

Influence of the Preparation on the Mechanical, Thermal, and Gas Permeation Properties of Polypropylene/Oligopinene Thin Films

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ABSTRACT: The mechanical, thermal, and gas permeation properties of polypropylene (PP)/oligopinene systems in the form of compression thin films 10 μm thick, which were prepared by quenching (with liquid nitrogen) and slow-cooling (15°C/min) techniques, were examined. The addition of oligopinene to PP changed the stress-strain curve of the polyolefin. Both for quenching and slow-cooling films, with a higher oligomer content, no more yielding was observed, and the elongation at break abruptly decreased with greater than 10% oligomer. The elastic modulus and stress at break changed according to the thermal conditions

of the film preparation. Thermal analysis revealed that the blend system had two glass-transition temperatures for both types of films. The values of permeation to CO₂ were independent of the film preparation and were practically unchangeable with the oligomer content in the blends, indicating that the overall decrease in the crystallinity was counterbalanced by the rigidity of the two amorphous phases. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2253–2260, 2003

Key words: poly(propylene) (PP); blends; oligomers

INTRODUCTION

Polyolefins are materials of great interest and numerous applications. Among commodity thermoplastics, polypropylene (PP) has been employed in a large range of uses because of its good physical, chemical, mechanical, insulating, and processing properties, in addition to its low cost. It is also used as an engineering material, alone or in blends, in the car industry (e.g., bumpers, internal lining, and panels).¹

Our group has studied blends of polyolefins with oligoresins from natural and synthetic sources. These oligomers are obtained by the oligomerization of monomolecular substances such as rosin, pinene, cumarone, indene, and cyclopentadiene. They find use in the paint, coating, and adhesive industry, mainly because of their tack characteristics.^{2–9} The goal of this study was to find a new material with respect to the evaluation property of PP after the addition of a sec-

ond component, to determine its possible use as a packing material, and to increase the applications of oligoresins. In this work, we focused on the effect of oligopinene,¹⁰ a low molecular mass resin, on PP when they were blended under selected conditions and in different film preparations. The mechanical, thermal, and gas permeation properties were evaluated.

EXPERIMENTAL

Materials

PP (Prolen) was supplied by Polibrasil Resinas [Rio de Janeiro, Brazil; number-average molecular weight (M_n) = 63,600 and weight-average molecular weight (M_w) = 445,400]. The density was 906 kg/m³, measured according to ASTM D 792. The degree of crystallinity (X_c) was 52%, calculated by differential scanning calorimetry (DSC). The Shore D hardness was 76, determined by ASTM D 2240.

The oligopinene resin, a synthetic low molecular mass resin, yellowish and amorphous, was composed mainly of β -pinene and was manufactured by Cloral S/A (Rio de Janeiro, Brazil; M_n = 570 and M_w = 920, calculated by gel permeation chromatography; density = 988 kg/m³, measured by ASTM D 792).

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Blend preparation

Mixtures of PP and oligopinene were prepared in a Haake Rheocord 9000 equipped with a tumble mixer in the molten state at 473 K and 30 rpm for 10 min. The nominal blend ratios were 100/0, 90/10, 80/20, 70/30, 60/40, and 50/50.

Film preparation

Films were produced in a Carver press at 473 K: the mixture was left for 5 min for softening, and then 5 kN of pressure was applied for 5 min so that the films would conform. Different conditions were given—quenching (with liquid nitrogen) and slow cooling (15°C/min) at room temperature—to the molten mass for film solidification, with the aim of evaluating the effect of the film preparation on the properties. The average thickness of the films was 10 μm .

Permeation testing

The CO₂ permeation through the polymeric films was measured with a traditional gas permeability analyzer.¹¹ The permeation cell consisted of two stainless steel compartments separated by the membrane under study. The gas was fed at a constant pressure (10⁵ N/m²) to the bottom cell, and the amount of gas that passed through the membrane was measured by the pressure increase on the downstream side with a pressure transducer. At a steady gas flow, the permeability (P/l) was determined from the slope (dp/dt) of the pressure–time plot:

$$\frac{P}{l} = \frac{dp}{dt} \left[\frac{V_{\text{system}}}{A \Delta p} \right] \left[\frac{T_{\text{STP}}}{T_{\text{ambient}} P_{\text{STP}}} \right]$$

where l is the film thickness, Δp is the pressure difference between the two film sides, A is the film area, V_{system} is the volume of the system, T_{ambient} is the ambient temperature, T_{STP} is the absolute temperature, and P_{STP} is the absolute pressure.

