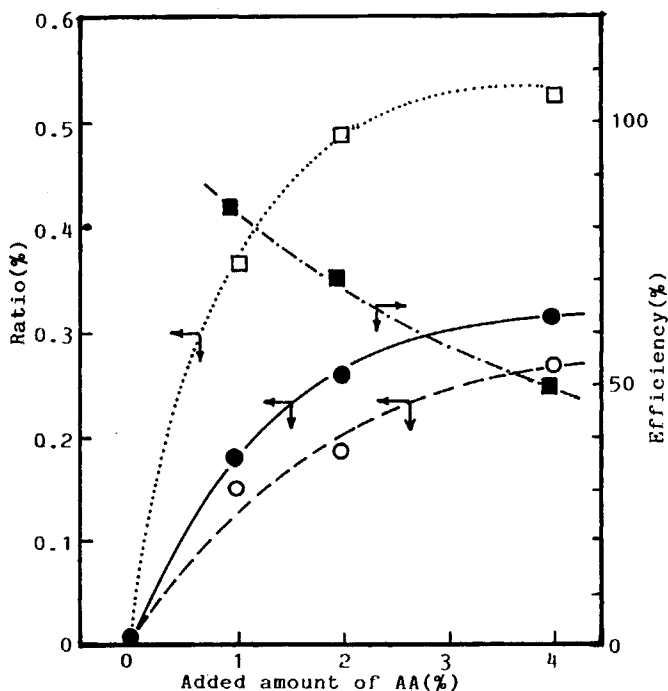


Fig. 3. Effect of AA on grafting ratio, grafting efficiency, PAA homopolymer ratio, and ratio of grafted AA + PAA: (●) grafting ratio; (■) grafting efficiency; (○) PAA homopolymer ratio; (□) ratio of grafted AA + PAA.

IR Spectra

IR spectra were obtained with a KBr disk on a JASCO Model A-202 Spectrophotometer.

Density Measurement

Density was measured at 21°C to calculate the specific gravity of the samples by the ASTM D792 test method as follows:

$$\text{sp gr } 21/21^\circ\text{C} = a/(a + w - b)$$

where a is the apparent weight of the specimen, without wire or sinker, in air, b is the apparent weight of the specimen (and of the sinker) completely immersed and of the wire partially immersed in pure water, and w is the apparent weight of the totally immersed sinker and of the partially immersed

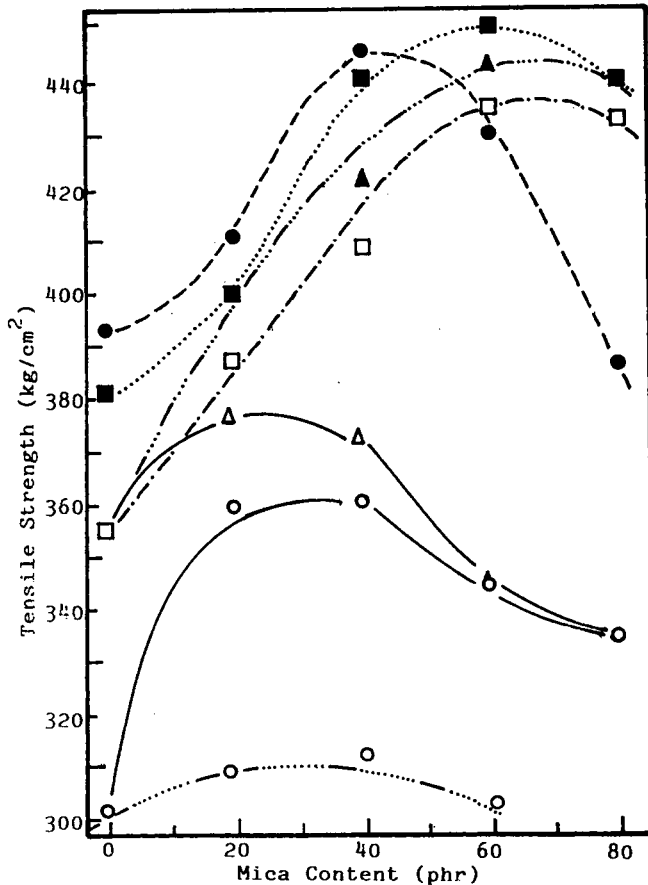


Fig. 4. Tensile strength as a function of mica content in reinforced polypropylene composites: (—○—○—) PP-g-0% AA/Z6020 (0.0%)—mica; (—○—) PP-g-0% AA/Z6020 (0.5%)—mica; (—□—□—) PP-g-1% AA/Z6020 (0.5%)—mica; (—●—●—) PP-g-2% AA/Z6020 (0.5%)—mica; (—■—■—) PP-g-4% AA/Z6020 (0.5%)—mica; (—▲—▲—) PP-g-2% AA/Z6020 (0.0%)—mica; (—△—△—) PP-g-2% AA/Z6020 (1.0%)—mica.

wire. Thus, the density of PP composite was calculated as follows:

$$D(\text{g/cc}) = \text{sp gr } 21/21^{\circ}\text{C} \times 0.9975$$

Mechanical Properties

Tensile properties were measured by the ASTM D638 test method with an Instron Universal Testing Machine Model 1130 under the conditions that the crosshead load was at 500 kg, speed at 5 cm/min, and chart speed at 100 cm/min. Notched Izod impact strength was measured by the ASTM D256 test method with an Izod Type Impact Tester under the conditions that the thickness was 2.9 ± 0.1 mm with a pendulum at 30 kg. Mold shrinkage was measured by the ASTM D955 test method. Hardness was measured by the ASTM D785A test method to obtain Rockwell hardness.

