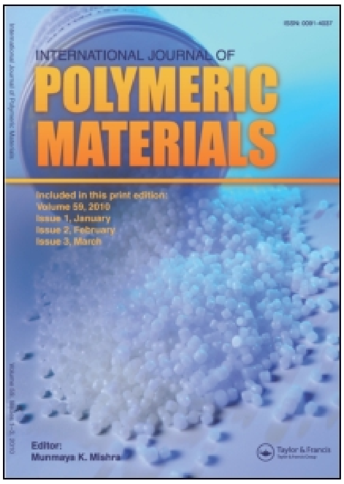

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^{13}C NMR Study PP/ROSIN Blends

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^{13}C NMR Study PP/ROSIN Blends

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The solid state NMR technique was employed to investigated the homogeneity level of the melting mixtures of polypropylene (PP) and glycerol ester of hydrogenated rosin (ester gum) prepared at different proportions and under selected conditions. The results were discussed in terms of the blend domains with distinct mobilities at kilohertz range. Up to 30% of rosin the blends revealed a slight increase in the proton spin lattice relaxation time in the rotating frame ($T_1^H\rho$) values caused by increasing the mobility process of PP domains. The presence of one phase at the time scale of that relaxation parameter suggests sample homogeneity. The $T_1^H\rho$ value for blend with 50% of rosin indicated incompatibility.

Keywords: Polypropylene; Rosin; nuclear magnetic resonance; blend; solid state NMR

INTRODUCTION

The aim of the our group is to study blends of commercial polyolefins and resins of low molecular weight, natural or synthetic. The morphology, mechanical and thermal behaviour of high density polyethylene (HDPE)/oligo(cyclopentadiene) (HOCP) and PP/HOCP blends were studied [1 – 3]. Both systems were partially miscible and an increase of elastic modulus was detected. The action of HOCP on the morphology of iPP/HDPE binary blends was also investigated [4]. The morphology, mechanical and rheological properties, thermal and dynamic-mechanical behaviour of HDPE/ROSIN (ester) blends prepared by melt mixing were shown in previous work [5, 6]. Recently, we

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prepared two papers on the mechanical and rheological properties and isothermal crystallization of PP/ROSIN blends [7, 8]. Solid state nuclear magnetic resonance spectroscopy (NMR) is a good source to obtain a response of blends compatibility. The combining techniques such as magic angle spinning (MAS) with cross polarisation (CP) are useful routines to obtain high-resolution solid state NMR. Proton spin-lattice relaxation time in the rotating frame are related to the nature and carbon nuclei environment and can provide detailed information on molecular and segmental motion of the blend components [9–15]. The main purpose of this work was to analyse the behaviour of PR/ROSIN blends at molecular level employing carbon-13 cross-polarisation/magic angle spinning and proton spin-lattice relaxation time in the rotating frame.

EXPERIMENTAL

Materials

Commercial polypropylene (PP) produced by OPP Petroquímica S.A., Brazil, density = 0.9 g/cm^3, degree of crystallinity = 40% (by DSC), rockwell hardness = 101 (R scale), melt flow index (MFI) = 3,5 g/10min.

Commercial glycerol ester of partially hydrogenated rosin (ester gum) was by Hercules Inc., Brazil; $M_w = 1190$, $M_n = 920$ (by GPC), density = 1.1 g/cm^3, color WG, acid number = 8.7, softening point = 101.5°C.

Blend Preparation

The blends were prepared by melt mixing in a Haake Rheocord 9000 at 200°C, 32 rpm for 10 minutes. The following PP/ROSIN w/w ratios were blended: 100/0, 90/10, 80/20, 70/30, 60/40 and 50/50.

Specimen Preparation

Sheets of 9 × 7 × 0.1 cm were compression moulded. The sample was left for 5 minutes at 220°C without pressure to melt completely. After this, 2.5 Mpa of pressure was applied for 5 minutes and then cooled in air until to 110°C. Finally, the mould was put in another press with water circulation to reach room temperature.

Solid State NMR Measurements

All NMR solid state spectra were obtained on a VARIAN spectrometer INOVA 300 operating at 299.9 MHz and 75.4 MHz for ^1H and ^{13}C, respectively. All experiments were done at probe ambient temperature and performed using gated high power decoupling. Zirconium oxide rotor of 7 mm diameter with Kel-F caps were used to acquire the NMR spectra at rates of 5 kHz. Carbon-13 spectra are referenced to the chemical shift of the methyl group carbons of the hexamethyl benzene (17.3 ppm). The ^{13}C were carried out in the cross-polarisation mode with magic-angle spinning (CP/MAS) with 2s of delay and variation contact time (VCT). A range of contact time was established as 200 to 8,000 μs. Proton $T_1\rho$ values were determined from the intensity decay of carbon-13 peaks with increasing contact-time.

RESULTS AND DISCUSSION

The carbon-13 CP/MAS NMR spectrum of PP showed three signals located on 44.2, 27.2 and 22.2 ppm respectively attributed to CH_2, CH and CH_3 groups. Rosin is natural resin consisting of mixture of monocarboxylic acids with diterpenic structures which abietic acid is the main component [16]. The carbon-13 NMR CP/MAS spectrum of glycerol ester of partially hydrogenated rosin (ester gum) is showed in Figure 1 and the assignments are listed in Table I.

