

# Viscosity Effect in Polyolefin Ternary Blends and Composites

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## SYNOPSIS

Ternary blends of PP(80)/rubber (EPM, EPDM)(10)/PE(10) and PP(80)/rubber(10)/CaCO<sub>3</sub>(10) composites were prepared in a twin-screw extruder. With polyethylene (PE) viscosity comparable to, or higher than that of rubber, the dispersed phase formed a reticulate structure with reduced size. On the contrary, when the viscosity of PE was significantly lower than that of rubber, the dispersed phase formed almost homogeneous morphology. With reticulate morphology, PE crystallinity content, hardness, modulus, and elongation at break of the ternary blend increased. In polypropylene (PP)/rubber/CaCO<sub>3</sub> composites, better dispersion of CaCO<sub>3</sub> in the PP matrix was obtained when the viscosity of rubber was significantly higher than that of matrix. With better dispersion, hardness and tensile properties were improved, but the impact strength more or less decreased. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Polypropylene (PP) blends have received widespread attention and valuable reviews are available.<sup>1-3</sup> Poor impact properties of PP, especially at low temperature, can be greatly enhanced by rubber addition. The rubber tougheners used mostly are ethylene-propylene copolymer (EPM) and ethylene-propylene-diene terpolymer (EPDM). With rubber inclusion, the tensile properties of PP, such as strength and modulus, are inevitably reduced.<sup>1,4,5</sup> The magnitude of tensile property decrease can be suppressed by adding the high-density polyethylene (PE) into the binary blends.<sup>6-8</sup>

When PE is added to the PP/rubber blend, PE is preferentially dissolved in the rubbery domain to form dispersed droplets, which is thermodynamically unstable and continues to grow in the melt state.<sup>5,9,10</sup> It has often been observed that, in such a thermodynamically unstable system, the component viscosity ratio has an important role in determining the morphology and mechanical properties of the blend. With regard to the viscosity effect, a number of contributions have been devoted to PP/rubber blends. However, to the knowledge of the present

authors, studies on the effect of the viscosity ratio in the PP/rubber/PE or PP/rubber/CaCO<sub>3</sub> system are sparse.

This paper considers the ternary blends of PP/rubber (EPM, EPDM)/PE and PP/rubber/CaCO<sub>3</sub> composites at a fixed composition of 80/10/10 by wt % (about 3.6 vol % CaCO<sub>3</sub> in the latter). Two types of PE and three types of rubber with different viscosities leading to different viscosity ratios of PE to rubber were employed. In this way, the effect of viscosity ratio on the morphology of the dispersed phase and the mechanical properties of the ternary blends can be analyzed.

The use of CaCO<sub>3</sub> instead of PE along the same path of preparation should provide data for sound comparison with the ternary blends. Data were analyzed in terms of rheology, morphology, and thermal and mechanical properties.

## EXPERIMENTAL

Commercial grades of PE, isotactic PP, EPM, and EPDM, listed in Table I, were used as received for blending. The microground calcium carbonates with calcitic structure were used without further treatments.

Blends were prepared by melt-mixing in a twin-

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**Table I** Molecular Characteristics of Base Resins

Polymer	$M_n$	$M_w$	Mooney Viscosity ML(1 + 4) (100°C)	Propylene Content (mol %)	I <sub>2</sub>	Producer
PP	$3.99 \times 10^4$	$3.12 \times 10^5$	—	—	—	Daehan Petrochemicals
PE(H)	$2.10 \times 10^4$	$2.35 \times 10^5$	—	—	—	Daehan Petrochemicals
PE(L)	$2.13 \times 10^4$	$1.83 \times 10^5$	—	—	—	Daehan Petrochemicals
EPM	—	—	—	50	—	EXXON
EPDM(H)	—	—	93	42	24	MITSUI
EPDM(L)	—	—	23	44	26	MITSUI

screw extruder with  $L/D = 30$ , at 30 rpm using a temperature profile 210, 220, 230, and 220°C of first, second, third, and die zones, respectively. The rpm approximately corresponds to a shear rate of  $200 \text{ s}^{-1}$ .

Blending was performed in two stages: For PP/rubber/PE blends, master pellets of PE(50)/rubber(50)/(by weight) were first prepared to mix with PP in the second stage. For PP/rubber/CaCO<sub>3</sub> systems, equal amount of CaCO<sub>3</sub> was first mixed with rubber to pelletize, followed by blending with PP. In either of the two cases, identical shear and thermal histories were provided for reliable comparison. Six combinations of ternary systems are listed in Table II.