Electrical Properties

The dielectric constant (ϵ) and the dielectric dissipation factor ($\tan \delta$) were measured according to the ASTM D150 test method at room temperature

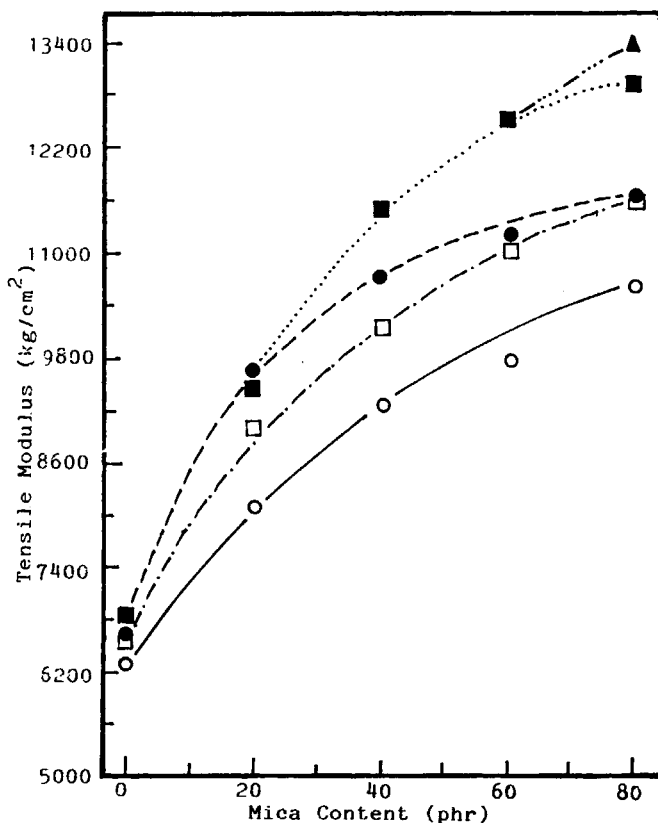


Fig. 5. Tensile modulus as a function of mica content in reinforced polypropylene composites: (—○—) PP-g-0% AA/Z6020 (0.5%)-mica; (- -□- -) PP-g-1% AA/Z6020 (0.5%)-mica; (- -●- -) PP-g-2% AA/Z6020 (0.5%)-mica; (· · · ■ · · ·) PP-g-4% AA/Z6020 (0.5%)-mica; (· · · · · ▲ · · · · ·) PP-g-2% AA/Z6020 (1.0%)-mica.

with the frequency at 3 MHz. Volume resistivity was tested by charging electricity at 500 V for 1 min.

Thermal Properties

A DuPont Instrument 1090B Analyzer equipped with a 910 differential scanning calorimeter (DSC) was used at a heating rate of $10^{\circ}\text{C}/\text{min}$ to measure the polymer melt temperature (T_m). A 951 thermogravimetric analyzer (TGA) was tested in the nitrogen atmosphere at a heating rate of $20^{\circ}\text{C}/\text{min}$ to measure the weight loss of PP composites.