DSC analysis

The thermal analysis of the films was carried out in a PerkinElmer DSC 7 calorimeter equipped with a data acquisition system. About 10 mg of a sample was put in an aluminum pan and run from 253 to 473 K at 10 K/min. The glass-transition temperature (T_g) and melting temperature (T_m) were taken from the DSC curves. X_c was evaluated for each mixture under the assumption that that melting enthalpy of 100% crystalline PP¹² was $\Delta H^0 = 165$ J/g. The crystallinity data were normalized with respect to the PP content.

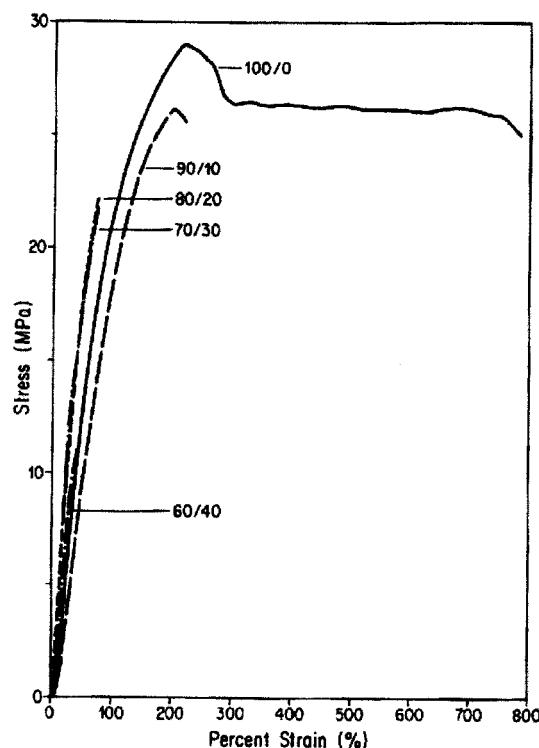


Figure 1 Stress–strain curves of PP/oligopinene blends (slow cooling).

Mechanical testing

The mechanical properties were evaluated according to ASTM D 882. The rate of gauge separation, grip distance, and sample specimen area were 10 mm/min, 30 mm, and 0.77 mm², respectively. The elastic modulus, stress and strain at yield, and break were calculated from the stress–strain curves. The values of the properties and standard deviations were calculated from the stress curves, with five or more specimens tested.

RESULTS AND DISCUSSION

In the evaluation of the mechanical properties, we observed that when oligopinene was mixed with PP, changes in the stress–strain curve of the polyolefin occurred (Figs. 1 and 2).

For slow-cooling films (Fig. 1), the mechanical curve of plain PP represented the classic behavior of a semi-crystalline polymer showing yield and necking formation, cold drawing, and finally rupture. Only the 90/10 PP/oligopinene blend curve showed yield and necking formation; the rupture occurred immediately after necking. For other blends, the curves did not present yielding, necking, and cold drawing; and rupture happened before necking. The slope of the curve became more prominent with oligopinene-enriched blends. This behavior indicates that the presence of the oligomer rendered the blends hard and changed the