Specimens for mechanical tests were prepared by injection molding. Dumbbell specimens of thickness 3 mm, width 25 mm, and gauge length 80 mm were punched out using a cutter. Tensile tests were performed using a Instron (4202) with a 1–500 kg load cell at a crosshead speed of 50 mm/min. Hardness, flexural modulus, and impact strength were determined following the standard procedures in ASTM. For mechanical tests, at least five runs were made and the results were averaged.

Morphologies of the blends and composites were observed using scanning electron microscopy (SEM). SEM micrographs were taken from cryogenically (in liquid nitrogen) fractured surfaces of injection-molded tensile specimens. The fractured surfaces were etched with *n*-heptane vapor (a selective solvent for rubber) for 1 min and sputtered with gold before viewing.

A differential scanning calorimeter (DuPont 1090B DSC) was employed to determine the thermal properties of the samples. Samples were first heated to 180°C and kept at that temperature for 5 min. The melted samples were cooled to room temperature at 20°C/min, recording the crystallization temperature ( $T_{cc}$ ). Melting peak temperature ( $T_m$ ) and heat of fusion ( $\Delta H_f$ ) were recorded during the second cycle at a heating rate of 10°C/min.

Rheological properties of the melt were measured from a Rheometrics Dynamic Spectrometer (RDS) 7700. A cone-and-plate fixture with cone angle of 0.1 rad and diameter of 2.5 cm was isothermally operated at 210°C, 15% strain level. The strain level was determined from a strain sweep to give maximum torque value within the linear viscoelastic limit.

**Table II** Thermal Properties of the Ternary Systems

No.	Sample Combination (80/10/10)	PE			PP		
		$T_m$ (°C)	$\Delta H_f$ (J/g PE)	$T_{cc}$ (°C)	$T_m$ (°C)	$\Delta H_f$ (J/g PP)	$T_{cc}$ (°C)
	PE(H)	135.1	189.7	113.4	—	—	—
	PE(L)	134.4	204.1	114.1	—	—	—
	PP	—	—	—	163.4	87.4	107.5
1	PP/EPM/PE(H)	129.3	147	112.6	162.0	88	112.6
2	PP/EPM/PE(L)	129.1	118	111.4	162.3	86	111.4
3	PP/EPDM(H)/PE(H)	130.9	116	112.8	163.3	83	112.8
4	PP/EPDM(L)/PE(H)	131.0	203	114.0	161.6	82	114.0
5	PP/EPM/CaCO <sub>3</sub>	—	—	—	164.1	118	111.9
6	PP/EPDM(L)/CaCO <sub>3</sub>	—	—	—	163.4	113	112.1

## RESULTS AND DISCUSSION

### Rheology

The complex viscosities of the components are shown in Figure 1. The viscosity of EPDM(H) is by far the highest, and PP has the lowest throughout the frequency range tested. At low frequency, viscosities are in the increasing order of PP < EPDM(L) < PE(L) < EPM < PE(H) < EPDM(H). The viscosities of PE(H) are greater than those of EPM at low frequency; however, they are lower at high frequency, resulting in a viscosity function crossover at approximately  $\omega = 1$  rad/s. Figure 2 shows the complex viscosities for the ternary blends, where EPDM blends (samples 3, 4, 6) give higher viscosities than do EPM blends (samples 1, 2, 5). However, it should be mentioned that when the measured viscosity was compared with the log-additivity rule<sup>11,12</sup> samples 1 and 4 gave positive and samples 2 and 3 gave small negative deviation from the additivity rule at low frequency. Following Han,<sup>13</sup> viscosities at a low rate of shear depend mainly on the state of dispersion, and with interlocked morphology, viscosity increases over the additive rule. From these points of view, the viscosity should be related to the morphology as discussed below.

A Cole-Cole plot of blends is also of a useful tool for rheological characterization.<sup>14-16</sup> When the out-of-phase components of the viscosities are plotted against the in-phase component in an ordinary coordinate, compatible blends often form a well-defined semicircle and immiscible blends show drifts from the semicircle. Such plots for the present system are given in Figure 3. Notably, no drift from the semicircle is found from the figure within the limit of our experiment, and the plot may not reflect on the state of miscibility but, rather, on the shape of the frequency relaxation spectrum.

