

Dynamic Mechanical and Mechanical Properties of Polypropylene/Poly(vinyl butyral)/Mica Composites

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ABSTRACT: Three-component composites consisting of polypropylene (PP) matrix, poly(vinyl butyral) (PVB) modifier, and mica filler at various ratios of matrix to modifiers and a constant mica content (30 wt %) were prepared by using two different kinds of PVB, viz., PVB and PVB-P. By correlating with the morphology, the dynamic mechanical and mechanical properties of the composites are studied in detail. PVB component in PP/PVB/mica composites cannot display a reinforcing effect to PP/mica binary composites, while impact strength of the composites are reduced further. It associates with incompatibility between PP and PVB, and as well as higher glass transition temperature of PVB. For PP/PVB-P/mica composites, stiffness decreases and, meanwhile, impact strength increases when PVB-P content is 7 wt %. The improvement of impact strength on PP/mica binary composites at the composition is due to a little affinity between the PP matrix and the plasticizer of PVB-P. Moreover, a minor amount of PP-g-MA in the 63/7/30 PP/PVB/mica composites only acts as an adhesion promoter.
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Key words: polypropylene/poly(vinyl butyral)/mica composites; dynamic properties; mechanical properties

INTRODUCTION

Polypropylene(PP)/mica binary composites have shown interesting performance improvement on PP; an addition of mica to PP increases stiffness,^{1–7} improves the chemical resistance, dimensional stability, and reduces the gas diffusivity of the resulting composites.^{5,8} However, the lowering of impact strength of the binary composites^{1,2} is a major problem in the application of the material. To improve toughness of PP/mica binary composites, some investigations have been done. One of the investigations was where a silane coupling agent was used in the system to get good interfa-

cial interaction between PP and mica. The result indicated that although the use of coupling agents improves tensile strength and modulus, the impact strength of the composites was poor,^{2,9,10} or changed very little with mica.¹¹ Wen-Yen Chiang et al.¹² developed the PP/mica composites with a diffuse interlayer between the matrix and the mica. The interlayer was created by the silane and acrylic acid (AA) treatment of the filler and the chemical modification of the polymer components; however, the impact strength of the composites was improved slightly only at high AA content. Another often-used method is the modification of the matrix by grafting or blending. Polypropylene can be grafted with acrylic acid, acrylic esters, or maleic anhydride^{13–15} to improve the interaction in composites. On the basis of the fact that the impact strength of unfilled polypropylene may be improved substantially by blending

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with ethylene-propylene monomer (EPDM) rubber, Faulkner¹¹ developed a family of rubber-toughened, mica-filled polypropylene composites by using EPDM as an impact modifier.

In this article, dynamic mechanical and mechanical properties of polypropylene(PP)/poly(vinyl butyral)(PVB)/mica ternary composites with 30 wt % mica content are studied using two different kinds of PVB, viz., PVB and PVB-P. The aim of the present work is to study the effect of two kinds of PVB and as well as minor quantities of PP-*g*-MA on the mechanical properties of mica-filled polypropylene by means of a dynamic mechanical analysis and an observation of SEM micrographs of the composites, in order to balance impact resistance and stiffness.

EXPERIMENTAL

Materials

In this work, polypropylene used is an ethylene-propylene block copolymer from Borealis Co. with the following specification: ethylene content in the copolymer: 6–13 wt %, molecular weight distribution (M_w/M_n): 780,000/85,000, melt flow index (MFI at 230°C): 0.50 g/10 min.

Poly(vinyl butyral) (PVB) is a terpolymer consisting of 80 wt % poly(vinyl butyral), 17–20 wt % poly(vinyl alcohol), and 0–2.5 wt % poly(vinyl acetate). Plasticized poly(vinyl butyral) (PVB-P) is soft PVB containing 25 wt % plasticizer. Both materials are from Monsanto Co. Polypropylene grafted with maleic anhydride(PP-*g*-MA) is from Eastman Chemical Co. MA content in PP-*g*-MA is 8–10 wt %, and molecular weight distribution (M_w/M_n) for the resin is 9100/3900.

An untreated (Mica 40) grade of phlogopite mica was supplied by Kemira Pigments Oy. The mica was highly delaminated into thin flakes, with an average diameter of 40 μm . Density of the mica was 2.8 g/cm³.

Sample Preparation

PP/PVB/mica ternary composites with 30 wt % mica content were made by melt-mixing PP, PVB (or PVB-P), and mica, in the requisite ratios, in the twin-screw extruder (Berstorff ZE 25*33D) at a screw speed of 160 min⁻¹ and a temperature zone (from feeding zone to the die): 250, 250, 230, 225, 215, 215, and 215°C. The specimens for tensile, bending, and impact test were injection

molded (the injection molding machine: Engel ES 240/65 ST CC 80; the barrel temperatures: 220, 235, 245, and 250°C; the mold temperature: 50°C).

