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2001

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William MacKnight, *University of Massachusetts Amherst*

E. Cascone

Donald J. David

M. L. Di Lorenzo

F. E. Karasz, et al.



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Blends of Polypropylene with Poly(vinyl butyral)

E. CASCONE,¹ D. J. DAVID,² M. L. DI LORENZO,¹ F. E. KARASZ,² W. J. MACKNIGHT,² E. MARTUSCELLI,¹ M. RAIMO¹

¹ Istituto di Ricerca e Tecnologia delle Materie Plastiche (CNR), Via Toiano, 6-80072 Arco Felice (NA), Italy

² Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003-4530

Received 13 December 2000; accepted 3 April 2001

Published online 2 October 2001; DOI 10.1002/app.2149

ABSTRACT: The thermal stability, crystallization behavior, and morphology of poly(vinyl butyral) (PVB) with differing compositions of vinyl alcohol and butyral units were investigated. It was found that the glass-transition temperature of PVB decreases with increasing concentration of butyral units, mainly because of the reduced number of hydrogen bonds between hydroxyl groups of the chains. PVB samples with high vinyl alcohol content ($\geq 63.3\%$ by weight) are crystallizable and present an endothermic melting peak in the range 170–220°C. The thermal stability of PVB is also influenced by composition and increases with the number of butyral units. The thermal and crystallization characteristics of PVB were compared with those of neat polyvinyl alcohol (PVA), and the differences explained in terms of molecular structure. Two amorphous PVB samples, containing 31 and 14 wt % of vinyl alcohol units, respectively, were blended with isotactic polypropylene grafted with maleic anhydride (PP-MA), the latter of which was present to favor compatibilization of the components through chemical reaction or dipolar interactions involving the anhydride groups of the PP-MA and the hydroxyl groups of PVB. Properties of PP-MA/PVB 90/10 blends, prepared by melt extrusion, were compared to those of neat PP-MA. Both the PVBs used were immiscible with PP-MA, as indicated by the invariance of glass-transition temperatures with the composition of the blends. However, a high level of compatibility between the components was achieved because the blends showed good mechanical properties that were comparable to, or even superior to, those of neat PP-MA. The analysis of the crystallization kinetics, performed both in isothermal and nonisothermal modes, showed that crystallization of polypropylene is only slightly influenced by the presence of the PVB phase. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2934–2946, 2001

Key words: blends; thermal properties; poly(vinyl butyral); polypropylene

INTRODUCTION

Poly(vinyl butyral) (PVB) is a derivative of polyvinyl alcohol (PVA), from which it may be obtained by reaction with butyral aldehyde.¹ The reaction is an intramolecular acetalization and involves glycolic groups of PVA in the 1–3 position, according to the following scheme:

Correspondence to: M. Raimo (raimo@irtemp.na.cnr.it).

Contract grant sponsor: Air Force Office of Scientific Research (AFOSR); contract grant number: 98-001.

Journal of Applied Polymer Science, Vol. 82, 2934–2946 (2001)
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Table I Codes, Composition, Crystalline Content, and Glass-Transition and Melting Temperatures of PVB Samples

PVB Sample No.	Vinyl Alcohol Content			X_c (%)	T_g (°C)	T_m (°C)
	Wt %	Mol %	Volume Fraction			
14	14.2	34.8	0.12	—	71	—
23	22.9	48.9	0.19	—	73	—
25	24.8	51.4	0.21	—	73	—
28	28.0	55.7	0.24	—	76	—
31	31.0	59.1	0.27	—	78	—
33	32.9	61.1	0.29	—	78	—
36	36.4	64.8	0.32	—	78	—
45	45.1	72.6	0.40	—	80	—
50	49.8	76.0	0.45	—	81	—
55	55.0	79.8	0.50	—	81	—
63	63.3	84.8	0.59	16	83	171
69	69.5	88.0	0.65	20	83	205
89	89.0	96.3	0.87	57	86	218

provided by Montell, Ferrara, Italy). It has a melt flow index of 50 g/10 min (Montell data).

Blends of PP-MA/PVB 90/10 (wt %) were obtained by extrusion at 210°C at a pressure of 5×10^5 Pa. Two PVB samples, PVB 31 and PVB 14, were used. The extruded materials were cooled with distilled water and dried in a vacuum oven for 24 h at 60°C. Small pieces (3–4 mm length) of the materials were compression molded to sheets of 1 mm thickness under the following conditions: $T = 200^\circ\text{C}$, $p = p_{\text{atm}}$ for 3 min; $T = 200^\circ\text{C}$, $p = 2 \times 10^7$ Pa for 1 min. Finally, dumbbell-shape specimens for tensile tests were cut from the sheets.

Films of 0.06 mm thickness for dynamic mechanical tests were obtained using the same conditions.

Procedures and Techniques

The thermal stability of PVB samples was measured by thermogravimetric analysis, using a TC 10A Mettler instrument, equipped with an M3 analytical thermobalance (Mettler-Toledo Inc., Columbus, OH). Each sample was heated from 40 to 600°C at a scan rate of 5°C/min in air.

Thermal analysis was performed under nitrogen by using a Mettler TA-3000 differential scanning calorimeter, equipped with a control and programming unit and a calorimetric cell. The apparatus was calibrated with pure indium, lead, and zinc standards at various scanning rates. Samples of about 15 mg of PVB, PP-MA, and their blends were studied with the following thermal protocol:

- Heating from 30 to 230°C at a scan rate of 10°C/min (Run I).
- Cooling from the melt to -50°C at a scan rate of 50°C/min (Run II).
- Heating from -50 to 230°C at a scan rate of 10°C/min (Run III).

Values of the glass-transition temperature (T_g) were determined from Run III, whereas the melting temperature (T_m) and the fusion enthalpy (ΔH_m) were determined from Run I.

Nonisothermal crystallization of PVB samples, containing high levels of vinyl alcohol units, was performed dynamically, at different scan rates (1, 5, and 10°C/min), by cooling from the melt after holding for 1 min in the molten state.