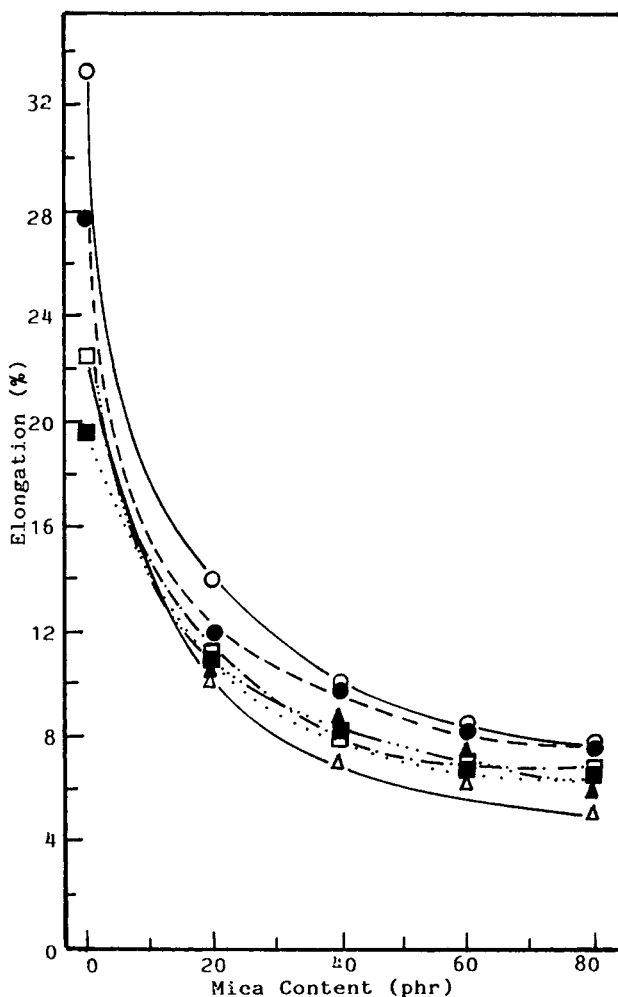


Fig. 6. Elongation as a function of mica content in reinforced polypropylene composites: (—○—) P-g-0% AA/Z6020 (0.5%)–mica; (---●---) PP-g-1% AA/Z6020 (0.5%)–mica; (-.-◻-.-) PP-g-2% AA/Z6020 (0.5%)–mica; (.....◼.....) PP-g-4% AA/Z6020 (0.5%)–mica; (—△—) PP-g-2% AA/Z6020 (0.0%)–mica; (-.-.-.-.-▲-.-.-.-.-) PP-g-2% AA/Z6020 (1.0%)–mica.

Measurement of Color Difference

The color difference (ΔE) was calculated at three values: L , a , and b were measured by a color and color difference meter model TC-50. ΔE was obtained from the following equation:

$$\Delta E_{12} = [(L_1 - L_2)^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2]^{0.5}$$

RESULTS AND DISCUSSION

Graft Copolymerization

Figure 1 shows that when the IR spectra of PP-*g*-AA is compared with that of PP resin, the difference is the most remarkable at 1720 cm^{-1} . The more the AA was added, the higher the intensity of the peak of $-\text{C}=\text{O}$. In view of the

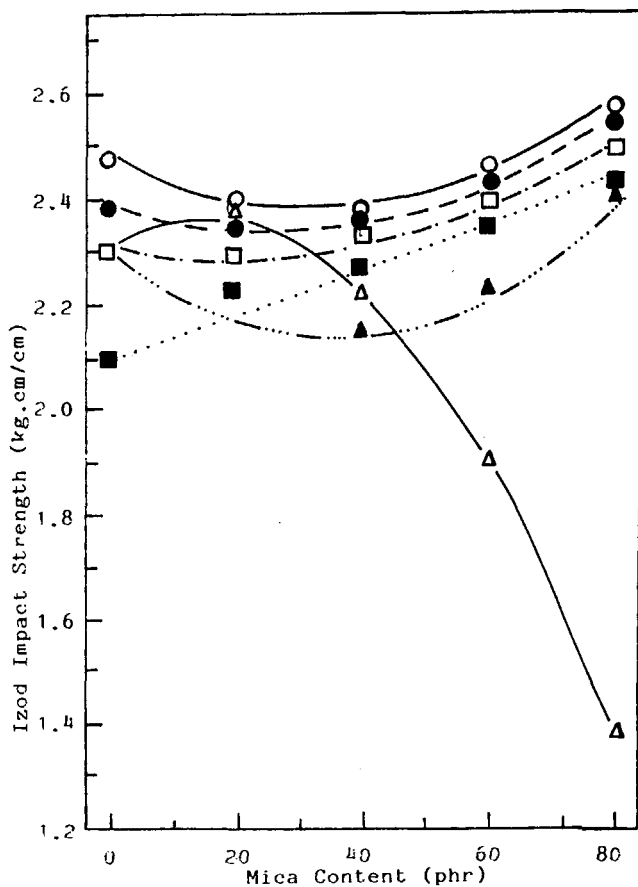


Fig. 7. Izod impact strength as a function of mica content in reinforced polypropylene composites: (—○—) PP-*g*-0% AA/Z6020 (0.5%)—mica; (---●---) PP-*g*-1% AA/Z6020 (0.5%)—mica; (-·-·-□-·-·) PP-*g*-2% AA/Z6020 (0.5%)—mica; (·-·-·■-·-·) PP-*g*-4% AA/Z6020 (0.5%)—mica; (—△—) PP-*g*-2% AA/Z6020 (0.0%)—mica; (-·-·-▲-·-·) PP-*g*-2% AA/Z6020 (1.0%)—mica.

fact that PP-*g*-AA had been extracted with xylene to remove PAA before the IR measurement was taken, it became obvious that AA must be grafted onto PP. The ratio of the absorption peak of —C=O to —CH_3 at $1720\text{ cm}^{-1}/1470\text{ cm}^{-1}$ (shown in Fig. 2) increased with the increase in the amount of AA added during the graft copolymerization. Figure 3 shows that the percentage of both grafting AA and PAA increases, but graft efficiency decreases with an increase in the amount of AA added during graft copolymerization. If the ratio of $1720\text{ cm}^{-1}/1470\text{ cm}^{-1}$ before extraction is subtracted from the ratio after extraction, the ratio will increase with the increment of AA added (Fig. 2). Therefore, it can be concluded that increasing the amount of AA in the course of graft copolymerization brings about the increase of homopolymerization of AA. Despite the decrease in the grafting efficiency, the amount of acrylic acid grafted onto PP will increase with the increase in the amount of AA added.