### Morphology

Figure 4 shows the SEM micrographs of the samples. It is of interest to find that the dispersed domains in samples 1 and 4 form reticulate structure, whereas those in samples 2 and 3 show almost homogeneous morphologies. Since samples 1-4 were prepared following the same shear and thermal paths, i.e., binary blending between rubber and PE, followed by blending with PP, the difference in morphology may be explained from the relative viscoelastic properties of the components. The viscosity of PE in samples 1 and 4 are close to (sample 1) or higher (sample 4) than those of rubber. This is opposite to samples

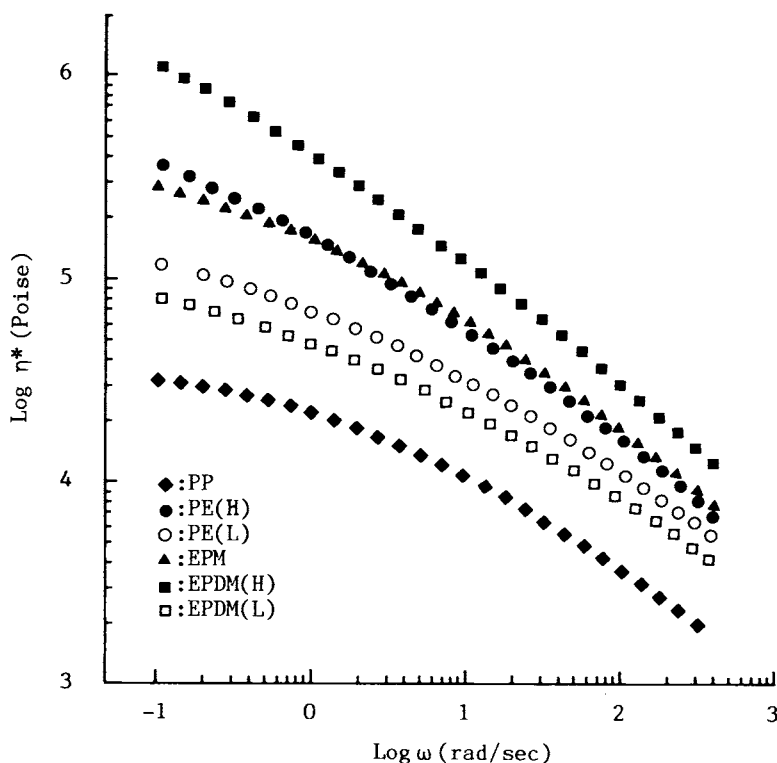


Figure 1 Viscosity functions for components.

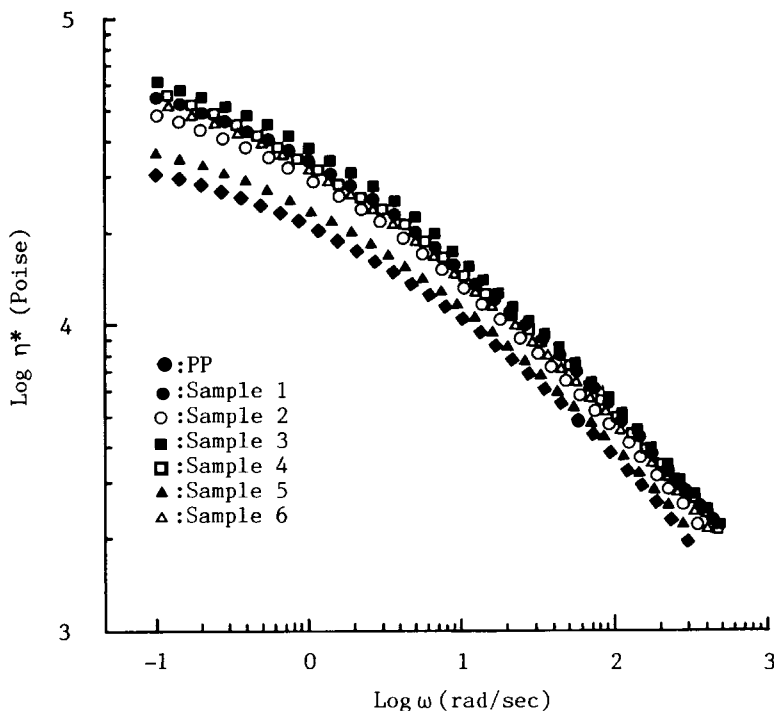


Figure 2 Viscosity functions for ternary systems.