The isothermal crystallization of polypropylene and PP-MA/PVB blends was carried out with the following thermal protocol:

- Heating to 190°C (or 200°C) at a scan rate of 20°C/min.
- Holding at the upper (190 or 200°C) temperature for 1 min.
- Cooling to selected temperatures to maximize crystallization.

Scanning electron microscopy (SEM) was performed with a Philips 501 SEM (Philips, The Netherlands), after vacuum metallization of the samples by means of a Polaron sputtering apparatus with Au-Pd alloy.

Wide-angle X-ray diffraction analysis was carried out using a Philips diffractometer (PW 1050) operating at the CuK_α radiation. Measurements of diffracted intensities were made in the angular range of $4\text{--}60^\circ$ (2θ), at room temperature and a scan rate of $1^\circ/\text{min}$.

Morphological investigations of the microstructure of the blends and spherulite growth rates were measured by means of a Zeiss polarizing optical microscope (Zeiss, Thornwood, NY) equipped with a Linkam hot stage (Linkam Scientific Instruments Ltd., UK).

To measure the growth rate of PP-MA spherulites, each sample was heated under dry nitrogen from 30 to 200°C at a rate of $30^\circ\text{C}/\text{min}$, held at 200°C for 1 min, then cooled to room temperature at $4^\circ\text{C}/\text{min}$. The radius of the growing crystalline entities was monitored during crystallization by photomicrography at appropriate intervals of time, using a JVC TK-1085E video camera. Spherulite radii were measured with the software Image-Pro Plus 3.0.

An Instron was used to perform room-temperature tensile tests according to ASTM D256 standards. The cross-head speed used was 5 mm/min. All the mechanical parameters were derived by averaging at least six experimental values for each composition.

Dynamic mechanical measurements were carried out by using an MK III dynamic mechanical thermal analyzer (Polymer Laboratories, UK), configured for automatic data acquisition. Parallelepiped-shape specimens ($4 \times 10 \times 0.06$ mm) were used. The experiments were performed in tensile mode with a work frequency of 1 Hz. The temperature range was -100 to 150°C .

RESULTS AND DISCUSSION

Properties of PVBs

Thermogravimetric analysis showed that the thermal stability of PVB copolymers increases as the number of butyral units in the polymer chain increases. The oxidative pyrolyses of PVB 89, PVB 55, PVB 50, and PVB 45, shown in Figure 1, indicate that the sample with the higher vinyl alcohol content starts to degrade at a lower temperature. Thus, PVB 89 undergoes a weight loss of 50% at a temperature 36°C lower than the corresponding value for PVB 45. Therefore it may be stated that the lower the number of hydroxyl groups, the lower the tendency of PVB to decom-

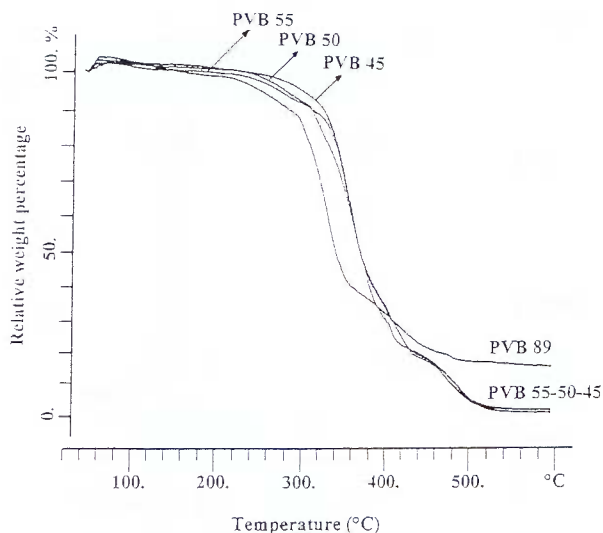


Figure 1 Relative weight of PVB samples as a function of temperature, in the range $40\text{--}600^\circ\text{C}$. The measurements were performed in air at a scan rate of $5^\circ\text{C}/\text{min}$.

pose by water elimination. As a consequence of the increased thermal stability, PVB samples offer, relative to PVA, the advantage of melt processability at higher temperature and/or longer times.

Table I reports glass-transition temperatures of PVBs, obtained by DSC, also as a function of the copolymer composition. The T_g increases with the number of hydroxyl groups, indicating a higher flexibility of the polymer chain containing butyral units compared to that of the polyvinyl alcohol homopolymer. This finding may be attributed both to the plasticization effect of the *n*-propyl groups attached to acetalic rings and to the decrease of the extent of inter- and intrahydrogen bonding.

The composition of PVB copolymers also affects the crystallinity, as shown in Table I. Indeed, only PVBs having a vinyl alcohol content $\geq 63.3\%$ by weight show an endothermic fusion peak and an exothermic crystallization peak on cooling. PVB samples with lower vinyl alcohol contents are essentially amorphous.

The melting temperatures T_m of crystalline samples, determined from the peak maxima, are reported in Table I for PVB 63, PVB 69, and PVB 89. For all the PVB samples the T_m results were lower than that of PVA measured under the same conditions (231°C). The decrease in melting temperature of crystalline samples of PVB with increasing vinyl butyral content indicates a lower