Measurements

Tensile and flexural properties and Charpy notched impact strength were measured according to the standards ISO 527, ISO 178, and ISO 179, respectively. The testing above were performed at room temperature (25°C).

Dynamic mechanical properties of the composites were measured by a dynamic mechanical thermal analyzer (Polymer Laboratories DMTA MkII) at fixed frequencies of 1, 3, and 10 Hz and a heating rate of 2°C min⁻¹ from -80 to +160°C.

Morphology of the fracture surfaces of the composites was examined with scanning electron microscopy (JEOL T100).

RESULTS AND DISCUSSION

Effect of PVB

Table I shows the effect of PVB on mechanical properties of PP/PVB/mica composites with 30 wt % mica content. It can be seen that PVB does not display a reinforcing effect to PP/mica binary composites because of no obvious change in tensile and bending strength and modulus with PVB content, whereas addition of PVB results in further deterioration of impact strength of PP/mica binary composites. The impact strength decreases gradually as PVB content in the ternary composites increases. Figure 1 displays SEM micrographs of a fracture surface of the composites. It is evident that the surface of mica in PP/mica binary composites is clean, indicating that an adhesion between PP and mica in the binary composites is poor. However, the mica flakes in the binary composites were not pulled out of the the matrix when the specimen broke. In PP/PVB/mica ternary composites, the mica flakes coated by the PVB disperse separately in the matrix. Although the coating layer of PVB on surface of the mica flakes appears to be thicker, the coated flakes were also pulled out of the matrix, and plastic deformation of the matrix obviously reduced. It also suggests poor adhesion between PP and mica flakes coated by the PVB. Figure 2 shows storage modulus E' and loss tangent $\tan \delta$ as a function of temperature at 1 Hz for the PP/mica binary and PP/PVB/mica ternary composites. In

Table I Effect of PVB on Mechanical Properties of the Composites with 30 wt % Mica Content

PVB Content (wt %)	Tensile Strength (MPa)	Tensile Modulus (GPa)	Bending Strength (MPa)	Bending Modulus (GPa)	Impact Strength (kJ/m ²)
0	25.2 ± 0.2	5.0 ± 0.7	44.8 ± 0.8	3.2 ± 0.2	9.5 ± 0.3
3.5	27.9 ± 0.2	4.9 ± 0.1	46.7 ± 0.6	3.2 ± 0.1	6.7 ± 0.2
7	26.9 ± 0.2	4.4 ± 0.5	46.5 ± 0.5	3.1 ± 0.1	6.5 ± 0.7
14	26.8 ± 0.1	4.9 ± 0.2	46.8 ± 0.5	3.3 ± 0.1	4.8 ± 0.1

the binary composites, the β_1 relaxation corresponding to the segment motion of an ethylene block and the α relaxation associating with the crystalline region for the copolymer matrix both are hardly discerned because of an addition of mica. Thus, only one relaxation, viz., the β_2 relaxation of the matrix, which attributed to the segment motion of a propylene block, obviously occurs in the $E'-T$ and $\tan \delta-T$ curves. Whereas the ternary composites exhibit two obvious relaxations in

the $E'-T$ and $\tan \delta-T$ curves, new ones at a higher temperature must correspond to the glass transition of the PVB component. As PVB concentration in the composites increases, a peak height of the β_2 relaxation of the matrix reduces and the one of PVB enhances. However, the peak temperature of the two relaxations, viz., T_{g2PP} and T_{gPVB} does not change with PVB concentration (as shown in Table II), indicating that the PP is incompatible with the PVB.