2 and 3, where viscosities of PE are significantly lower than those of rubber. Therefore, PE should form the continuous phase in samples 2 and 3, whereas rubber forms a continuous phase in samples

1 and 4. It is likely that the rubber, when it forms a continuous phase, behaves as an effective compatibilizer. In this regard, it may be noted that the dispersed domain in sample 4 is smaller than that

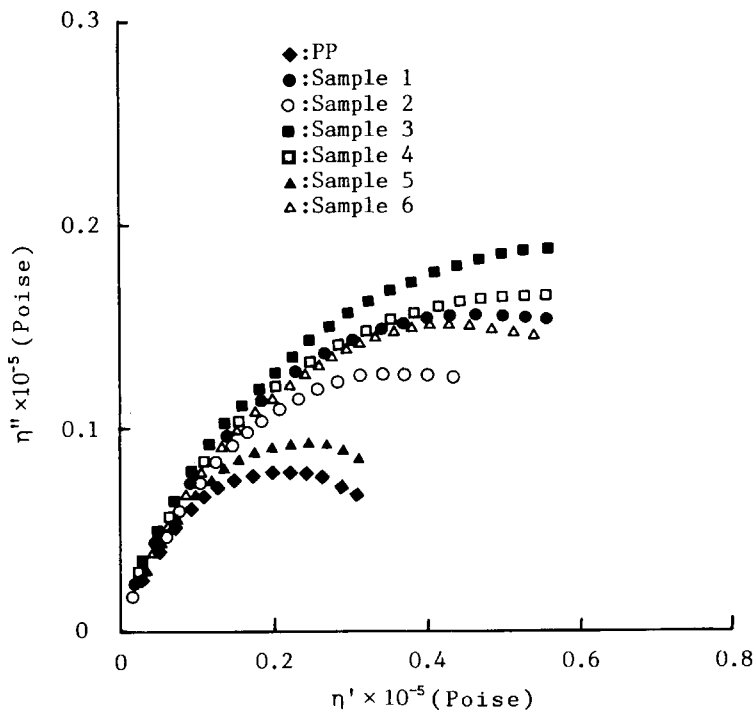
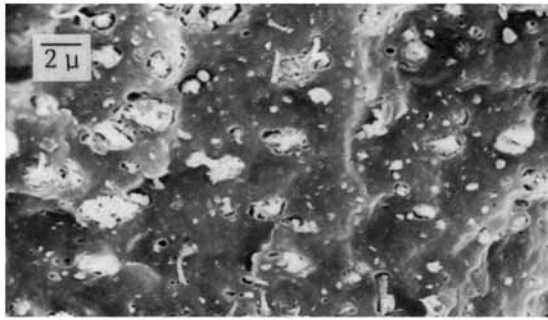
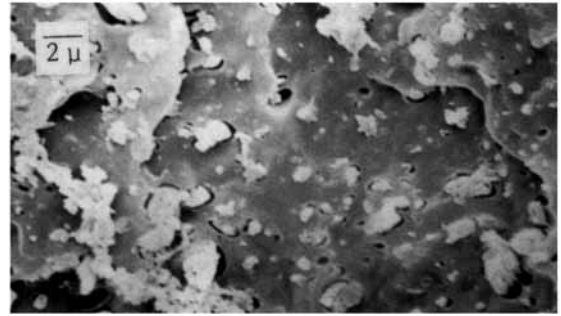


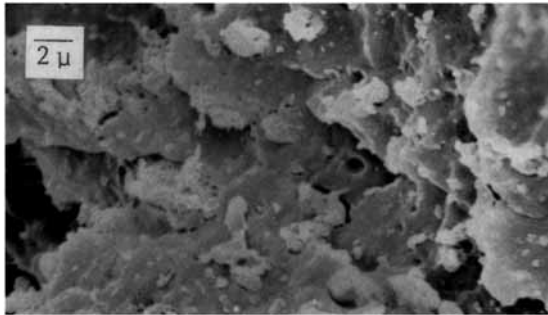
Figure 3 Cole-Cole plots for ternary systems.