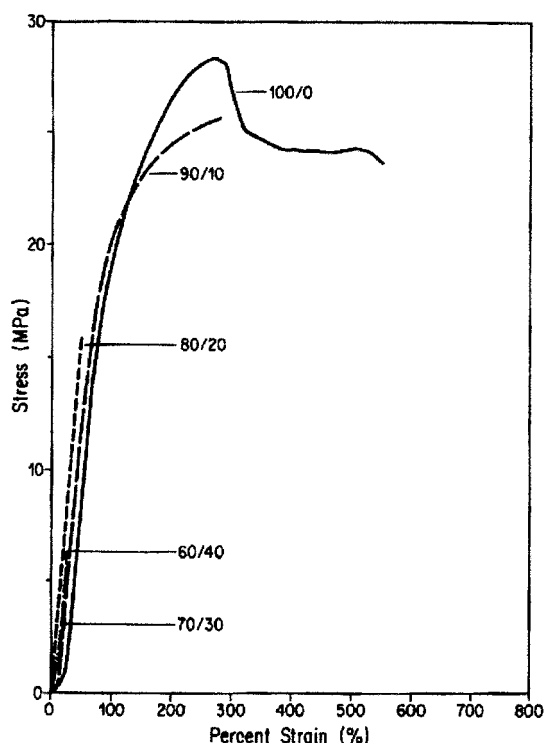


Figure 2 Stress-strain curves of PP/oligopinene blends (quenching).

PP characteristic from ductile to brittle. For quenching films (Fig. 2), the mechanical curve of plain PP showed a behavior similar to that of the slow-cooling film, except that rupture occurred at a lower value of elongation. The curves of the blends followed a behavior similar to that observed for slow-cooling films, except for the 90/10 PP/oligopinene blend, which did not show necking formation and ruptured before this point. We should emphasize that we did not have mechanical data for oligopinene alone because it did not form a film on account of its low molar mass and glassy nature. When the material was removed from plates, it broke into fragments similar to pieces of glass.

In Tables I and II, we summarize the mechanical parameters of the quenching and slow-cooling films, respectively.

For quenching films (Table I), the values of the elastic modulus for plain PP and the 90/10 PP/oli-

gopinene blend were similar and for other blends showed a tendency to increase because of an increasing crystallinity index and a hardener effect of the oligomer molecules on the PP molecules. Both the stress and elongation at break decreased with the amount of oligopinene, and the loss reached 72 and 93%, respectively. The discontinuity of the molecular size between the PP and oligopinene molecules was the main reason for the drop in the end properties during the stretching.

For slow-cooling films (Table II), the elastic modulus increased continuously with the amount of oligopinene and also contributed to increasing the crystallinity index and hardener effect of the oligopinene molecules. The stress at break remained practically constant up to 10% oligopinene and then decreased for other contents. The elongation at break decayed continuously for all compositions with oligomer-enriched blends. The losses in the stress and elongation at break were approximately 40 and 90% at the highest oligomer content. Also, the discontinuity in the molecular size between the oligomer and PP was the main reason for these drops. The results indicated that the mechanical properties of the slow-cooling films were slightly better than those of the quenching films, and they agreed with the results for a PP/oligopinene system (plate samples) published in a recent article of ours.¹³

The thermal curves of plain PP, plain oligopinene, and 80/20 and 60/40 PP/oligopinene blends for the slow-cooling films are arranged in Figure 3. For the slow-cooling films (Fig. 3), the curve of plain oligopinene presented a thermal transition at about 333–343 K as a peak. The curve of PP alone showed a melting peak containing a shoulder that could represent another crystalline form of PP or a crystal with a different lamellar thickness. The curves of the blends presented a baseline variation from approximately 283 to 353 K, showing a broadened peak at about 323–353 K. This temperature interval corresponded to the T_g region and showed the presence of two T_g 's. In the blends, PP molecules crystallized even in the presence of the oligomer. A shoulder was observed in the melting peak of the 80/20 PP/oligopinene blend, the nature of which was explained previously. We inserted

TABLE I
Mechanical Properties of Quenching PP/Oligopinene Blend Films

PP/oligopinene blend	Elastic modulus (MPa)	Stress at yield (MPa)	Elongation at yield (%)	Stress at break (MPa)	Elongation at break (%)
100/0	31 ± 4	28.5 ± 0.9	295 ± 15	24.7 ± 1.1	429 ± 73
90/10	30 ± 5	—	—	25.7 ± 1.9	272 ± 53
80/20	38 ± 5	—	—	14.4 ± 1.4	49 ± 10
70/30	26 ± 8	—	—	4.0 ± 1.6	23 ± 7
60/40	32 ± 10	—	—	7.0 ± 1.0	26 ± 4

