Oligobetapinene as Barrier Improver to CO_2 of HDPE in Thin Films of Binary Blends

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Abstract: Quenched thin films (about 100 microns thick) of high-density polyethylene (HDPE) / oligobetapinene (OBP) blends were prepared by melt mixing with the amount of OBP varying from 0 to 40%. The results of CO_2 permeation, thermal behavior and morphology are reported. From -130 to -100 °C we observed two peaks in DSC measurements, the lower one being ascribed to γ-transition of HDPE. The upper one attributed to Tg which was shift at high contents of OBP. The OPB molecules also displayed another transition at higher temperatures. The normalized degree of crystallinity of HDPE remained constant while the overall crystallinity of the blends was reduced in all blends. We have hypothesized that three distinct phases coexist, viz. a HDPE-amorphous phase with some amount of OBP molecules, OBP-amorphous phase with polyolefin and HDPE-crystalline phases. The permeation test revealed a decrease in permeability to CO_2 independent of the amount of OBP in the blends. The reduction of gas permeation could be explained mainly by the rigidity of the OBP rich phase that has counterbalanced the decrease of overall crystallinity of the film blends.

Keywords: *High density polyethylene, oligobetapinene, permeability, thermal properties, blends.*

Introduction

Oligoresins from natural and synthetic sources are materials that, along the three last decades, have gained scientific and commercial importance. The coumarone-indene, petroleum resins and resins originated from renewable sources such as rosin and terpenes, has been found applications in pressure-sensitive adhesives, coatings, sizing and rubber compounding. Some of them have been chemically modified to increase their industrial application. Within the terpene resins family the alpha and beta pinenes are the compounds of greatest commercial importance. These monomers are cyclic substances present in turpentine oil, which is extracted from pinewood. When polymerized by cationic process, the monomers produce resins with low molecular mass and degree of polymerization in the range 10-15. The products vary from partially fluid to clear, pale yellow, brittle resins that are resistant to acids and alkalis. Their particular properties make them attractive for several applications such as sheet carbon and copying paper, paints and varnishes, plasticizers, floor wax, chewing gum base, concrete curing, rubber belts and hoses, among others[2-3]. They can also be used in some reactions as cross-linker agents and precursors for light and thermal stabilizers[4,5]. As adhesion modifier these resins find applications in adhesives for nicotine delivery and surface-active agent in polymer/metal and polymer/polymer systems[6-8]. The relationship among phase structure, morphology, thermal behavior, rheology and crystallization with mechanical and permeation properties of mixtures of polyolefins with various oligoresins has been extensively investigated[9-11]. Recently, a terpenic resin, oligobetapinene (OBP), was mixed with PP and HDPE and the results on phase structure, thermal and crystallization behavior and their correlation with mechanical and permeation properties were published[12,13]. The poly(α-pinene) and poly(d-limonene) were blended with PP and the results on crystallization growth rates, phase structure, thermal and viscoelastic properties were discussed[14-15].

The focus of the present work was the preparation of quenched thin films of HDPE and OBP blends in order to investigate the influence of the addition of OBP on gas permeation, thermal behavior and morphology of HDPE and the possible application of these blends as packing material.

Experimental

Materials

The high density polyethylene (HDPE), grade BT 003, was kindly supplied by Polialden, Brazil. The density[16] was 967 kg/m^3, according to ASTM D 792; the degree of crystallinity and melt flow index were 63% and 0.3 g/10min, respectively.

The oligobetapinene (OBP) obtained by cationic polimerization of natural β-pinene monomer was manufactured by Cloral S/A, Brazil, under the form of

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transparent and yellowish small stones, with average molecular masses of $\overline{Mn}$ = 570 and $\overline{Mw}$ = 920 g/mol, determined by size exclusion chromatography (SEC), and density[16] of 988 kg/m^3.

Blend preparation

Mixtures of HDPE and OBP were prepared in a Haake Rheocord 9000 equipped with an internal mixer, in molten state at 200 °C, 30 rpm during 5 minutes. The blend nominal ratios were 100/0, 90/10, 80/20, 70/30 and 60/40.