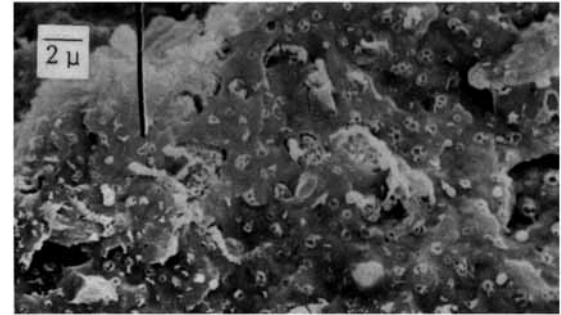
PP/EPM/PE(H)



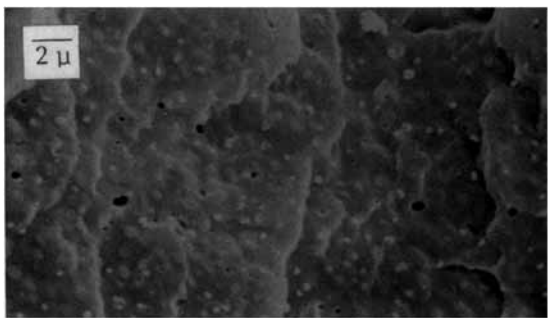
PP/EPM/PE(L)



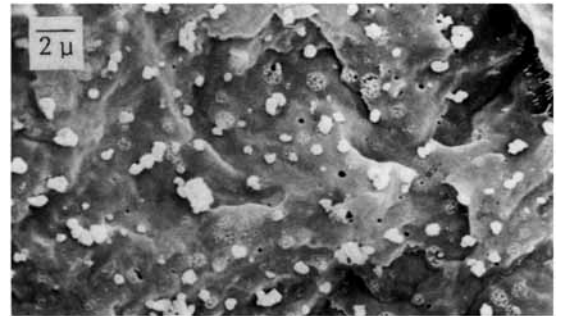
PP/EPDM(H)/PE(H)



PP/EPDM(L)/PE(H)



PP/EPM/CaCO<sub>3</sub>



PP/EPDM(L)/CaCO<sub>3</sub>

**Figure 4** SEM micrographs of the fractured surfaces.

in sample 3. In samples 1 and 2, domain size is similar. In sample 1, EPM may form a continuous phase in binary blends with PE(H); however, due to its higher viscosity, the breakup of the dispersed phase in the final mixing stage should be difficult.

SEM micrographs for filler-loaded samples show that CaCO<sub>3</sub> particles in sample 5 are separately imbedded in the PP matrix, whereas those in sample 6 form agglomerates and show poor wetting by the matrix. Since the chemical affinity of rubber is pre-

sumably greater for PP than for  $\text{CaCO}_3$ , rubber is preferentially dispersed in PP. This is more feasible when the viscosity of rubber is similar to that of PP, as is the case for EPDM(L) (sample 6). On the other hand, the viscosity of EPM is significantly higher than for PP (sample 5), and rubber could be interposed at the PP/ $\text{CaCO}_3$  interfaces to enhance the interfacial adhesion and dispersion as well. To explain the vastly different morphology of samples 5 and 6, analysis based on structure, interfacial energy, etc., is desired.