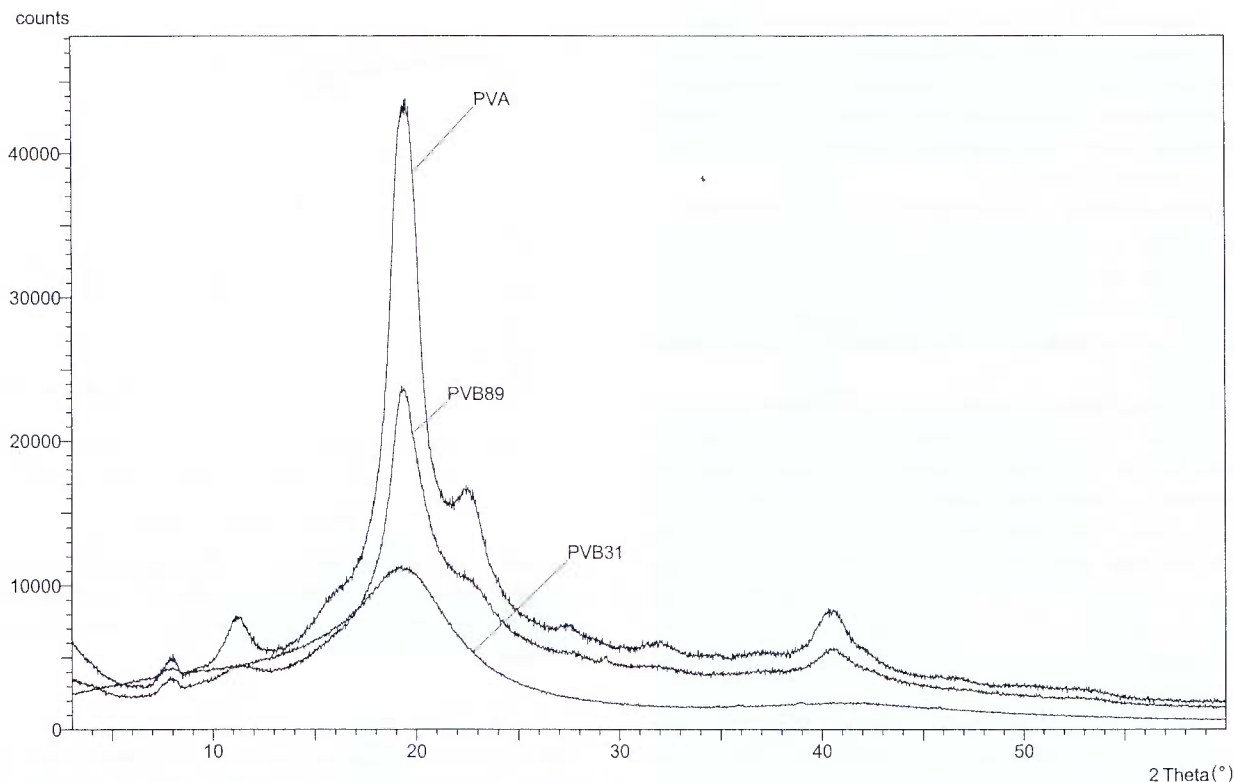


Figure 2 X-ray diffractograms of PVA, PVB 89, and PVB 31.

degree of perfection of crystals and/or different lamellar thicknesses.⁵ Further investigations are needed to discriminate between such hypotheses. Comparing the thermal properties of PVB and PVA, it is possible to conclude that the former should be easier to process. Because of the narrow range between processability and degradation temperatures, PVA is difficult to melt-process. The introduction of acetalic cyclic groups in the PVB copolymer interrupts the chain regularity of the vinyl alcohol sequences and changes their physicochemical characteristics. The glass-transition and melting temperatures are reduced in PVB relative to PVA, causing an improvement in thermal stability and permitting easier melt-processability.

The observed fusion enthalpies obtained from the area of the melting peaks of the PVBs, divided by the theoretical fusion enthalpy per vinyl alcohol units (ΔH_u), taken as 6.98 kJ/mol (143 J/g),⁶ results in crystallinity content ranging from 16 to 57%, as reported in Table I.

X-ray diffractograms of some representative PVB samples are shown in Figure 2. PVBs with high content of butyral units, such as PVB 31, present a broad peak that is not attributable to

crystalline structure. As expected, the bulky butyral units are not able to participate into a crystalline lattice and thus PVB samples with low vinyl alcohol units are substantially amorphous. Conversely, PVB 63, PVB 69, and PVB 89 show sharp and resolved peaks, implying a persistence of the monoclinic structure of PVA.⁷

Thermal and Morphological Investigations of Maleic Anhydride-Modified Polypropylene

The melt temperature T_m , the glass-transition temperature T_g , the fusion enthalpy ΔH_m , and the crystallinity level X_c of the PP-MA sample, obtained by differential scanning calorimeter, are shown in Table II.

The crystallinity X_c was obtained by using a theoretical value⁸ of 190 J/g for the enthalpy of fusion of 100% crystalline maleic anhydride-

Table II Thermal Parameters of PP-MA

T_m (°C)	T_g (°C)	ΔH_m (J/g)	X_c (%)
169	8.5	56	30

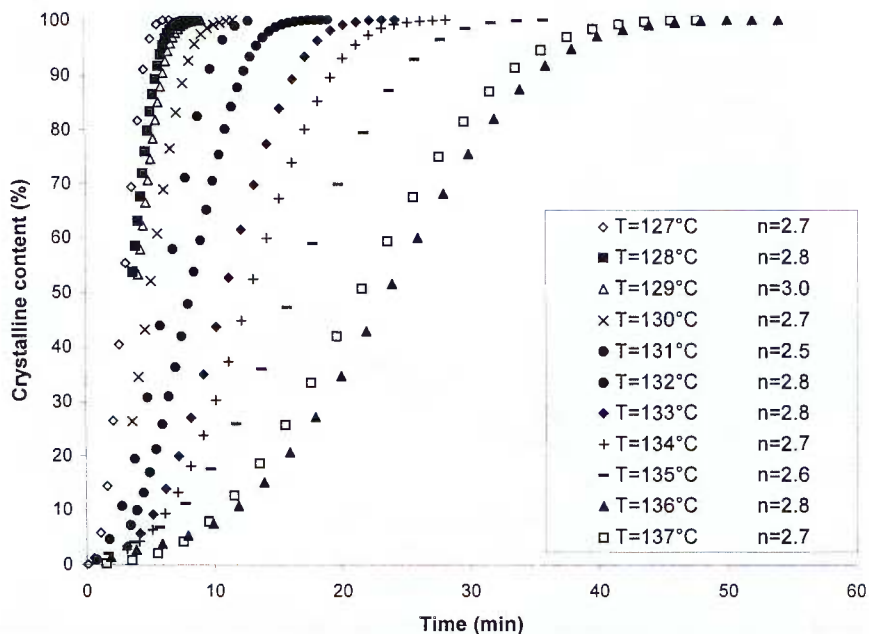


Figure 3 Crystallinity development as a function of time of PP-MA at different temperatures.

modified polypropylene. The rather low crystalline content of the PP-MA sample used here is probably attributable to the influence of polyethylene blocks on the crystallization process of the polypropylene units.