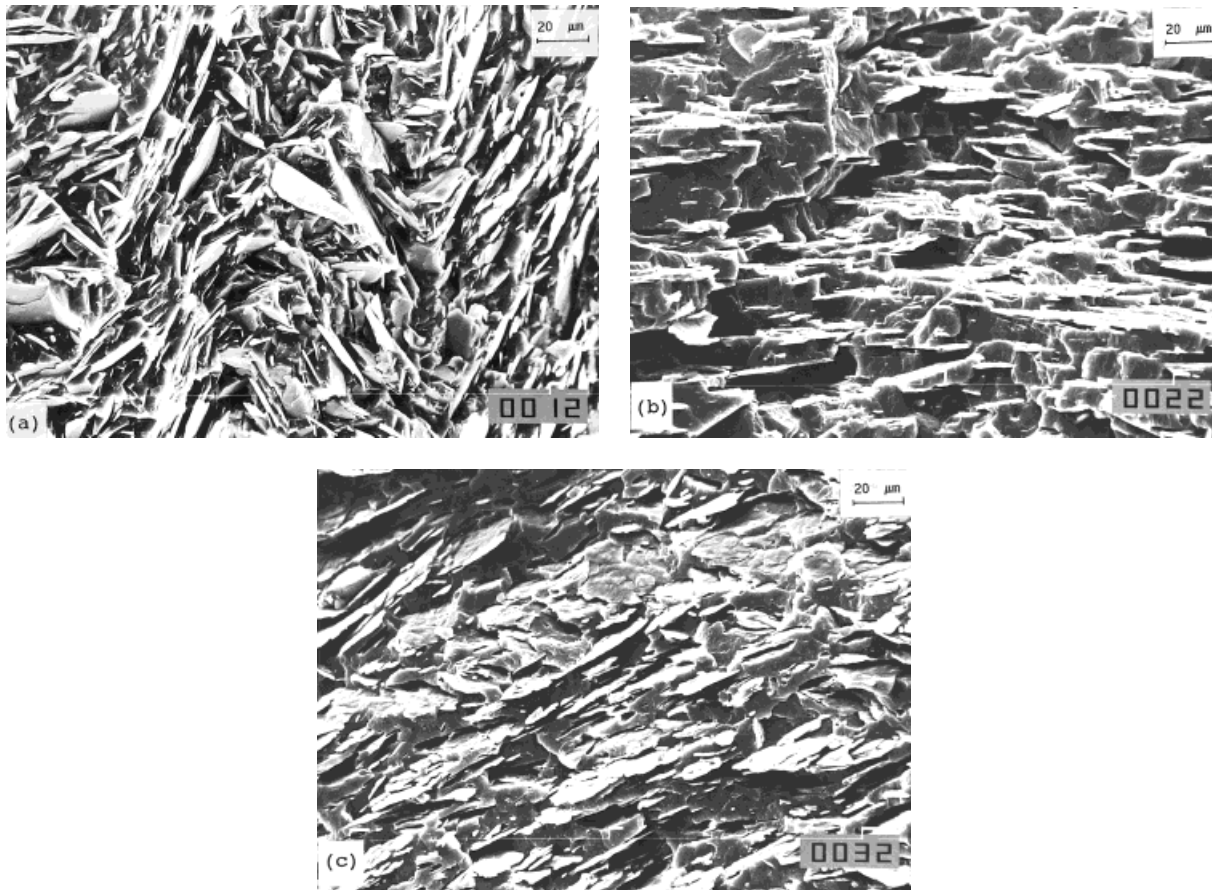


Figure 1 SEM micrographs of PP/PVB/mica composites at various PVB contents (wt %): (a) 0; (b) 7; (c) 14.