Mechanical Properties

Figure 4 shows the synergistic effect of the coupling agent and the AA grafting ratios on the improvement of the tensile strength of the composites as compared with unmodified PP composites. It also shows that the enhancement occurs when both the amount of mica treated with a coupling agent and the amount of AA added to the graft copolymerization. That is tensile strength increases with an increase of mica content. Incidentally, maximum values occur at 30–60 phr. These effects can also be observed in the stress–strain curves. When the mica content is lower than 40 phr, the addition of 1% AA is better than the addition of 2 or 4% AA. This is so because the PP-*g*-AA with a polar group of —COOH can easily produce hydrogen bonding in PP matrixes and can form ionic bonding with mica even though only 1% of AA is added. Increasing AA from to 2% or 4% in the graft copolymerization will increase the homopolymerization, which brings about PAA. PAA existing

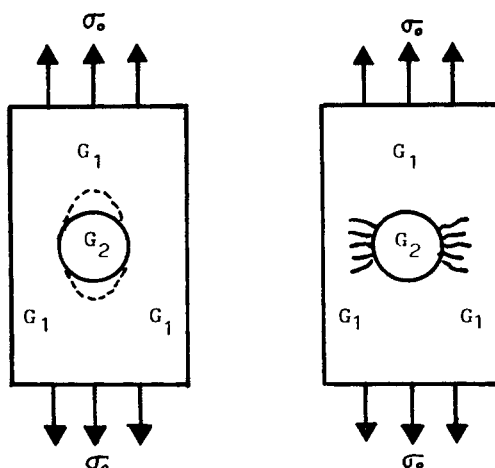
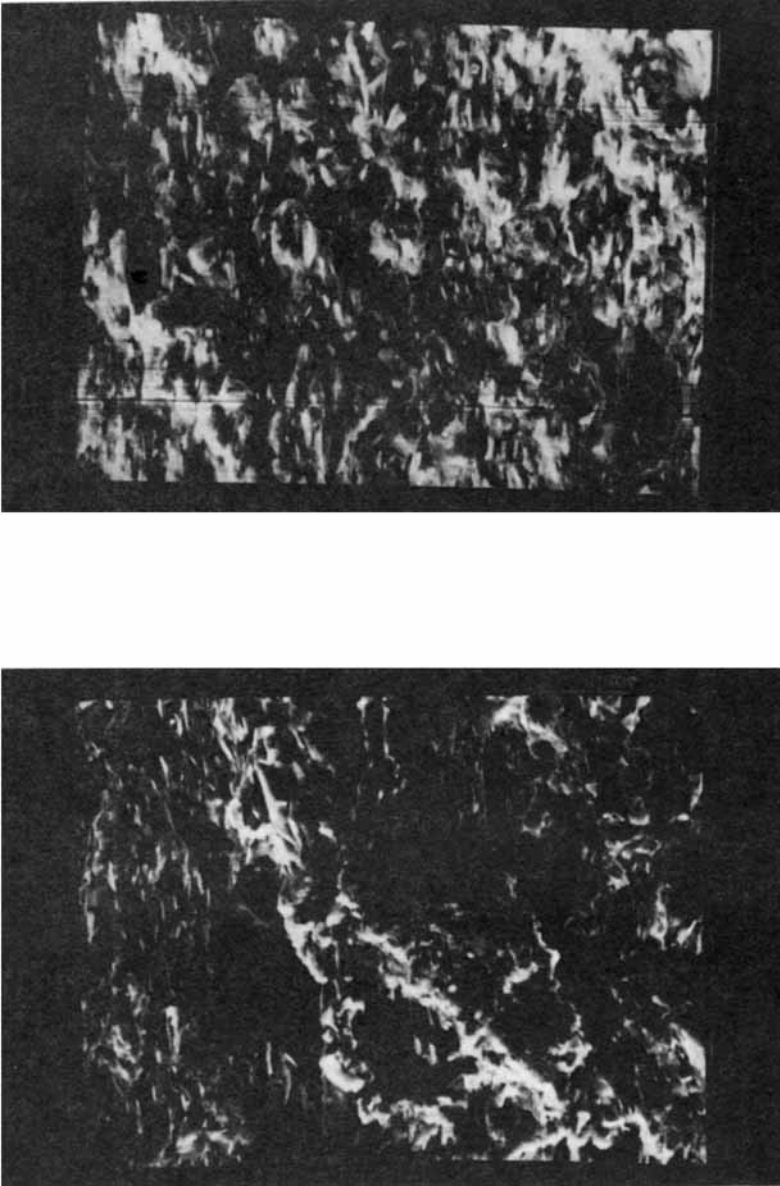
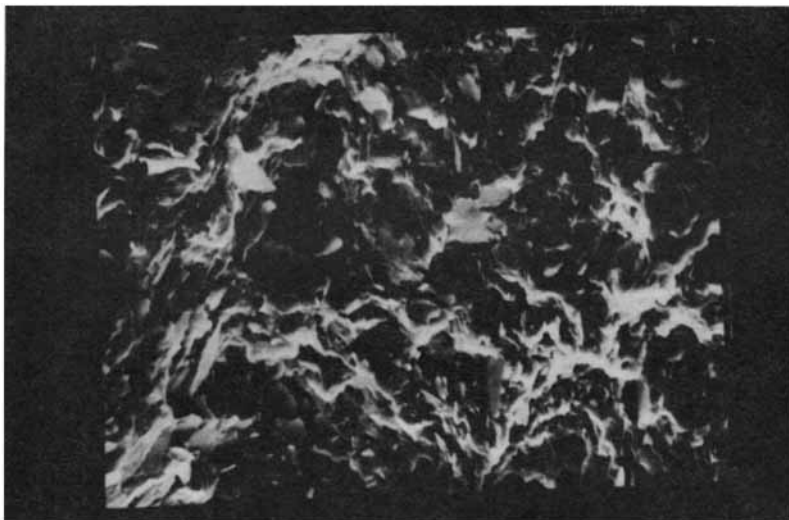