The carbon-13 CP/MAS spectrum for PP/Rosin 50/50 is shown in Figure 2. Only two signals, with very low intensity, belonged to rosin was detected: one at 37.7 ppm (CH_2) and the second located at 176.9 ppm (carbonyl group). The three NMR signals of PP was also detected, and the intensity proportions were very high. Another point shows that the chemical shifts for the PP NMR signals in the PP/rosin blend did not change when compared to PP itself, which is a first indication that this sample presents phase separation.

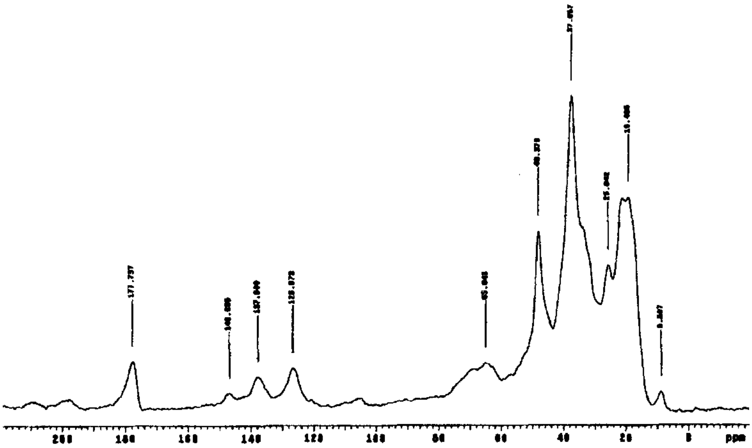

FIGURE 1 Carbon-13 CP/MAS NMR spectrum of Rosin.

TABLE I Assignments of Rosin structure by carbon-13 CP/MAS NMR spectrum

δ (*ppm*)	*Carbon*-13 *group*
177.7	$C{=}O_{(ester)}$
146.9	$C{-}C{=}C$
137.8	$C{=}C{-}CH_3$
126.8	$C{=}C{-}H$
65.0	$CH_2{-}O$
48.3	CH_2
37.6	CH_2
25.8	CH_2
21.8	CH_3
19.4	CH_3
8.8	$CH_{3(branching)}$

Proton $T_1\rho$ values for rosin are listed in Table II. It was observed high values of $T_1^H\rho$, which is an indication that it is mainly constituted by a large domain with high mobility. The distribution form of the decay intensities of carbon-13 in the array of contact-time corroborates this observation.

The $T_1^H\rho$ values of blends measured from variable contact-time experiment are listed in Table III. The values are referred to assignments of methylene, methyne and methyl groups of PP since the polyolefin dominates the relaxation process. Up to 30% of rosin, the blends present a slight increase in $T_1^H\rho$ values caused an increase in

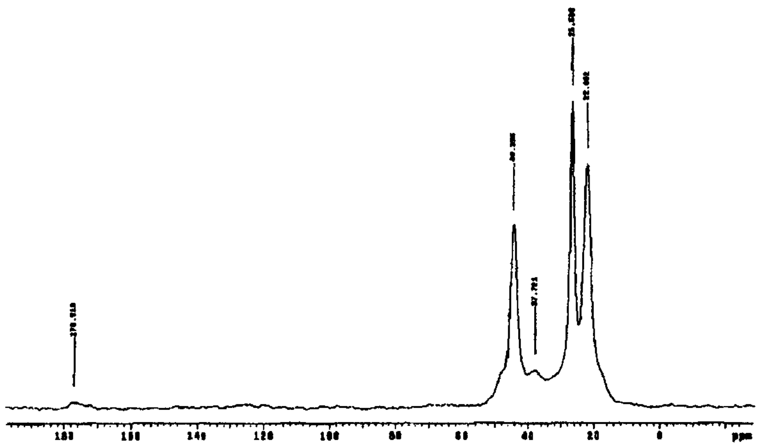

FIGURE 2 Carbon-13 CP/MAS NMR spectrum of 50/50 PP/Rosin blend.

TABLE II $T_1^H\rho$ values for Rosin

δ (ppm)	$T_1^H\rho$ (μs)
177.7	41.7
137.8	21.6
126.6	24.7
48.3	13.1
37.6	20.0
25.8	18.5
21.8	19.6

TABLE III $T_1^H\rho$ values for PP/Rosin blends

PP/Rosin blend	$T_1^H\rho$ (μs)		
	Methylene	*Methyne*	*Methyl*
100/0	9.2	12.6	15.2
90/10	10.2	13.5	17.0
80/20	12.7	17.0	18.9
70/30	–	–	26.9
50/50	10.7	12.2	14.2

the mobility process of PP domains that can be attributed to rosin amount effect. These results show some interaction between both blend components and one phase at the time scale of this parameter is a consequence of sample homogeneity. For 50/50 PP/Rosin blend the values of $T_1^H\rho$ becomes very similar to that PP alone which can be attributed to the blend incompatibility. These results corroborate the isothermal crystallization data where above 30% of rosin the spherulite radial growth rate increased showing that the demixing was induced at large rosin content [8].

CONCLUSION

The study of carbon-13 NMR solid state of PP/Rosin mixture indicated phase separation. The data of relaxation time of blends showed that the polyolefin and rosin have some interaction. Up to 30% of rosin the blends revealed a slight increase in $T_1^H\rho$ values caused by increasing the mobility process of PP domains. The presence of one phase at the time scale of that relaxation parameter suggests sample homogeneity. The $T_1^H\rho$ value for blend with 50% of rosin indicated incompatibility. The ^{13}C NMR results corroborated the isothermal crystallization data, where above 30% of rosin the spherulite radial growth rate increased showing that the demixing was induced at large rosin content.

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