Film preparation

Films were produced in a Carver press at 200 °C where the mixture was left for 1 minute in order to softening the material. Then, 50 kN of load was applied during 4 minutes to conform the film. From the molten state, the film was quenched (with liquid nitrogen) and left to reach room temperature. The thickness of the films varied in a range from 0.010 to 0.016±0.002 microns.

Permeation test

The CO_2 permeation through the polymeric films was measured using a traditional gas permeability analyzer[17]. The permeation cell consists of two stainless steel compartments separated by the membrane under study. The gas was fed at constant pressure (10^5 N/m^2) to the bottom cell, and the amount of gas pass through the membrane was measured by the pressure increase on the downstream side with a pressure transducer. At steady gas flow, the permeability (P/l) was determined from the slope (dp/dt) of pressure *vs.* time plot using the following equation, where the symbols are listed at the end of the text[18]:

$$\frac{P}{l}=\frac{dp}{dt}\cdot\left(\frac{V_{system}}{A.\Delta p}\right)\cdot\left(\frac{T_{STP}}{T_{ambient}.p_{STP}}\right)$$

Morphology analysis

The morphology evaluation was carried out using a scanning electron microscope JEOL JMS 5610 LV. A small specimen was cut from the molded film and fractured after freezing (30 minutes) in liquid nitrogen. The fractured piece was sputtered with a thin layer of gold/palladium alloy before SEM observation.

DSC analysis

The thermal analysis of the films was carried out in a Perkin Elmer calorimeter DSC 7 equipped with data acquisition system and computer program for calculation. About 10 mg of sample were put in an aluminum pan and run from -150 ºC to 0 ºC and 0 to 170 ºC at 10 ºC/min. The glass transition and melting temperatures (T_g and T_m) were taken from the DSC curves. The blend crystallinity was obtained from DSC and the crystallinity degree (X_c) was normalized taking into account HDPE content for each mixture considering ΔH = 290 J/g the melting enthalpy[19] of HDPE 100% crystalline.

Results and Discussion

The samples were frozen in liquid nitrogen for 30 minutes, immediately broken and the surfaces were submitted to SEM observations. The broken surface of HDPE showed ductile fracture, as expected. For the blends, the same type of fracture has occurred as illustrated in the photomicrograph of fractured surface of 80/20 HDPE/OBP blend (Figure 1, x500), where a rough surface is seen and showed rupture by shearing. The Figure 2 shows the HDPE as matrix surrounded to the oligobetapinene phase (see the white arrows in dark areas on the photo). The shape of the dispersed domains is irregular with size from 1µm. The micrograph shows that the OBP domains are satisfactory welded to the matrix. This is probably due to the fact that part of HDPE chains is also present into second phase, leading to a material well interlaced and compact. The SEM observations indicate that the HDPE / OBP blend is a system with phase separation.

DSC curves were evaluated considering two temperature intervals being one at T_g of HDPE (-150 to 0 ºC) and another corresponding to T_g of oligobetapinene and melting peak of HDPE (0 to 170 ºC). For T_g calculation, the first derivative function was applied on DSC traces of HDPE, 80/20 and 60/40 HDPE / OBP blends and the results are shown in Figure 3. All

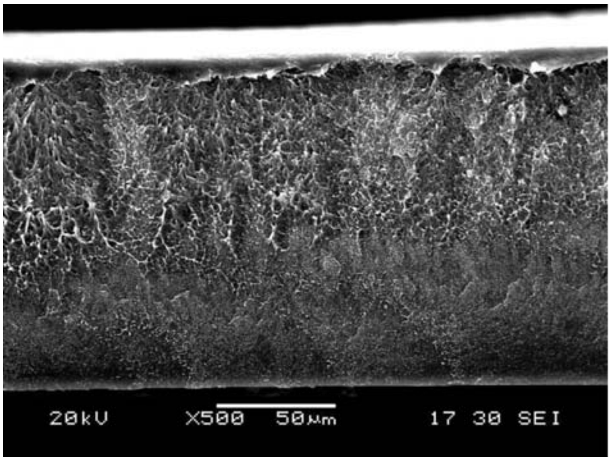

Figure 1. SEM photomicrograph of 80/20 HDPE/OBP film (x500)