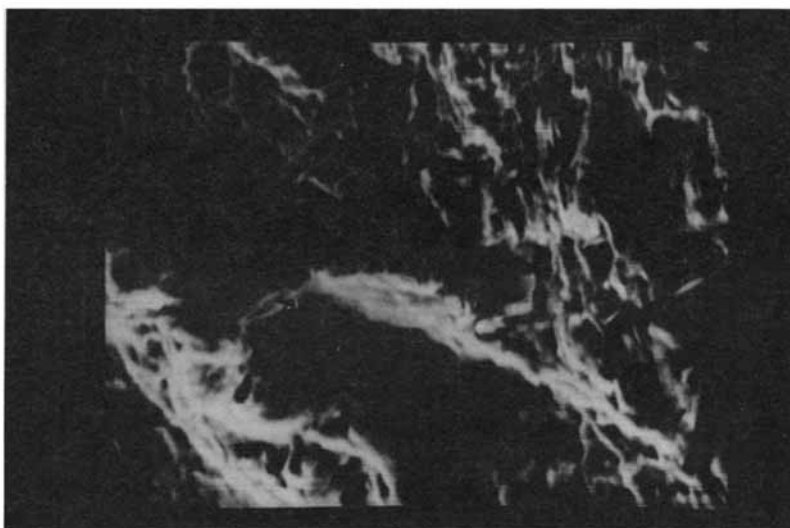
Fig. 8. (A) dewetting of a rigid filler particle in a matrix of lower modulus; (B) crazing of a polymer around a filler particle (or void) when the matrix has a higher modulus than the filler particle. G_1 = polymer matrix; G_2 = rigid filler; σ_0 = force.



(a)
Fig. 9. Scanning electron micrographs of FRPP: (a) PP/mica 80 phr; (b) PP/Z6020-mica 80 phr; (c) PP-g-2% NAA/mica 80 phr; (d) PP-g-2% AA/Z6020-mica 80 phr.



(d)



(c)

Fig. 9. (Continued from the previous page.)

in a composite will produce an interface between matrix and filler, thus decreasing the tensile strength. However, when the mica content is increased to more than 40 phr, 1% PP-*g*-AA will be unable to maintain good ionic bonding with mica and the tensile strength will decrease.

The surface of the filler (mica) treated with the coupling agent will get more desirable dispersion in the polymer matrix and will enhance wetting adhesion between filler and polymer, thus improving the interface of both and increasing the mechanical properties. When the mica content is increased, the effects of the coupling agent will become all the more obvious. By grafting AA onto PP and using the coupling agent to treat the filler, a synergistic effect is obtained as a result of good adhesion and interaction between filler and polymer. The SEM photograph shows that when the mica is increased, the interface will be gradually formed. Therefore, three factors are found to influence the tensile strength: (1) AA content, (2) intermolecular H bonding, and (3) ionic bonding between PP-*g*-AA and mica. When the mica content is low, factor (3) works as usual: with factor (1) more influential than factor (2), 1% AA will contribute to higher tensile strength. When the mica content is increased, factor (2) remains unchanged but factor (3) is more influential than