TABLE II
Mechanical Properties of Slow-Cooling PP/Oligopinene Blend Films

PP/oligopinene blend	Elastic modulus (MPa)	Stress at yield (MPa)	Elongation at yield (%)	Stress at break (MPa)	Elongation at break (%)
100/0	28 ± 3	29.2 ± 0.9	286 ± 54	25.9 ± 2.0	645 ± 148
90/10	30 ± 8	—	—	26.4 ± 3.0	188 ± 39
80/20	45 ± 4	—	—	23.5 ± 1.6	89 ± 19
70/30	52 ± 7	—	—	21.1 ± 4.1	63 ± 20
60/40	45 ± 6	—	—	14.8 ± 4.0	44 ± 7

the curve of the 80/20 PP/oligopinene blend (Fig. 4) to illustrate better what was described.

The calorimetric curves of plain PP, plain oligopinene, and 80/20 and 60/40 PP/oligopinene blends for the quenching films are arranged in Figure 5. For the quenching films (Fig. 5), the calorimetric behavior was similar to that observed for the slow-cooling films. The curve of plain oligopinene showed its T_g around 333–343 K as a peak. The curve of plain PP also showed a melting peak with a slight shoulder. The curves of the blends presented baseline variations in the same temperature interval and showed the presence of two T_g 's. In the blends, PP molecules crystallized even in the presence of the oligomer, and the 80/20 PP/oligopinene blend showed an additional shoulder. We included the curve of the 60/40 PP/oligopinene blend (Fig. 6) to illustrate better what was described.

The evaluation of T_g was performed with a trace of the curves between 253 and 373 K for both types of

films. For slow-cooling films, the curve of plain oligopinene showed a peak at about 333–343 K. This peak disappeared when the sample was reheated, showing a baseline variation similar to that observed for T_g in the polymers. For us, this transition corresponded to T_g of oligopinene, as found in a previous article.⁹ T_g of plain PP was calculated with the computer program of the DSC equipment. The presence of a T_g (upper) value for PP was not observed in our experiment.¹⁴ For the blends, the thermal curves were composed of two distinct portions indicating the presence of two T_g 's. The first baseline variation was attributed to T_g of the amorphous PP-rich phase. The second one was ascribed to T_g of the amorphous oligopinene-rich phase. For T_g , the calculation of the amorphous PP-rich phase used the computer program of the DSC equipment. T_g of the amorphous oligopinene-rich phase was considered the maximum of the peak because it was difficult to select an adequate baseline. In Figures 7 (slow-cooling film) and 8

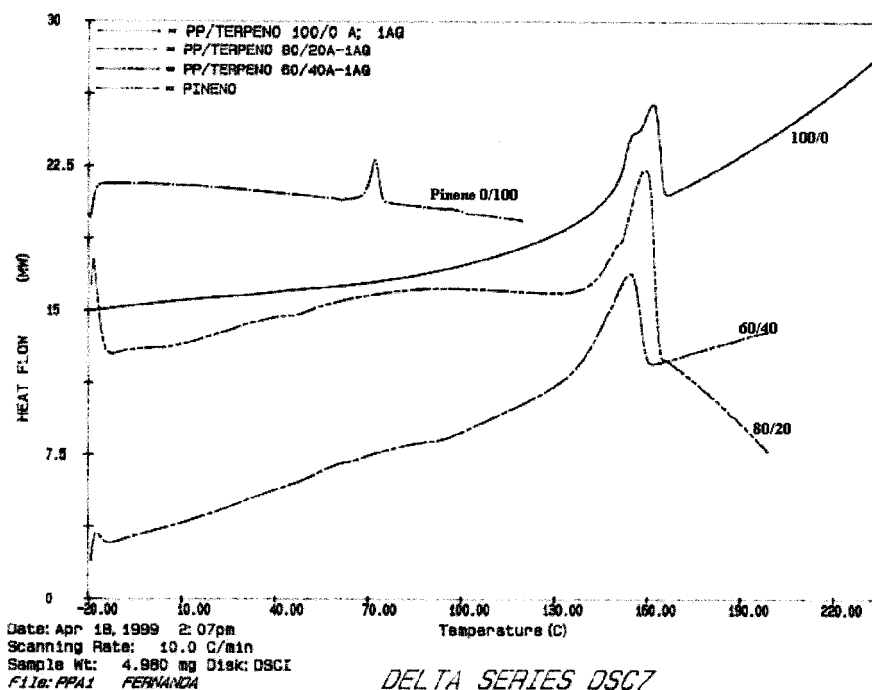


Figure 3 Calorimetric curves of PP/oligopinene blends (slow cooling).