### Thermal Properties

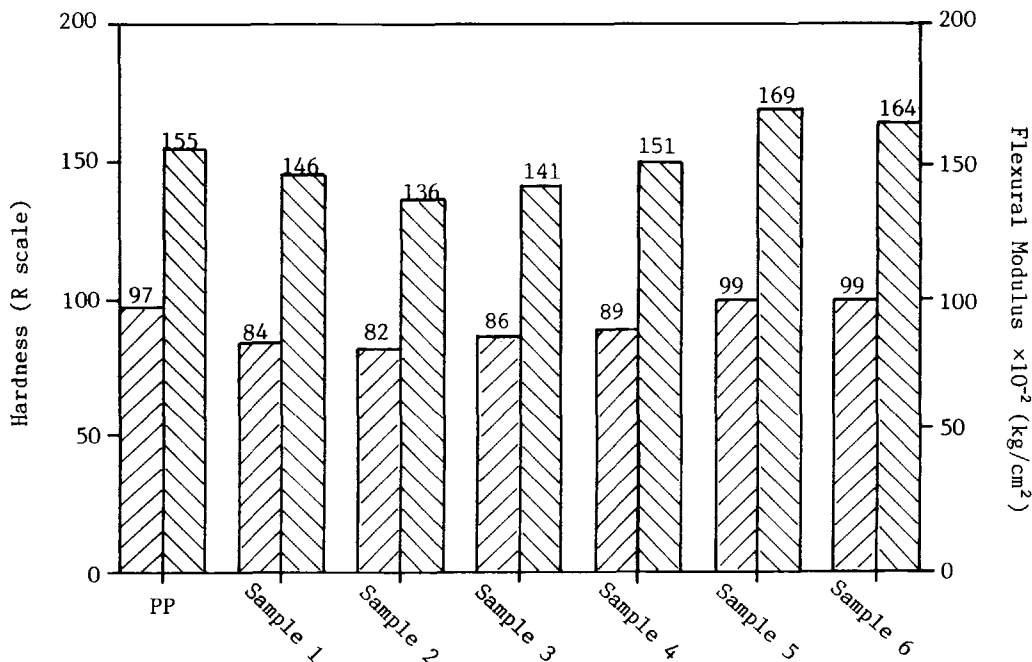
Thermal properties of the samples, determined from DSC, are summarized in Table II. The melting peak temperature ( $T_m$ ) of PE in samples 1–4 is lower than that of the homopolymer by approximately 4–5°C. However, the  $T_m$  decrease of PP in the blends is insignificant. This clearly indicates that rubber is more intensively mixed with PE than with PP or that PE is preferentially dispersed in the rubber domain. The  $T_m$  decrease of PE is accompanied by a reduced heat of fusion ( $\Delta H_f$ ) in the blends except for sample 4, where  $\Delta H_f$  of PE increased in the blend. When one compares samples 1 and 2, and samples 3 and 4, samples 2 and 3 show more reduction in  $\Delta H_f$  than do samples 1 and 4, respectively. More reduction in the total crystallinity content of sam-

ples 2 and 3 indicates intimate mixing in these samples, as evidenced from the SEM micrographs.  $T_{cc}$  peaks of PE and PP were not resolved in the DSC thermogram in samples 1–4.

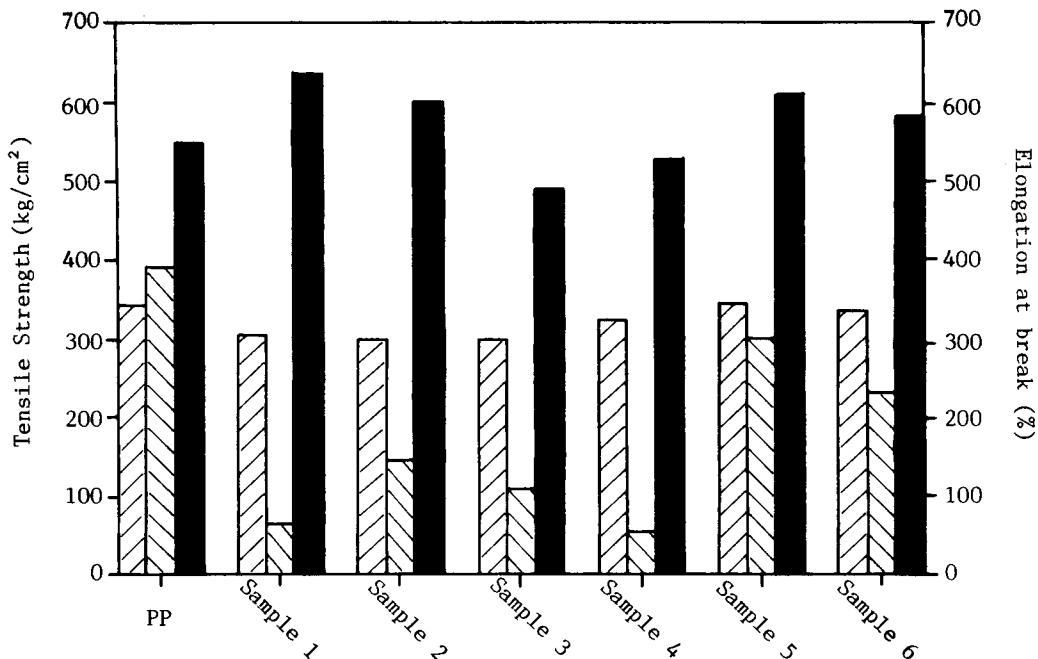
In PP/rubber/ $\text{CaCO}_3$  composites, the crystallinity content ( $\Delta H_f$ ) of PP is significantly increased due to the nucleating effect of  $\text{CaCO}_3$ . The increase of total crystallinity is not necessarily driven by the increased rate of crystallization. However, in the PP/rubber/ $\text{CaCO}_3$  system,  $\Delta H_f$  and  $T_{cc}$  simultaneously increased.