The isothermal crystallization of PP-MA was investigated in the range 127–137°C at two melting temperatures, 190 and 200°C. From the DSC measurements the fraction $X(t)$ crystallized at time t , at constant temperature T_c , was obtained using

$$X(t) = \frac{\int_0^t (dH/dt) dt}{\int_0^\infty (dH/dt) dt} \quad (1)$$

where the numerator is the enthalpy developed during crystallization up to time t , whereas the denominator is the heat generated on complete crystallization. The experimental values can be interpreted by using the following Avrami equation:

$$1 - X(t) = e^{-kt^n} \quad (2)$$

where n gives an indication of the type of nucleation and the geometry of the growing crystals,

whereas the constant k is related to the global crystallization rate v , that includes both nucleation and growth rates, by means of the relationship

$$k = v^n \ln 2 \quad (3)$$

The global crystallization rate is defined as the inverse of the half-transformation time $t_{0.5}$, defined as the time needed to reach half of the final crystallinity; thus eq. (3) can be rewritten in the following way:

$$k = \ln 2/t_{0.5}^n \quad (4)$$

The fraction of PP-MA crystallized as a function of time is shown in Figure 3 at different temperatures, whereas Figure 4 illustrates the dependence of $t_{0.5}$ from the crystallization temperature.

The values obtained for the Avrami parameter n are approximately 3, compatible with an instantaneous nucleation and a spherical geometry of the growing crystals, as evidenced by the optical microscopy analysis discussed later, in agreement with previous results.⁹ As frequently pointed out, nonintegral n values are probably attributable to experimental difficulties in determining the onset time for isothermal crystallization.¹⁰

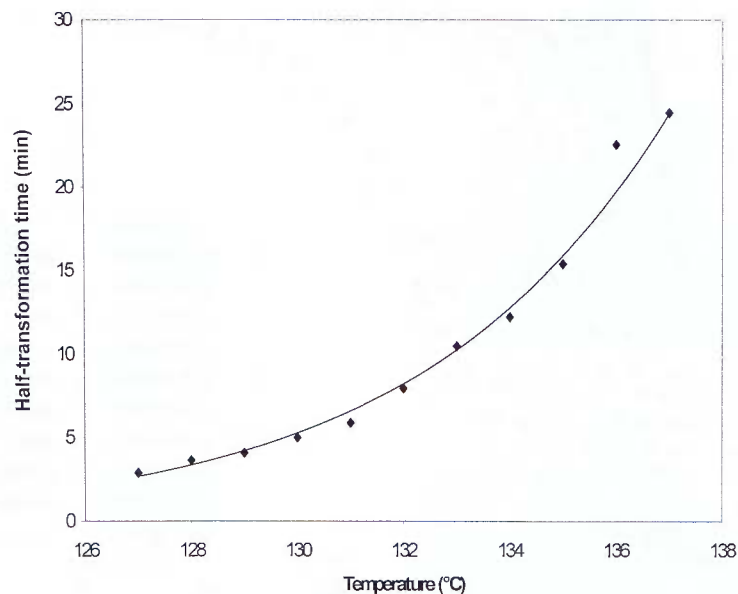


Figure 4 Half-transformation time of PP-MA as a function of crystallization temperature (see text).

PP-MA/PVB Blends

Miscibility

The morphology of PP-MA/PVB 90/10 blends was first observed in the melt state, under a nitrogen atmosphere using an optical microscope. Optical micrographs of PP-MA/PVB blends at 200°C are shown in Figure 5. For both blends, discrete particles homogeneously distributed within the matrix are observable, clearly indicating the presence of two separated liquid phases.

Thermal properties of PP-MA/PVB 90/10 blends are reported in Table III, in which the T_g values correspond to the PVB phase, whereas T_m , ΔH_m , and X_c correspond to the polypropylene matrix.

From DSC experiments only one glass-transition temperature was detected for all the blends, and these values do not differ from the T_g of neat PVB. It was not possible to observe by DSC the T_g of PP-MA in the extruded materials. Besides the constancy of the glass transitions of the blend components, other indications of immiscibility are the invariability of the fusion temperature and the crystallinity level of PP-MA in the blends. Moreover, the presence of PVB only slightly affects the nonisothermal crystallization process of PP-MA. In fact, the PP-MA crystallization peaks in the neat matrix and in PP-MA/PVB 31 blend overlap, whereas the maximum of the crystallization peak of the PP-MA/PVB 14 blend (Fig. 6) is

shifted to higher temperature, indicating a slight reduction of the crystallization rate of PP-MA.

In Figure 7 the trend of $\tan \delta$, obtained by dynamic mechanical analysis (DMA), with temperature for PP-MA and PP-MA/PVB 90/10 blends is shown. Comparison of the curves indicates that the blends exhibit three transitions, almost independent of composition, as expected for immiscible polymers in the amorphous phase. The $\tan \delta$ peaks at higher temperature (87°C for PP-MA/PVB 14 and 84°C for PP-MA/PVB 31, respectively) correspond to the glass transition of PVB, whereas the transitions at 15 and -34°C relate to the PP-MA phase. The peak at 15°C is associated with the glass transition of polypropylene, whereas the transition at -34°C may be attributed to the glass transition of polyethylene blocks in the PP-MA.¹¹

Crystallization Kinetics

The solidification rate of PP-MA/PVB blends was investigated by DSC isothermal crystallization. The half-time of crystallization of PP-MA and blends is exhibited in Figure 8. As found in the nonisothermal crystallization procedures, the crystallization rate of the PP-MA/PVB 31 90/10 blend at constant temperature was very close to that of neat PP-MA, whereas a small decrease is observed in the PP-MA/PVB 14 90/10 blend.