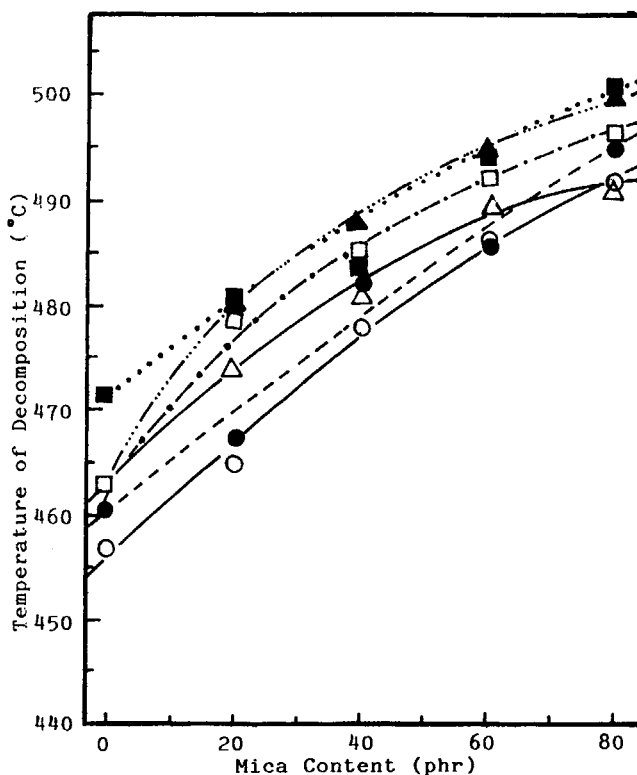


Fig. 10. Temperature of decomposition 50% as a function of mica content in reinforced polypropylene composites (heating rate 20°C/min): (—○—) PP-*g*-0% AA/Z6020 (0.5%)–mica; (---●---) PP-*g*-1% AA/Z6020 (0.5%)–mica; (-·-□-·-) PP-*g*-2% AA/Z6020 (0.5%)–mica; (···■···) PP-*g*-4% AA/Z6020 (0.5%)–mica; (-·-·-·-▲-·-·-) PP-*g*-2% AA/Z6020 (0.0%)–mica; (—△—) PP-*g*-2% AA/Z6020 (1.0%)–mica.

factor (1). Thus 2% or 4% AA will contribute to higher tensile strength than 1% AA.

In general, many equations¹²⁻¹⁵ show that the tensile modulus of composites will increase with increase of filler content, an observation confirmed by our experiments. The tensile modulus also increases with the increase in the grafting ratios and the coupling agent used (Fig. 5). However, Figure 5 shows irregular results on coupling-agent contents. This may be attributed to the result of the formation of microfailure, which is caused by the existence of vacuoles and crazes between interfaces. As vacuoles are considered to be a very soft material, the stiffness of the composite will be decreased, i.e., the modulus will be decreased. However, when the filler is treated by a coupling agent, the interface of the matrix and the filler will be improved, and the vacuoles will be decreased. As a result, the stiffness will be increased, i.e., the modulus will be increased. At the same time, because the bond between the matrix and the filler will be reinforced by the effects of the coupling agent, the modulus will also be increased. The coupling agent can also wet the interface. However, a small amount (0.5%) of the coupling agent can only act as a plasticizer rather than serve to wet the surface. Thus the interaction of molecular chain is weakened, and the modulus is decreased. However, when the amount of the coupling agent is increased to 1%, void-cancelling and bonding effects may overshadow the effects of plasticizing, thus resulting in the uplift of the modulus.

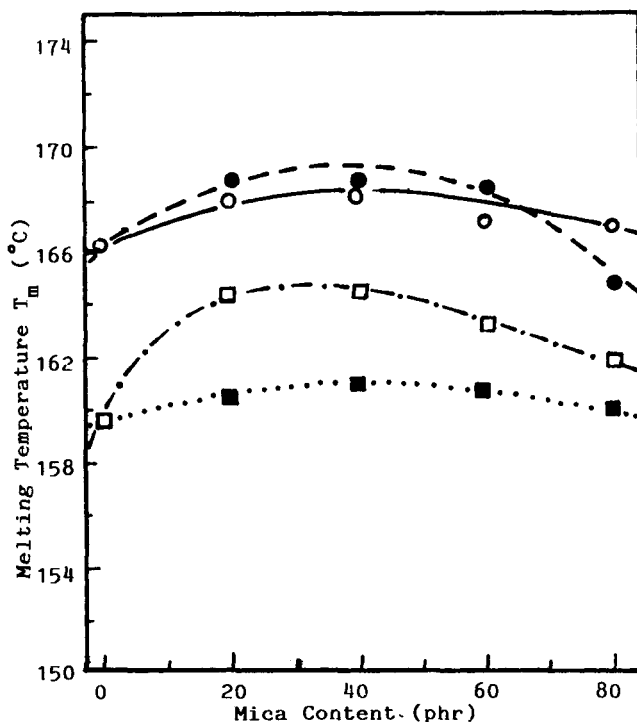


Fig. 11. Melting temperature as a function of mica content in reinforced polypropylene composites (heating rate 10°C/min): (—○—) PP/mica; (---●---) PP/Z6020-mica; (-·□-·) PP-g-2% AA/mica; (···■···) PP-g-2% AA/Z6020-mica.