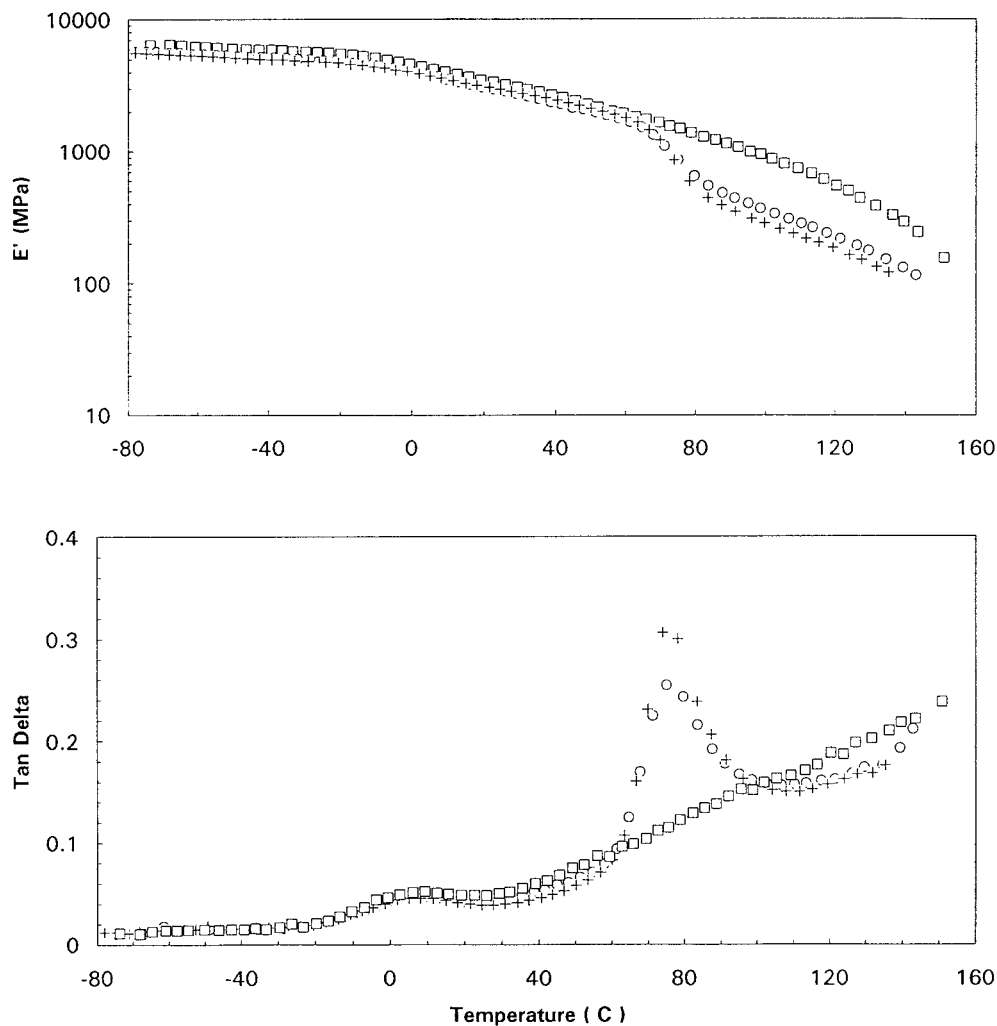


Figure 2 E' and $\tan \delta$ as a function of temperature for PP/PVB/mica composites at 1 Hz and varying PVB content (wt %): (\square) 0; (\circ) 7; (+) 14.

In light of the observation of SEM, and the analyses of dynamic mechanical and mechanical properties for the composites, the role of PVB component in the ternary composites can be reasonably discussed. The PVB is a polar terpolymer that consists of 80 wt % poly(vinyl butyral), 17–20 wt % poly(vinyl alcohol) and 0–2.5 wt % poly-

(vinyl acetate). The annexed polar groups of PVB molecular chains make strong interaction between PVB and mica; thus, mica was well bonded by the coating layer of PVB. On the other hand, PP is a nonpolar polymer; the difference in the structure between PP and PVB leads to incompatibility of PP with PVB (same as the analysis in

Table II Effect of PVB Content on $T_{g2\text{PP}}$ and $T_{g\text{PVB}}$ of the Composites

PP/PVB/Mica	$T_{g2\text{PP}}$ (°C)			$T_{g\text{PVB}}$ (°C)		
	10 Hz	3 Hz	1 Hz	10 Hz	3 Hz	1 Hz
70/0/30	11.4	10.3	7.7			
63/7/30	11.5	9.0	6.5	82.2	79.1	75.0
56/14/30	12.2	9.4	8.1	82.1	77.6	73.9

the dynamic mechanical properties) and, hence, poor adhesion between the PP and the coated mica (as shown in the SEM micrographs). Thus, the layer of PVB with a higher glass transition temperature (about 80°C) and poor adhesion between PP and the coated mica does not favor relieving some stresses by deforming, even though it diminish property gradient relative to PP/mica interface more or less. Consequently, the impact strength decreases with increasing PVB concentration.

Moreover, Figure 2 also shows variation of storage modulus of the composites with PVB content. Storage modulus E' slightly reduces with an increase of PVB content in a temperature region between -80 and the β_2 relaxation of the matrix, while, in a temperature region between the β_2 relaxation and 20°C (before relaxation of PVB), $E'-T$ curve of 56/14/30 PP/PVB/mica composites locates between the two curves of 70/0/30 PP/PVB/mica and 63/7/30 PP/PVB/mica composites. After the relaxation of PVB, E' values of PP/PVB/mica ternary composites decrease notably compared with the PP/mica binary composites. Before relaxation of PVB in the dynamic mechanical spectra, the phenomenon may be due to the mismatch in the thermal expansion coefficients of the components.¹⁶ The mismatch causes the PVB near the surface of the filler particle to be subjected to strong tensile force in the tangent direction; consequently, the modulus of the composites is less than what is expected. However, when the temperature is near to the glass transition temperature of PVB, the tensile force subjected disappears in some degree because of a molecular relaxation. Therefore, the more obvious the increasing of modulus in the temperature range, the higher PVB concentration in the composites. The obviously decreasing of storage modulus for the ternary composites above the glass transition temperature of PVB assigns to softening of the coating layer of mica.