**PP-MA/PVB 31
90/10**

100 μm



**PP-MA/PVB 14
90/10**

Figure 5 Optical micrographs of 90/10 PP-MA/PVB 14 and PP-MA/PVB 31 blends at 200°C.

To clarify the influence of PVB on the crystallization process of PP-MA, spherulite growth rates G of neat PP-MA and of PP-MA/PVB blends were measured during cooling from melt, using a recently described nonisothermal procedure.¹²⁻¹⁴ Briefly, for each sample the radii of the growing spherulites were recorded as a function of temperature and G was calculated by taking the first derivative at each point of the radius versus temperature plot. This

method is more rapid than the conventional isothermal method because, for the latter, each experimental point implies a sequence of radius measurements, whereas the nonisothermal procedure obtains G data over a rather large temperature range with a single experimental measurement. It was also shown that very good agreement exists between data measured by both methods.¹²⁻¹⁴ The spherulite growth rates of neat PP-MA and of PP-MA/PVB 90/10 blends as a function of temperature are shown in Figure 9. On the same plot, spherulite growth rates measured isothermally at 130°C are reported for comparison, to show the reliability of the nonisothermal procedure.

G values of the PP-MA/PVB 31 90/10 blend are very close to those of plain PP-MA, whereas a small decrease in G is observed in the PP-MA/PVB 14 90/10 blend, in agreement with the behavior observed with DSC analysis. In Figure 10 the optical micrographs of the blends isother-

Table III Thermal Parameters of PP-MA/PVB Blends

Blend	T_g (°C)	T_m (°C)	ΔH_m^a (J/g)	X_c (%)
PP-MA/PVB 31	75	168	55	29
PP-MA/PVB 14	74	167	63	33
Neat PP-MA	—	168	58	30

^a Normalized to PP-MA content.

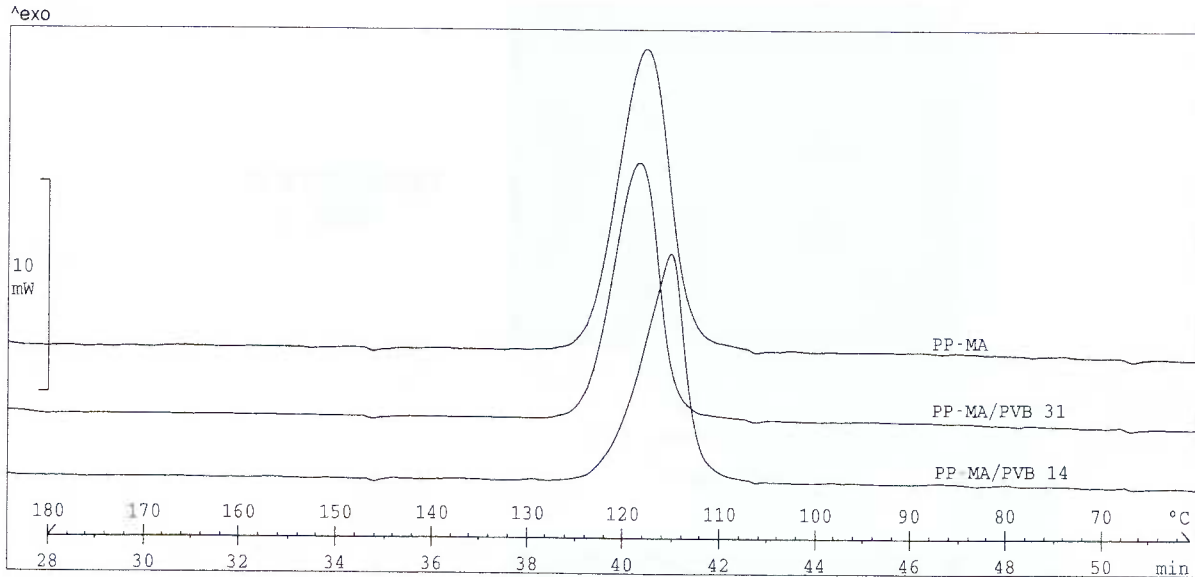


Figure 6 Nonisothermal crystallization peaks of neat PP-MA and PP-MA/PVB blends. Scan rate: 5°C/min.

mally crystallized at 130°C are shown. No significant difference in the morphology of the spherulites is observable and also the number of PP-MA spherulites per unit area (nucleation density)

seems unaffected by the addition of PVB. As the overall nucleation rate depends on the nucleation and radial growth rate and PVB seems to have little or no influence on the nucleation of PP-MA,