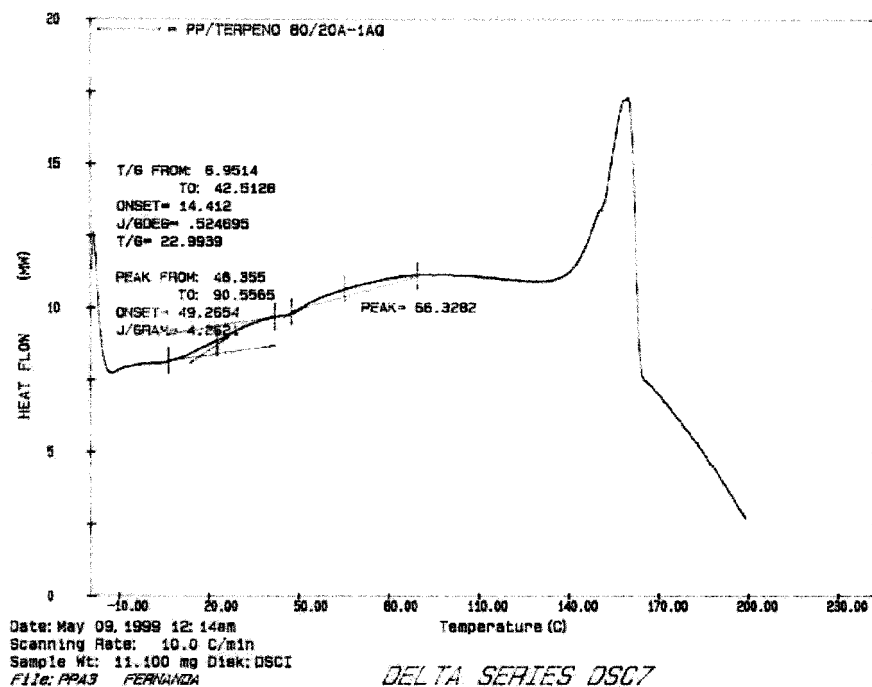


Figure 4 Calorimetric curve of an 80/20 PP/oligopinene blend (slow cooling).

(quenching film), we show two selected DSC curves to illustrate the calculations used in the determination of T_g 's of the samples.

The results of the thermal analysis of the quenching and slow-cooling samples are listed in Table III. For both, T_m 's of the blends decreased with the oligopinene content; this indicated that the oligomer re-

tarded the crystallization process of PP during the solidification of the molten mass.⁹ X_c increased slightly for both types of films and, as expected, the crystallinity values for the slow-cooling films were the highest. The blends showed two T_g 's for both types of films. The addition of oligopinene to the polyolefin caused a displacement to a higher temperature for T_g