Elongation decreases with an increase in the amount of AA added in graft copolymerization but increases with the use of the coupling agent. With elongation, the compatibility of the matrix and the filler is improved, resulting in a plasticizing effect. However, the effect is insignificant because the composites with a highly stiff filler added will easily form a stress-concentration point and will be rapidly fractured when stress is placed. Therefore, elongation will be decreased abruptly, as shown in Figure 6.

Figure 7 shows that grafting will make PP brittle because when mica is used as a reinforcement a partial ionic-bond crosslinking will be formed. As a result, impact strength will be decreased. PP-g-AA in Figure 7 shows that without coupling-agent treatment the notched Izod impact strength decreases with the increase in the mica contents. However, the mica with coupling-agent treatment not only shows no deterioration but also increases with the increase of the amount of mica added. This fact is brought about by the coupling agent which decreases vacuoles. This decrease indicates that the impact strength is largely determined by dewetting, which reduces microcraze phenomena. As illustrated in Figure 8, a tensile stress produces a type of stress concentration that results in dewetting and cavitation at the poles of a spherical particle. With dewetting, the change of stress concentration takes place, an occurrence that tends to produce cracks or crazing at the equator of the particles. SEM shows that a filler treated with a coupling agent has better uniformed

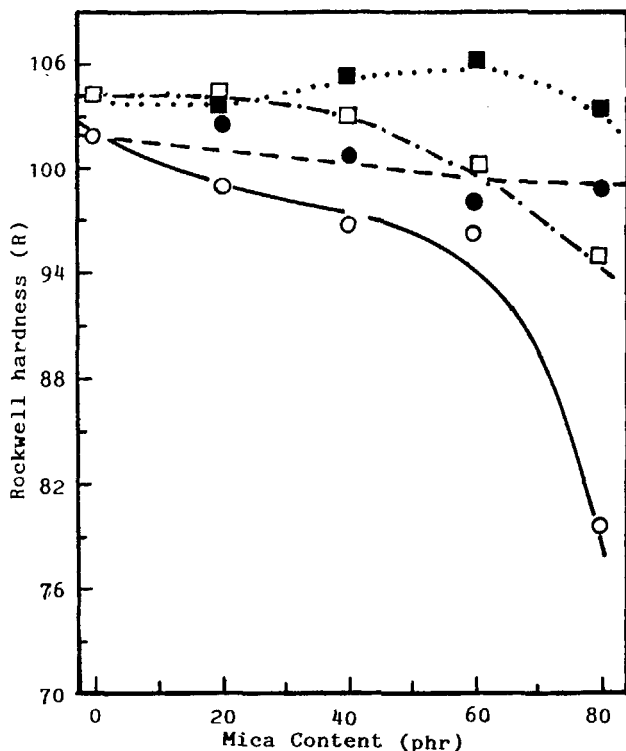


Fig. 12. Effect of acrylic acid and coupling agent on Rockwell hardness: (—○—) PP/mica; (---●---) PP/Z6020-mica; (-·-□-·-) PP-g-2% AA/mica; (···■···) PP-g-2% AA/Z6020-mica.

dispersion, a feature coming from better wetting and adhesion. As a result, good mechanical properties are obtained, especially the high mica contents, as shown in Figure 9.

Thermal Properties

TGA was used to measure three stages of weight loss: initial stage, medial (50% weight loss), and final stage. As shown in Figure 10, the temperature of 50% weight loss rises with the increase of mica contents and the grafting of AA as well as the coupling agent treatment. The effect is brought about by bonding between matrix and filler as well as the improvement on the interface by coupling-agent treatment. As a result, the heat stability is improved. The effect is much better when both AA grafting and coupling agent are applied. Thus a synergistic effect is observed. DSC measurements show that the T_g of composites of PP with AA graft-copolymerization and the filler used with coupling-agent treatment is lower than that of PP without AA grafting. This phenomenon comes from the fact that the grafted side chain increases the molecular spacing, flexibility, and rotation. Their appearance increases ΔS_m but decreases ΔT_m as shown in Figure 11.