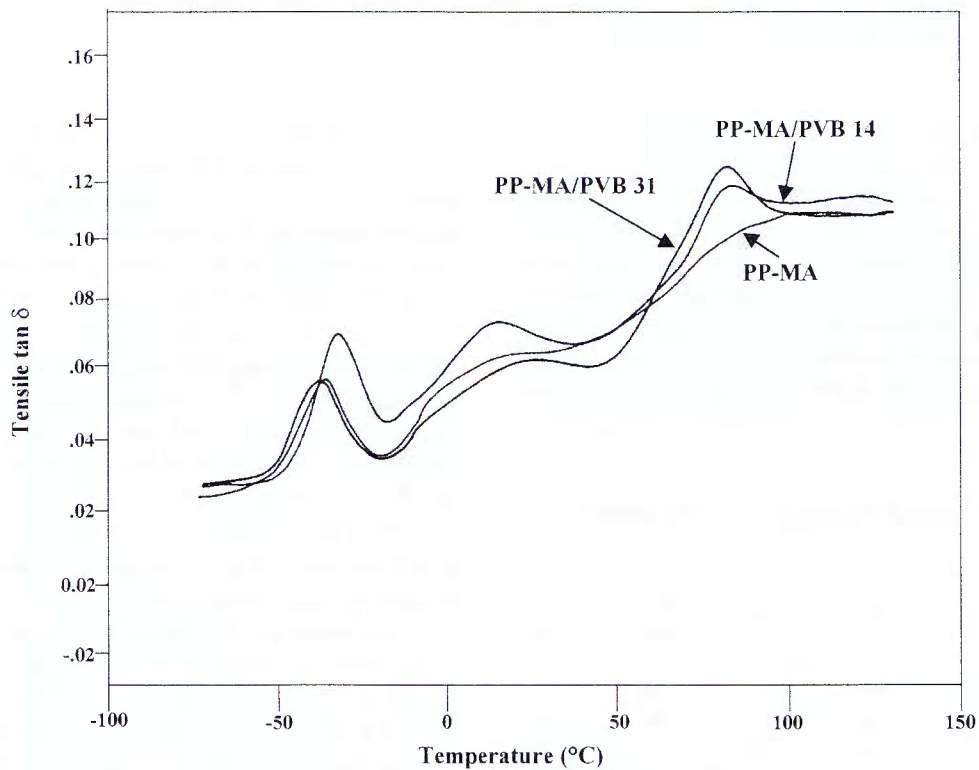


Figure 7 DMA curves for neat PP-MA, 90/10 PP-MA/PVB 14, and PP-MA/PVB 31.

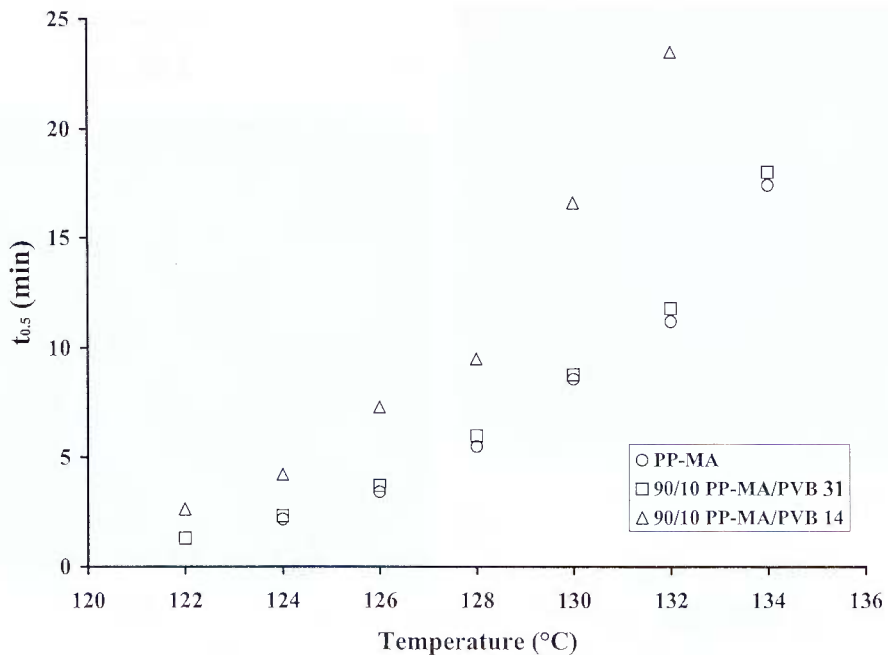


Figure 8 Half-time of crystallization of maleated polypropylene in neat PP-MA, PP-MA/PVB 14, and PP-MA/PVB 31 blends as a function of temperature.

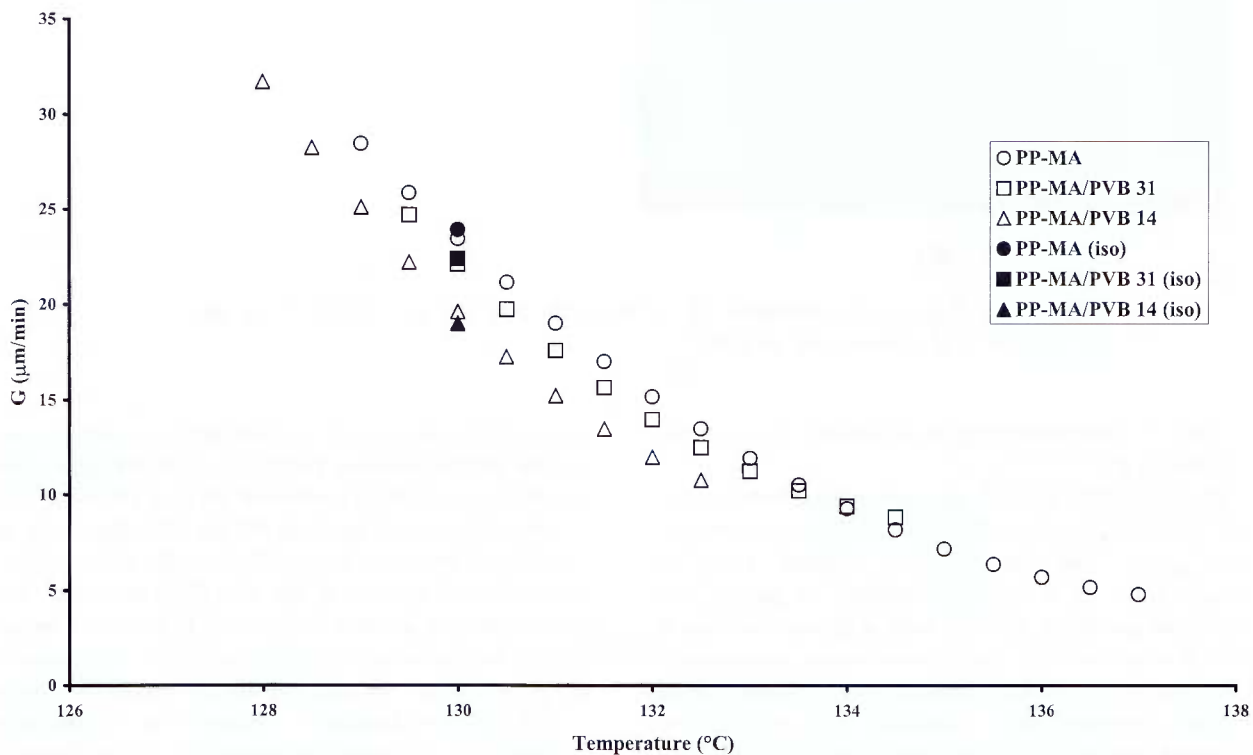


Figure 9 Growth rate of PP-MA spherulites in neat PP-MA, 90/10 PP-MA/PVB 14, and PP-MA/PVB 31.