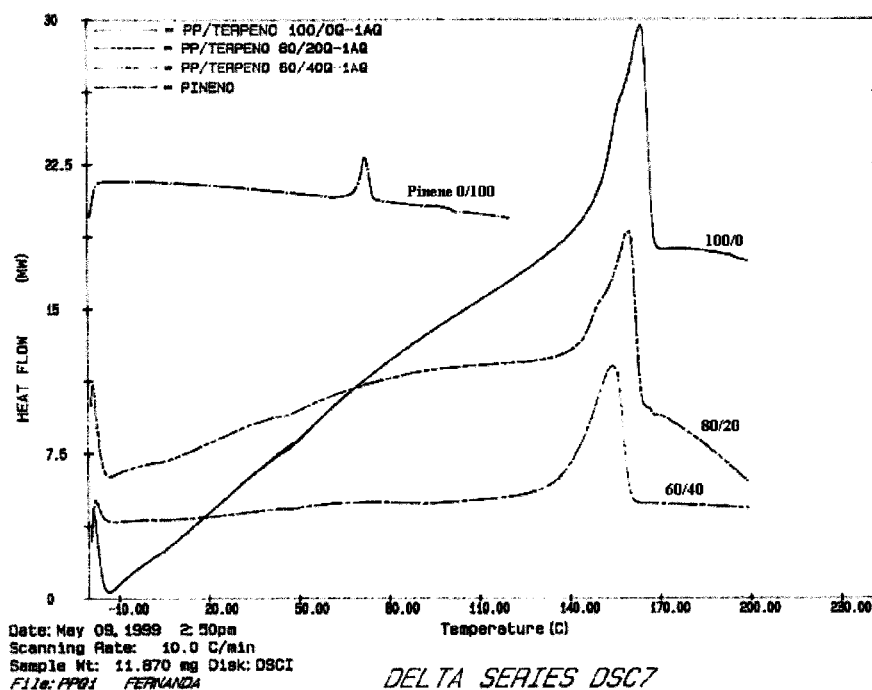


Figure 5 Calorimetric curves of PP/oligopinene blends (quenching).

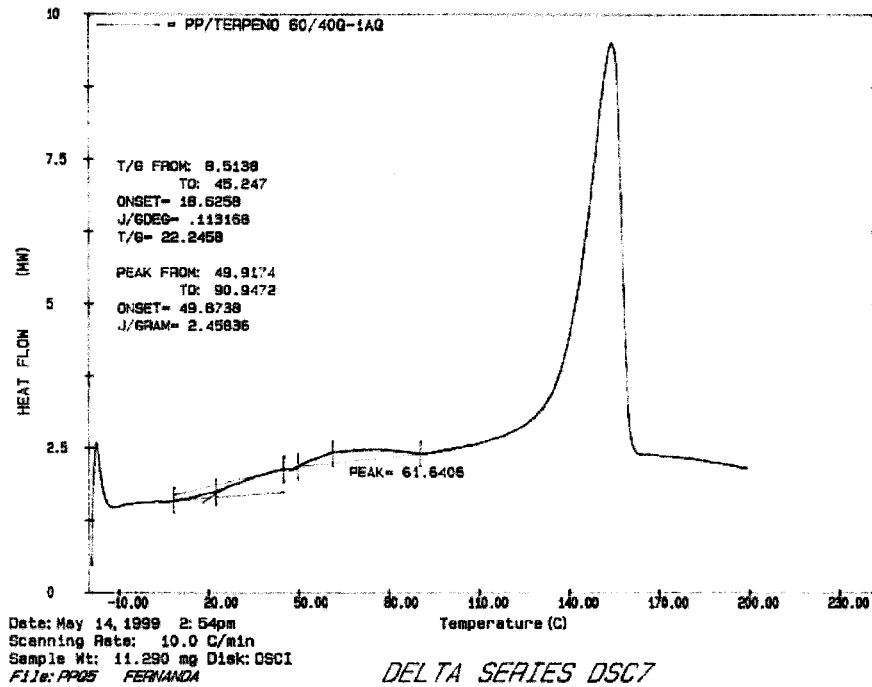


Figure 6 Calorimetric curve of a 60/40 PP/oligopinene blend (quenching).

of PP. The T_g values were practically the same, regardless of the film preparation and composition. The blend curves clearly showed an additional transition at about 333–343 K and a tendency to decrease with the oligopinene content for both films. The increase of the crystallinity could be attributed to the crystallization of PP molecules in the oligomer phase. Despite

many attempts, we did not manage to determine T_g of the amorphous PP-rich phase for the slow-cooling films. The thermal results confirmed what was proposed and published in our recent article.⁹ The PP/oligopinene blends formed a partially miscible system consisting of at least three phases: one amorphous PP-rich phase, another amorphous oligopinene-rich