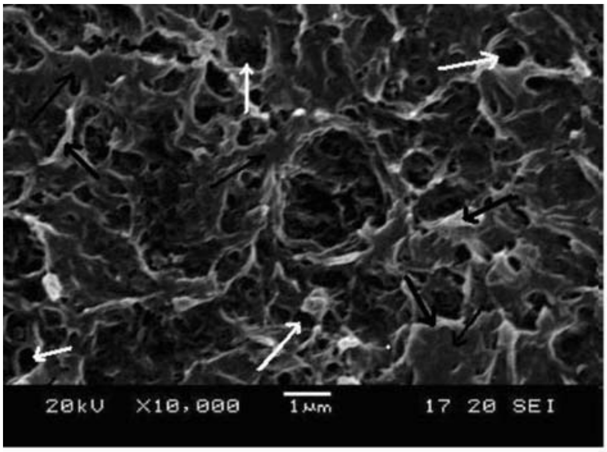

Figure 2. SEM photomicrograph of 80/20 HDPE/OBP film (x10000)

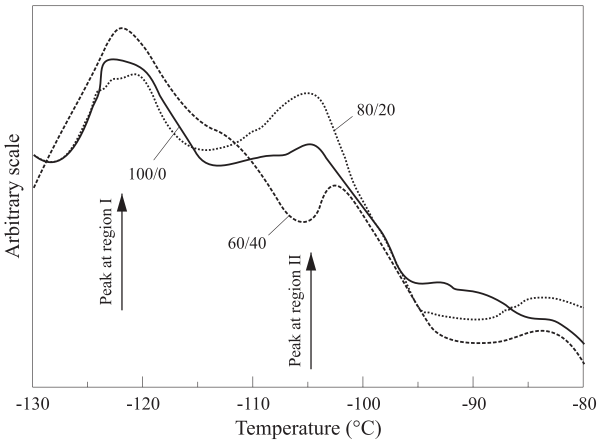

Figure 3. First derivative function of DSC curves of HDPE/OBP films (-130 to -80°C

samples have shown two peaks. The first one (peak at region I) was centered in the range from -130 to -110 °C and second one (peak at region II) in the range from -110 to -95 °C. The first peak was ascribed to γ-transition of HDPE and the second one was attributed to T_g of HDPE[20-23]. The effect of OBP on the HDPE amorphous phase can be seen in the curve of 60/40 HDPE / OBP blend. The first peak was more pronounced and the second one showed tendency to be displaced to higher temperatures. Figure 4 presents calorimetric curves of HDPE and OBP, 90/10, 80/20 and 60/40 HDPE / OBP films, from 0 to 170 °C. The melting peak of HDPE was observed for all samples indicating that crystallization occurred independent of oligobetapinene content. Table 1 summarizes the results of melting points and crystallinity indices of these blends. The melting peaks and crystallinity indices decreased continuously with an increase in the amount of OBP in blends. The normalized degree of crystallinity showed values quite similar. The T_g of OBP appeared at 70 °C in agreement with results found in literature[11,15]. Careful observation in the DSC curves from 0 to 100 °C indicated the presence of another transition (Figure 5). The HDPE curve showed a slight inflection at about 30-50 °C that was attributed to its α-relaxation[24]. At the same temperature interval, each blend presented a transition that became more evident when the amount of OBP increased. This transition was ascribed to T_g of oligobetapinene amorphous phase in the blends and the respective values are listed in Table 2.

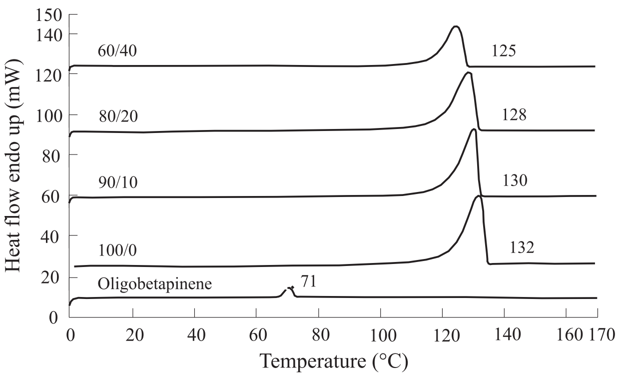

Figure 4. DSC curves of HDPE/OBP films (0 to 170°C)