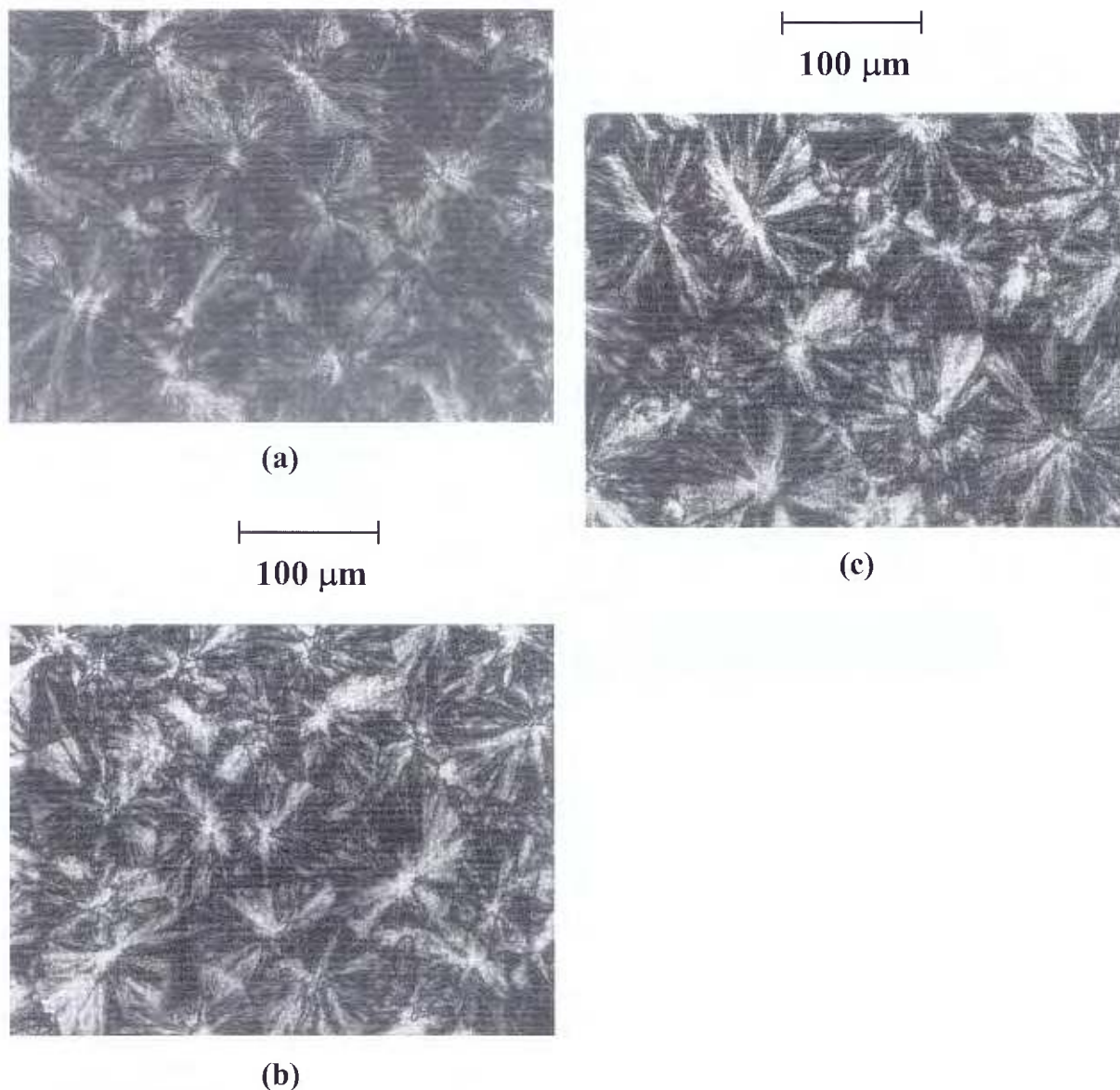


Figure 10 Optical micrographs of (a) neat PP-MA, (b) PP-MA/PVB 14, and (c) PP-MA/PVB 31 crystallized at 130°C.

the global crystallization rate reflects that of the spherulite growth rates.

In immiscible blends an amorphous component may perturb the crystallization of the other component, given that the growing crystals have to change their path to reject and/or to engulf the dispersed particles.^{15,16} In only a few cases has it been found that the noncrystallizable component does not influence the growth rate of spherulites of the crystallizable polymer; the poly((D)-3-hydroxybutyrate)/ethylene-propylene rubber binary blend can be cited as an example.¹⁷ In the present immiscible PP-MA/PVB blends the addi-

tion of PVB also seems to have little or no influence on the crystallization growth rate of PP-MA. The small decrease of G observed for the PP-MA/PVB 14 blend, relative to that of the PP-MA/PVB 31 blend, can probably be ascribed to the difference in thermal conductivity of the two PVB samples. The lower thermal conductivity of PVB 14 could be the reason for the observed decrease of PP-MA spherulite growth rate, as was previously shown for other binary polymer blends.¹⁸ Indeed, if a crystallizing polymer is surrounded by a material of low thermal conductivity, the crystallization rate slows. Comparing literature data, PVA should have a thermal