Effect of PVB-P

The mechanical properties of PP/PVB-P/mica ternary composites at various PVB-P contents (wt %) are shown in Table III. Tensile and bending strength and modulus of the composites decreases as the PVB-P content increases; this is due to a low tensile and bending strength of the PVB-P, whereas a variation of impact strength with PVB-P content is different from the one of the tensile and bending strength and modulus. Maximum impact strength of the composites occur when PVB-P content is about 7 wt %. It should note that the impact strength decreases with an increase of PVB-P content from 0 to 3.5 wt %, then increases with an increase of PVB-P content from 3.5 to 7 wt %, and decreases again as PVB-P content increases further. SEM micrographs of PP/PVB-P/mica composites are shown in Figure 3. When PVB-P content in the composites is 3.5 wt %, mica flakes coated by the PVB-P separately disperse in the matrix. Separately dispersed mica flakes disappear when PVB-P content in the composites is 7 and 14 wt %, demonstrating that PVB-P encapsulates mica flakes. Figure 4 and Table IV show dynamic mechanical data of PP/PVB-P/mica composites. It is very clear that 66.5/3.5/30 PP/PVB-P/mica composites exhibit lower T_{g2PP} (the peak temperature for the β_2 relaxation of PP component in the composites) compared with one of PP/mica composites, and much higher T_{gPVB-P} (the peak temperature for the glass transition of PVB-P component in the composites) compared with one of pure PVB-P. As PVB-P content in PP/PVB-P/mica ternary composites increases, the β_2 relaxation of the PP component drifts to the higher temperature, viz., T_{g2PP} increases slightly; on the other hand, the glass transition of the PVB-P component shifts to the lower temperature, viz., T_{gPVB-P} decreases and tends to that of pure PVB-P.

The PVB-P is a soft plastic because of an addi-

Table III Effect of PVB-P on Mechanical Properties of the Composites with 30 wt % Mica Content

PVB-P Content (wt %)	Tensile Strength (MPa)	Tensile Modulus (GPa)	Bending Strength (MPa)	Bending Modulus (GPa)	Impact Strength (kJ/m ²)
0	25.2 ± 0.2	5.0 ± 0.7	44.8 ± 0.8	3.2 ± 0.2	9.5 ± 0.3
3.5	24.2 ± 0.1	3.4 ± 0.1	41.7	3.1	6.4 ± 0.5
7	23.4 ± 0.2	2.8 ± 0.2	40.1 ± 0.3	2.6 ± 0.1	11.4 ± 0.5
14	21.8 ± 0.1	3.3 ± 0.6	36.9 ± 0.3	2.5 ± 0.1	6.5 ± 0.1