### Mechanical Properties

Figure 5 shows the hardness and flexural modulus of the samples. In samples 1–4, hardness and flexural modulus are lower than those of PP, due to the rubber inclusion. However, comparisons between samples 1 and 2, and samples 3 and 4, indicate that the worsening of these properties have, more or less, been effectively suppressed in samples 1 and 4, respectively. Since these properties are governed mainly by the crystallinity content of the polymer, morphologies and thermal data should properly explain the results. In short, reticulate morphology of the dispersed phase and relatively large values of  $\Delta H_f$  measured for samples 1 and 4 should account for this. Addition of  $\text{CaCO}_3$  to PP/rubber binary blends gave values of hardness and modulus greater



**Figure 5** Hardness and flexural modulus for ternary systems: (▨) hardness; (▩) flexural modulus.

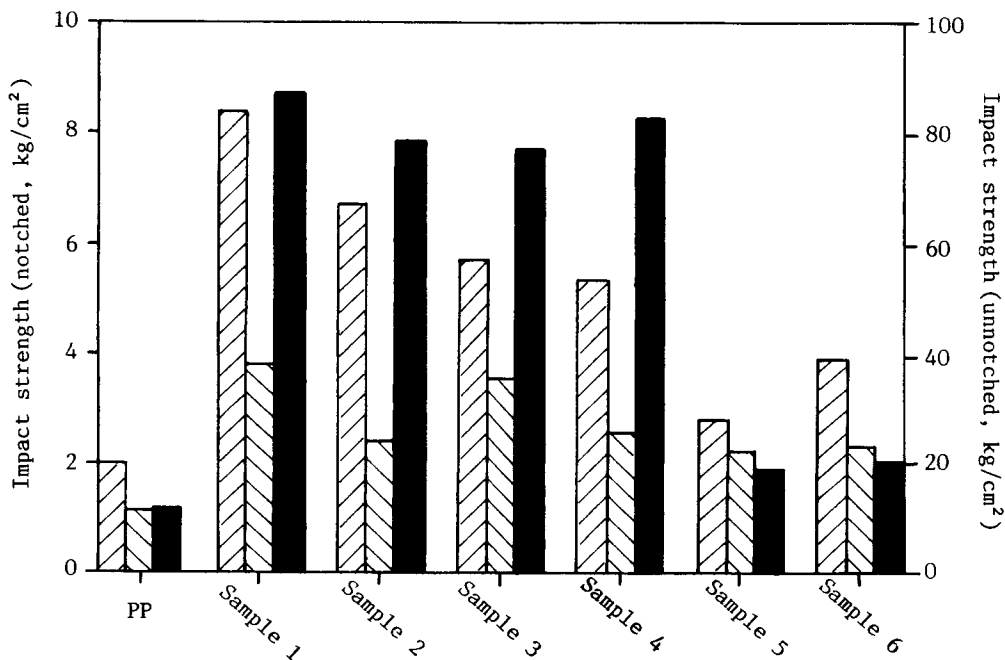


**Figure 6** Tensile properties for ternary systems: (▨) yield strength; (▩) break strength; (■) elongation at break.

than those of PP. This is due mainly to the presence of the hard particle, as well as a nucleating effect of CaCO<sub>3</sub>.

Figures 6 and 7 show the tensile properties and impact strength of the samples. It is seen that the

drops in break strengths due to the rubber inclusion have significantly been compensated by adding CaCO<sub>3</sub>. Addition of rubber to the PP matrix is primarily aimed to increase the impact strength via stress concentration, leading to multiple crazing and



**Figure 7** Impact strengths for ternary systems: (▨) notched at 23°C; (▩) notched at -10°C; (■) unnotched at -10°C.

yielding. This is clearly demonstrated in Figure 7. It is also of interest to note that the PE crystallinity in the rubbery domain does not give effects on impact strength. This may imply that the outer layer or the dispersed domain is effectively surrounded by rubber.<sup>16</sup> Filler particles facilitate the initiation of local crack and reduce the matrix fraction that covers plastic deformation during the fracture.<sup>15</sup> Therefore, filler reduces and rubber raises the impact strength of the ternary systems. For the systems under investigation, the effect is positive.

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