Table 1. Calorimetric parameters of HDPE/OBP films (0 to 170°C)

HDPE/OBP	Tm (°C)	χ_b (%)	χ_c (%)
100/0	132	63	63
90/10	130	56	62
80/20	128	53	66
60/40	125	39	65

T_m - melting temperature; χ_b - blend crystallinity; χ_c - HDPE normalized crystallinity

Table 2. T_g of oligobetapinene phase of HDPE/OBP films (0 to 100 °C)

HDPE/OBP	Tg (°C)
0/100	70
90/10	42
80/20	41
60/40	46

The thermal results indicated that the HDPE / OBP blend is a partially miscible system. The amorphous phases are likely HDPE amorphous rich phase with some amount of OBP material and OBP amorphous rich phase with some amount of HDPE. A third phase is related to HDPE crystalline phase. The results corroborate the SEM analysis.

As the overall crystallinity decreased in blends, the sorption and diffusion processes of the gas through the film could favorably reduce the barrier property. An unexpected behavior was observed, the permeability to CO_2 of the films decreased (Table 3) independently of the OBP content in blends. The crystallinity of HDPE practically remained constant for all blends but the presence of OBP material had an important role on the permeation process. It must be considered that at the temperature of the test (23 °C) the OBP rich phase is in the glass state ($T_g \cong 45$ °C), then its restrict mobility hinders the gas diffusion through the film. Thus, the formation of a rigid OBP rich amorphous phase restrains the gas diffusion, produces a gain in the CO_2 barrier property, counterbalancing the loss of overall blend crystallinity.

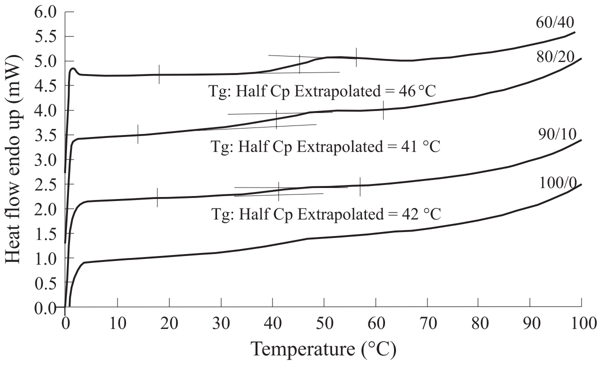

Figure 5. T_g graphic determination on DSC curves of HDPE/OBP films (0 to 100 °C)

Table 3. CO_2 Permeation of HDPE/OBP films

HDPE/OBP	P x 10^{10} $cm^3.cm/cm^2.s.cmHg$
100/0	3.44
90/10	1.44
80/20	1.59
60/40	1.97

Conclusion

The permeability to CO_2, thermal properties and morphology of HDPE / OBP blends were evaluated. The gas permeation decreased with amount of OBP. DSC and SEM analyses showed phase separation in the blends. Two amorphous phases coexist being one formed by HDPE-amorphous with some amount of OBP and the other one composed of OBP-amorphous with some amount of polyolefin. A third phase is formed by HDPE-crystalline. The OBP amorphous phase ($T_g \cong 45^oC$) was considered responsible for improving of gas permeation in blends due to its rigidity that restricts molecular mobility. The loss in overall crystallinity of blends was counterbalanced by the presence of rigid OBP amorphous phase.

Nomenclature

Symbols

P	permeability coefficient; ($cm^3.cm/cm^2.s.cm$ Hg)
l	film thickness; (cm)
d*p*/dt	gradient of the linear region (steady-state gas flow) of the pressure *versus* time plot; (cm Hg/s)
Δp	pressure difference between the two film sides; (cm Hg)
A	film area; (cm^2)
V	volume system; (cm^3)
T	temperature of test; (23^oC)
T_{STP}	absolute temperature; (0^oC)
P_{STP}	absolute pressure (76 cm Hg).

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