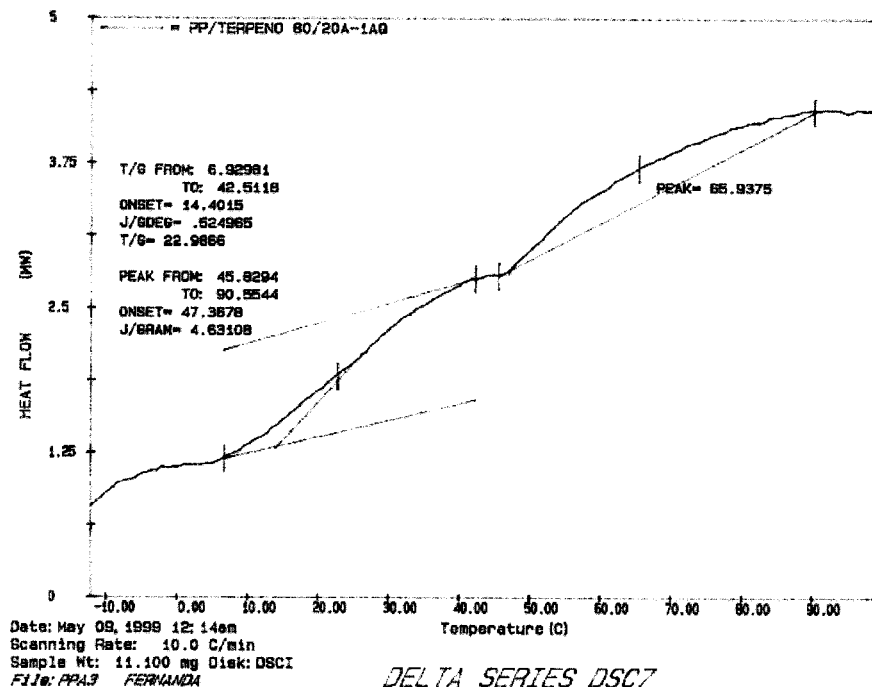


Figure 7 Calorimetric curve of an 80/20 PP/oligopinene blend (slow cooling) at 253–373 K.

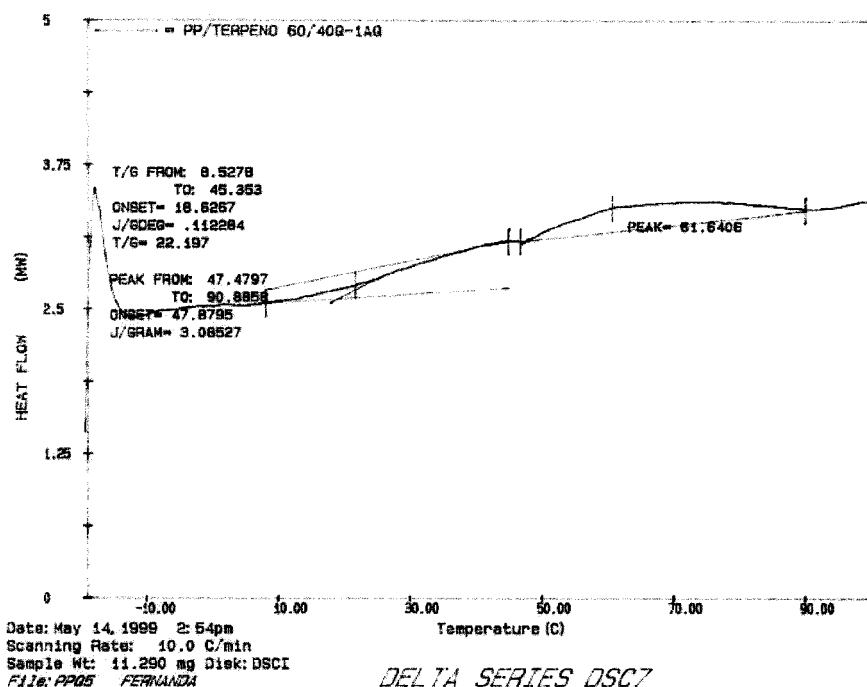


Figure 8 Calorimetric curve of a 60/40 PP/oligopinene blend (quenching) at 253–373 K.

phase, and a third phase corresponding to the crystalline PP phase.