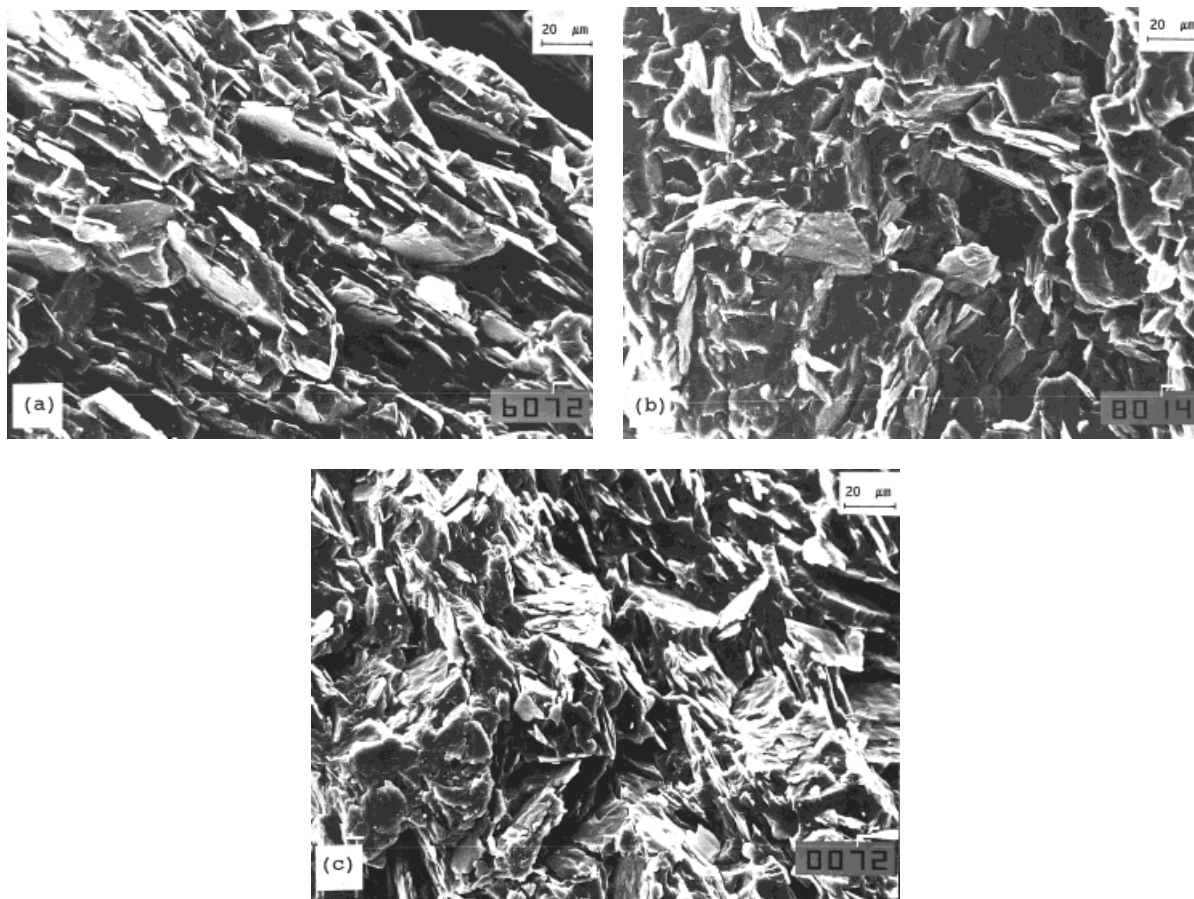


Figure 3 SEM micrographs of PP/PVB-P/mica composites at various PVB-P contents (wt %): (a) 3.5; (b) 7; (c) 14.

tion of a plasticizer. In PVB-P, polar groups of PVB and the plasticizer can produce interaction with mica; hydrocarbon groups of the plasticizer has a little affinity with PP. It was not found that there is loss of PVB-P plasticizer during blending. However, it is worth noting that the plasticizer of the PVB-P in the processing temperature may migrate into the PP phase during preparation of the composites, which is one of the important factors that affect dynamic mechanical and mechanical properties of PP/PVB-P/mica composites. When PVB-P content in PP/PVB-P/mica composites is 3.5 wt %, only a thin coating layer of PVB-P exists on the surface of mica; because of low PVB-P content (as shown in Fig. 3), it is easy for the plasticizer of the layer to migrate into the PP phase. The notably increase of $T_{g\text{PVB-P}}$, which is close to $T_{g\text{PVB}}$, and as well as the lowering of $T_{g2\text{PP}}$ (which also is an indication of no loss of PVB-P plasticizer during blending) suggest that there is almost no plasticizer in the layers at the blend composition; thus, the layer is similar to one of

PP/PVB/mica composites. The morphology of the composites should result in the decreasing of impact strength. The mica flakes were encapsulated by PVB-P when PVB-P content in the composites is 7 wt %, thus forming a thick interlayer between the matrix and the filler and, hence, restraining the migration of plasticizer to some degree, so that the two relaxation peaks shift inward in the dynamic mechanical spectra of the composites. In this case, a little affinity between the matrix and the hydrocarbon groups of the plasticizer in encapsulated particles plays a role in toughening, leading to the improving of impact strength. However, when PVB-P content in the composites is 14 wt % and size of the encapsulated particles is getting larger, the stress concentrator effect of the particles surpasses the influence of the plasticizer on the interfacial interaction between PP and the particle, resulting in the reduction of the impact strength. In addition, variation of the modulus with composition for PP/PVB-P/mica composites and as well as the explanation on the variation