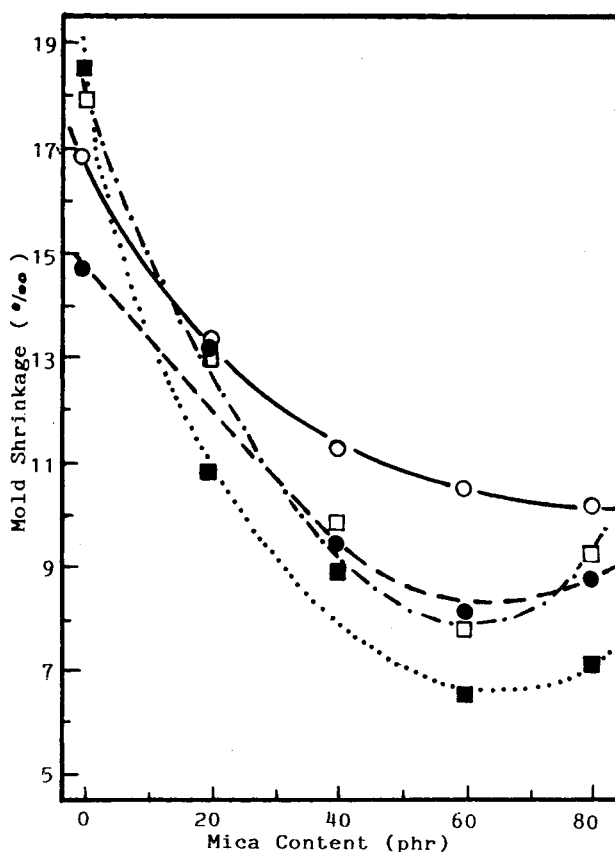


Fig. 13. Mold shrinkage of PP-g-AA filled with silane Z6020-treated mica after molding for 48 h at 21°C: (—○—) AA 0%; (---●---) AA 1%; (-·-□-·-) AA 2%; (····■····) AA 4%.

Electrical Properties

The dielectric constant correlates with the ionization of polar compounds.¹⁶ Because the conductivity of mica is better than PP, the dielectric constant of the composites decreases but the dielectric dissipation factor deteriorates with increase in mica content. However, these properties are improved by grafting AA onto PP and by coupling-agent treatment of the filler to improve the adhesion between the components in the composites.

Other Properties

The density of the composite will increase with the increase of the filler.¹⁷ It will also increase with the amount of AA grafter onto PP as well as with coupling-agent treatment of the filler. This characteristic comes from the good interface adhesion between polymer matrix and filler and from the reduction of voids and vacuoles, which results in the formation of a more packed composite. PP without the grafting of AA or using mica without a coupling agent for reinforcement shows that the hardness decreases with increase in mica content. However, hardness and mold shrinkage are improved by the

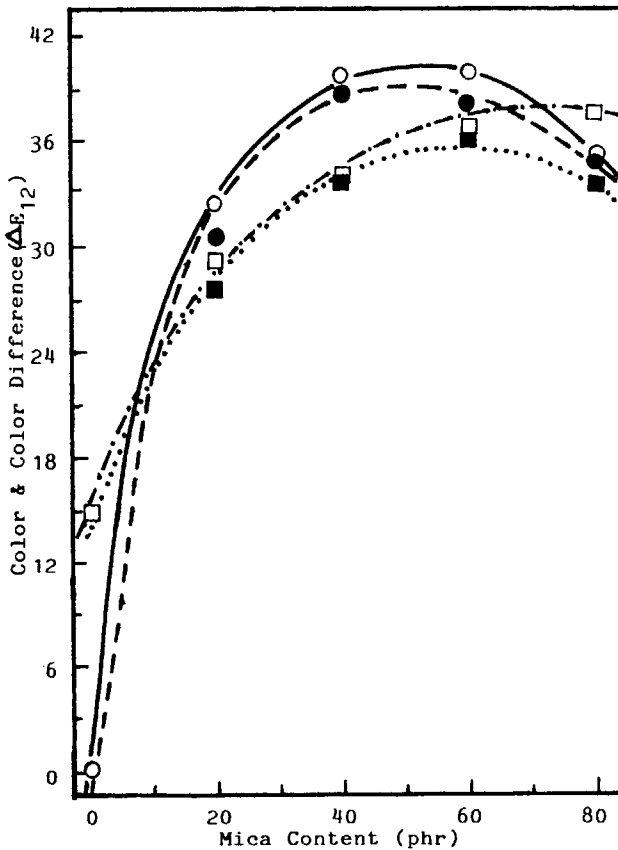


Fig. 14. Measured color and color difference of reinforced polypropylene composites: (—○—) PP/mica; (---●---) PP/Z6020-mica; (- - □ - -) PP-g-AA/mica; (···■···) PP-g-AA/Z6020-mica.

grafting of AA and coupling-agent treatment as shown in Figures 12 and 13. The increase in the mica contents gives coloring to the composites. However, this phenomenon could be reduced by the grafting of AA and coupling-agent treatment. From experimental results, as shown in Figure 14, the reduction may be attributed to better blending, which improves the adhesion between the interfaces.

CONCLUSIONS

By using solvent extraction, titration, and IR measurements, acrylic acid grafted onto PP was confirmed. When the amount of added AA increases, the percentage of grafting increases, but polyacrylic acid (PAA) is formed simultaneously. The grafting efficiency decreases with an increase of added AA.

Compared with the original PP, PP composites made by grafting acrylic acid onto PP (PP-*g*-AA) and reinforcement treated with a coupling agent can remarkably enhance the mechanical, thermal, electrical, and physical properties.

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