The results for the gas permeability of PP/oligopinene blend films are listed in Table IV. The gas permeability values were practically independent of the film preparation. The values of the permeability, related to the composition, were practically unchangeable with the oligomer content; the variations were considered negligible, showing that the presence of the oligomer did not affect the transport properties of the films. Generally, the gas permeation in the polymers took place only in the amorphous phase; the crystalline phase was a barrier to gas diffusion. The sorption and diffusion process of CO₂ through the films could be kept unchangeable because of both the similarity of the chemical structures of the blend components (hydrocarbon nature) and the glass nature of oligopinene; both effects could affect the gas diffusion through the film because of the restricted segmental mobility of macromolecules in the amorphous phase.

Only a slight increase in X_c of the blend films was not capable of modifying the permeability to CO₂. The PP/oligopinene blends were partially miscible. In fact, T_g of oligopinene was about 343 K; at room temperature, it was in a glassy state and was more rigid than PP. In the blends, at the test temperature, both amorphous PP and oligopinene chains were in a glassy state, and the lower molecular mobility in these phases should have produced a higher barrier to CO₂. Then, the loss in the overall crystallinity was counterbalanced by the presence of two rigid amorphous phases, which resulted in a negligible influence of oligopinene on the permeability of PP.

The results corroborate what we have published in two previous articles^{9,13} on the PP/oligopinene system.

CONCLUSIONS

Oligopinene changed the stress–strain curve of PP and caused a drop in its mechanical properties for both

TABLE III
Calorimetric Parameters of PP/Oligopinene Blend Films

PP/oligopinene blend	T_m (K)		X_c (%)		T_g (K)			
					Quenching film		Slow-cooling film	
	Quenching film	Slow-cooling film	Quenching film	Slow-cooling film	PP-rich phase	Oligopinene-rich phase	PP-rich phase	Oligopinene-rich phase
100/0	435	437	49	44	274	—	—	—
80/20	433	433	53	50	296	339	293	340
60/40	427	427	53	47	297	334	295	335
0/100	—	—	—	—	—	343	—	343

TABLE IV
CO₂ Permeability of PP/Oligopinene Blend Films
[cm³ (CNTP)/cm² s cmHg]

	PP/oligopinene				
	100/0	90/10	80/20	70/30	60/40
Slow cooling	9.981	9.986	9.214	9.986	9.605
Quenching	10.051	9.835	9.860	9.463	—

film preparations. With more than 10% oligomer, the polyolefin did not show yielding, necking formation, or cold drawing, its behavior being modified from ductile to brittle. For the quenching films, the elastic modulus was dependent on the composition. The stress and elongation decreased continuously with the amount of the oligomer in the blend. For the slow-cooling films, the elastic modulus had a tendency to increase. The stress at break was practically constant up to 20% oligomer, and the elongation at break showed a behavior similar to that observed for the quenching films. For both film preparations, the results revealed that the blends of PP and oligopinene formed a partially miscible system containing two T_g 's. The lowest value of T_g was attributed to the PP amorphous phase, which seemed to attain a constant value. The highest value of T_g was ascribed to the amorphous oligomer phase, in which the T_g value decreased when the blend was enriched with an oligopinene component. For both film preparations, PP macromolecules crystallized; T_m decreased and X_c increased slightly with the oligomer content. The permeability values were independent of the film preparation and were practically unchangeable with the oligomer content in the blends. The loss in the overall crystallinity was counterbalanced by the presence of two rigid amorphous phases, which resulted in a negligible influence of oligopinene on the permeability of PP.

NOMENCLATURE

A	film area
dp/dt	gradient of the linear region (steady-state gas flow) of the pressure–time plot

l	film thickness
M_n	number-average molecular weight
M_w	weight-average molecular weight
P/l	permeability
T_{ambient}	ambient temperature
T_g	glass-transition temperature
T_m	melting temperature
T_{STP}	absolute temperature
P_{STP}	absolute pressure
V_{system}	volume of the system
X_c	degree of crystallinity
ΔH^0	melting enthalpy of 100% crystalline polypropylene
Δp	pressure difference between the two film sides

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