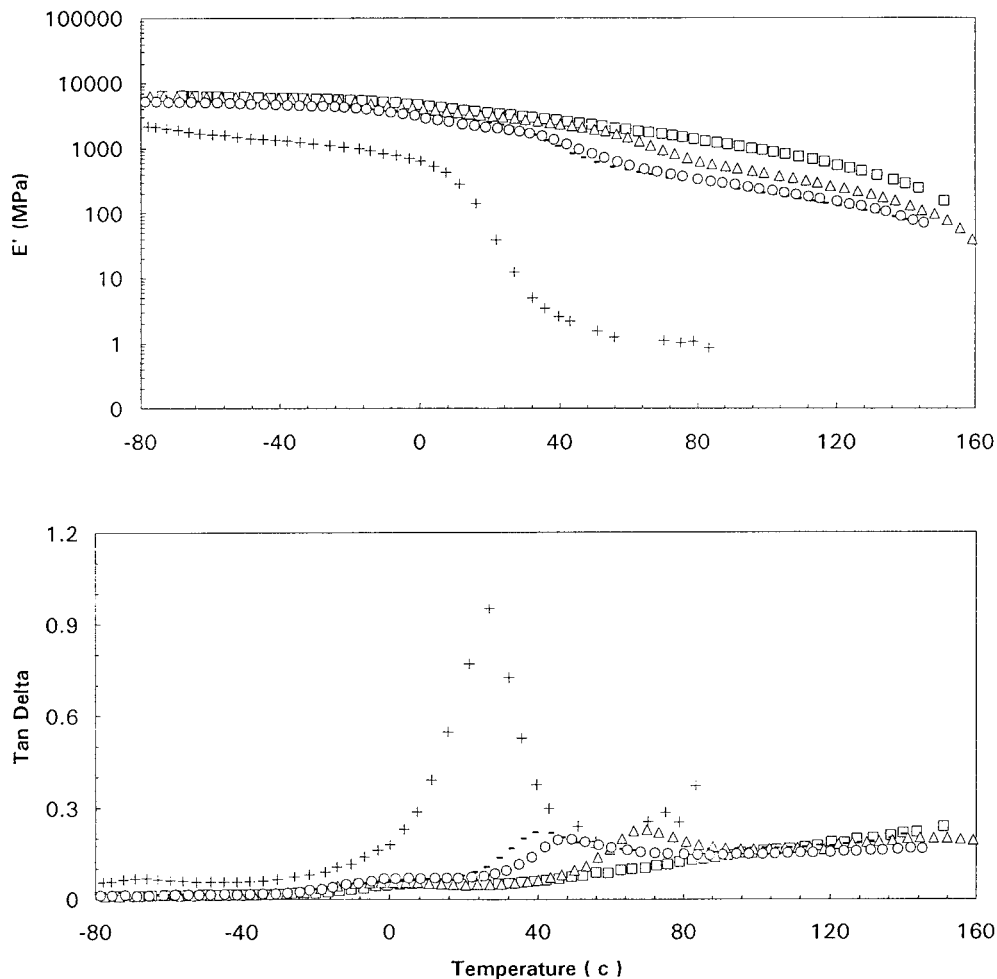


Figure 4 E' and $\tan \delta$ as a function of temperature for PP/PVB-P/mica composites at 1 Hz and varying PVB-P content (wt %): (□) 0; (Δ) 3.5; (○) 7; (+) 14.

are the same as the ones for PP/PVB/mica composites.

Effect of Minor PP-g-MA Component

Table V shows the effect of minor PP-g-MA components on mechanical properties of 63/7/30 PP/

PVB-P/mica ternary composites. It is clear that the minor amount of PP-g-MA in the composites can slightly improve tensile and bending strength and modulus. Nevertheless, the impact strength decreases with increasing PP-g-MA content. Dynamic mechanical data for the composites are demonstrated in Figure 5 and Table VI. Owing to

Table IV Effect of PVB-P Content on T_{g2PP} and T_{gPVB-P} of the Composites

PP/PVB-P/Mica	T_{g2PP} (°C)			T_{gPVB-P} (°C)		
	10 Hz	3 Hz	1 Hz	10 Hz	3 Hz	1 Hz
70/0/30	11.4	10.3	7.7	—	—	—
66.5/3.5/30	6.3	3.6	0.9	75.8	72.6	69.9
63/7/30	7.3	4.3	3.4	53.4	50.4	49.3
56/14/30	10.8	9.6	—	45.2	42.2	38.7
0/100/0	—	—	—	—	31.3	26.7

Table V Mechanical Properties of 63/7/30 PP/PVB-P/Mica Composites with Minor Amount of PP-g-MA

PP-g-MA Content (wt %)	Tensile Strength (MPa)	Tensile Modulus (MPa)	Bending Strength (MPa)	Bending Modulus (MPa)	Impact Strength (kJ/m ²)
0	23.4 ± 0.2	2.8 ± 0.2	40.1 ± 0.3	2.6 ± 0.1	11.4 ± 0.5
0.35	24.0 ± 0.3	3.0 ± 0.2	42.2 ± 0.3	2.8 ± 0.1	10.6 ± 0.4
0.70	24.8 ± 0.1	3.5 ± 0.4	43.1 ± 0.3	3.0 ± 0.1	8.2 ± 0.2

addition of 0.35 wt % PP-g-MA, resulting composites display higher storage modulus E' in a temperature range from 40 to 160°C; on the other hand, the β_2 relaxation of the matrix and the glass transition of PVB-P component drifts to a high temperature, respectively. The dynamic mechanical properties of the composites is very consistent

with its mechanical properties. PP-g-MA in the interlayer between the matrix and the filler plays a role in the crosslinking agent because MA groups of PP-g-Ma chains may react with OH groups of poly(vinyl alcohol) in PVB, resulting in hardening of the interlayer. In addition, a propylene segment of PP-g-MA is the same as the one