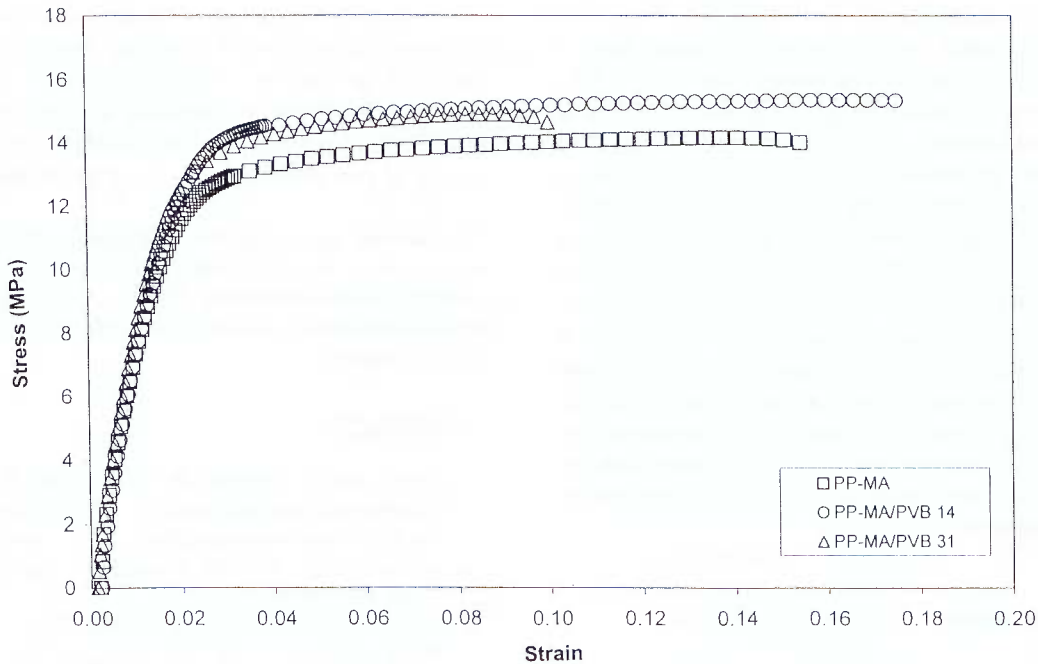


Figure 11 Stress-strain curves of neat PP-MA, 90/10 PP-MA/PVB 14, and PP-MA/PVB 31.

conductivity slightly higher than, or comparable to, that of polypropylene,^{8,19} although this trend is probably inverted for vinyl alcohol-vinyl butyral copolymers (for which no data concerning thermal conductivity are available) with a high percentage of vinyl butyral units.

Tensile Properties

Mechanical properties of crystallizable polymer blends mainly depend on composition and on the level of phase segregation that results from both liquid-liquid and liquid-solid phase-separation processes. In the case of multicomponent polymer systems showing amorphous phase separation in addition to a crystalline phase, the large-strain properties, such as elongation and stress at break, are particularly related to the dispersion level of the phases present in the material,

whereas the low-strain properties, such as Young's modulus and yield stress, are much more dependent on the adhesion between the phases. Therefore, when two or more amorphous phases are present, excellent tensile properties such as tensile strength and toughness could be expected, if the domains are small in size and randomly dispersed in the matrix and provided there is a high level of adhesion between the components. For the present PP-MA/PVB 90/10 blends, optical observations showed that the amorphous PVB has a good level of dispersion within the crystalline matrix of PP-MA, and thus it was expected that the blends were mechanically compatible.

Nominal stress-strain curves of PP-MA and PP-MA/PVB 90/10 blends tested at room temperature are shown in Figure 11. The Young's modulus, stress to break σ_B , and strain to break ϵ_B

Table IV Tensile Parameters of PP-MA/PVB Blends

Sample	Vinyl Alcohol in PVB (wt %)	E (MPa)	Improvement of Modulus with Respect to PP-MA (%)	σ_B (MPa)	ϵ_B (%)
PP-MA	—	739	—	13.7	15
PP-MA/PVB 31	31	917	24	15.4	11
PP-MA/PVB 14	14	855	16	15.5	17

values are summarized in Table IV. For PVB having an elastic modulus higher than that of polypropylene, the Young's modulus of the PP-MA/PVB 90/10 blends is also higher than that of PP-MA. Moreover, PP-MA/PVB 90/10 blends have stress to break values higher than that of neat PP-MA. Finally, the strain to break slightly decreases for the PP-MA/PVB 31 blend, whereas it increases for the PP-MA/PVB 14 blend. Thus PP-MA/PVB 90/10 blends show mechanical properties comparable to, or even superior to, those of neat PP-MA. This finding agrees with the fine domain dispersion of the phases present in the samples (Fig. 5) and suggests good adhesion between the two components of the blends that are mechanically compatible, though thermodynamically immiscible.

CONCLUSIONS

The results show that composition determines molecular flexibility, thermal stability, and crystallinity content of PVB copolymers. Thus, PVBs with a high content of butyral units are less crystalline (or even completely amorphous) and more flexible and thermally stable than PVA. The lower melting point and the higher degradation temperatures give PVBs a larger processability window than that of PVA. This also facilitates the preparation of PVB blends with polypropylene by melt mixing, and overcomes the drawbacks connected to solvent casting preparation, the common procedure for PVA blending.¹⁹ The compatibility of PP-MA and PVB was demonstrated by means of morphological and mechanical investigations. Good compatibility and improved mechanical properties of PP-MA/PVB blends relative to those of neat PP-MA may result in future applications. In particular, the blend with PVB 14 seems very interesting, given that its mechanical properties are better than those of neat PP-MA. Indeed, the 90/10 blend has an elastic modulus higher than that of neat PP-MA, combined with an unexpected enhancement of tensile strength. Further work is needed to assess the gas permeability of PP-MA/PVB blends, a very important parameter for practical applications. Blends in which a polyolefin is the major component, modified by addition of a more expensive polymer to enhance gas-barrier properties, are of great industrial interest.²⁰ It is well recognized that the presence of a high-barrier polymer such as poly(vinyl alcohol), poly(vinylidene chloride), and

polyamides may greatly reduce the gas permeability of a polymer. Therefore, the improved mechanical properties of PP-MA/PVB blends encourage the further blending of PVB with other polyolefins so that low-cost materials with a wide range of gas permeability may be obtained.

The authors gratefully thank Gennaro Romano, Carlo Mancarella, Giuseppe Orsello, and Dr. A. Sarkar for their technical assistance. F.E.K. thanks the Air Force Office of Scientific Research (AFOSR; Grant 98-001) for partial support.

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