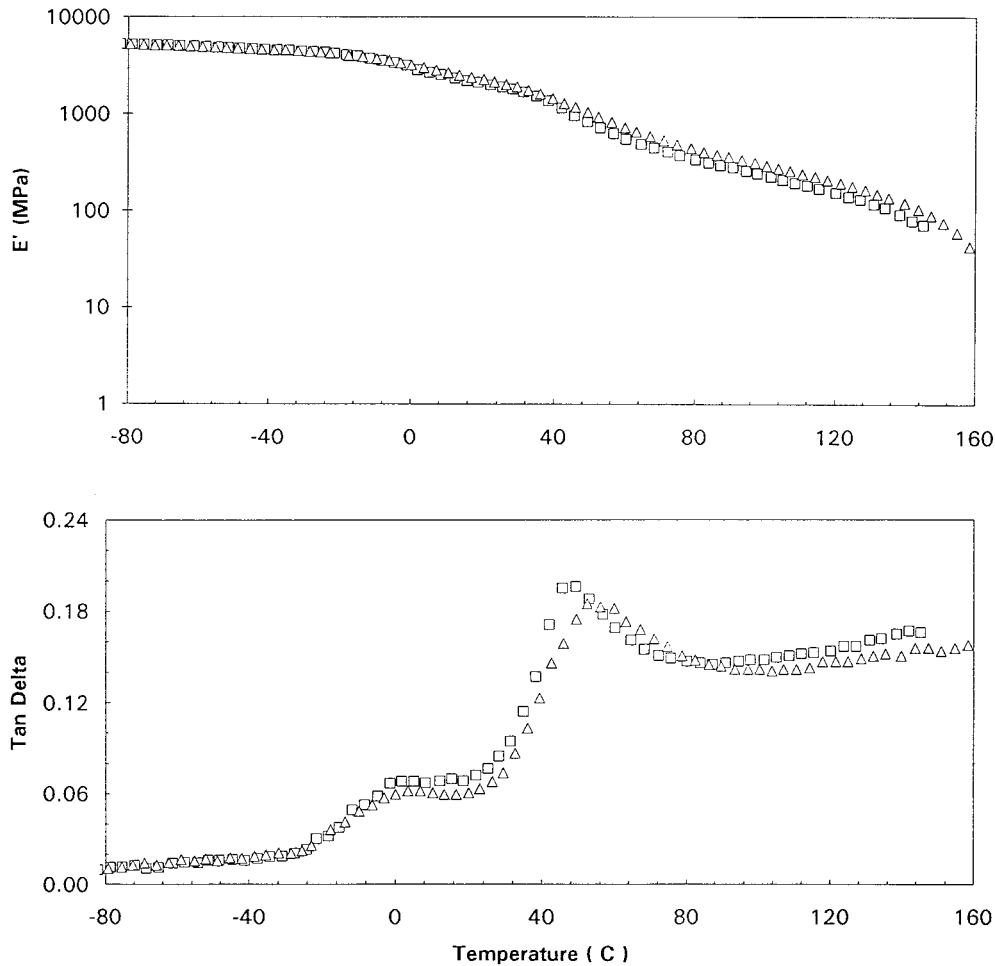


Figure 5 Effect of a minor amount of PP-g-MA on dynamic mechanical properties of 63/7/30 PP/PVB-P/mica composites at 1 Hz: (□) 0 wt % PP-g-MA; (△) 0.35 wt % PP-g-MA.

Table VI Effect of Minor Amount PP-g-MA on $T_{g2\text{PP}}$ and $T_{g\text{PVB-P}}$ of 63/7/30 PP/PVB-P/Mica Composites

PP-g-MA Content (wt %)	$T_{g2\text{PP}}$ (°C)			$T_{g\text{PVB-P}}$ (°C)		
	10 Hz	3 Hz	1 Hz	10 Hz	3 Hz	1 Hz
0	7.3	4.3	3.4	53.4	50.4	49.3
0.35	9.0	6.2	5.0	62.0	55.4	52.4

of PP; thus, minor PP-g-MA slightly increases interaction between the matrix and the filler. The hardening of the interlayer between PP and mica leads to the increase in modulus and the drawback in impact strength of the composites.

CONCLUSIONS

The dynamic mechanical and mechanical properties of PP/PVB/mica ternary composites are studied using polypropylene copolymer as the matrix, poly(vinyl butyral) as the modifier, and mica as the filler, in order to improve the mechanical properties of PP/mica binary composites. In addition, the effect of minor amount of PP-g-MA on mechanical properties of the ternary composites is observed. The following conclusions are obtained:

1. Compared with the binary composites, PP/PVB/mica ternary composites do not display a reinforcing and toughening effect to PP. β_2 relaxation of the matrix and the glass transition of the PVB component in the dynamic mechanical spectra of the ternary composites remain unchanged with the blend composition, and as well as the mica flakes coated by PVB were pulled out of the matrix in the micrographs of the composites, suggesting that PP is incompatible with PVB.
2. Suitable amounts of PVB-P in PP/PVB-P/mica ternary composites can improve the impact strength, whereas the stiffness of the composites reduces. The dynamic mechanical analysis and the observation of the morphology of the composites indicate the improvement of impact properties, which is attributed to a little affinity between PP matrix and the plasticizer of PVB-P.
3. Minor amounts of PP-g-MA in 63/7/30 PP/PVB-P/mica ternary composites slightly improve stiffness, whereas the impact strength of the resulting composites drops due to the addition of PP-g-MA.

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