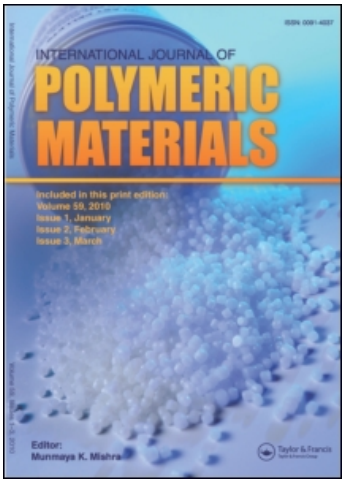

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Mendes, L. C. , Cardoso, R. S. , Chagas, B. S. and Moraes, G. F.(2000) 'PP/ROSIN Blends: Isothermal Crystallization', International Journal of Polymeric Materials, 46: 3, 801 — 808
To link to this Article: DOI: 10.1080/00914030008033915
URL: http://dx.doi.org/10.1080/00914030008033915

Intern. J. Polymeric Mater., 2000, Vol. 46, pp. 801–808
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PP/ROSIN Blends: Isothermal Crystallization

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(Received 28 February 1999)

The isothermal crystallization of polypropylene (PP) melt blended with a glycerol ester of hydrogenated rosin (ester gum) (PP/ROSIN) were prepared under select conditions using up to 50% of rosin revealed phase separation. The presence of rosin changed the radial growth rate and size of PP spherulites. The rosin-separated domains were noticed in the intraspherulitic and interspherulitic regions and increased in size when the oligomer enriched the blends. Up to 30% of rosin, samples isothermally crystallized at 125°C showed a decrease of spherulite radial growth rate and above that amount an increase was observed.

Keywords: Polypropylene; rosin; blends; isothermal crystallization

INTRODUCTION

The low cost, good properties and versatility make the polyolefins attractive materials for scientific and technological studies. Our subject of study are mixtures of polyolefins and low molecular weight resins. Recently, the morphology, mechanical and thermal behavior of high density polyethylene (HDPE)/oligo (ciclopentadiene) (HOCP) and PP/HOCP blends were studied [1–3]. These systems were partially miscibles 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

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properties of HDPE/ROSIN (ester) blends prepared by melt mixing were shown in previous work [5]. The morphology, thermal and dynamic-mechanical behavior of HDPE/ROSIN (ester) mixtures were presented in another paper [6]. An article showing the mechanical and rheological properties of PP/ROSIN (ester) blends [7] was prepared previously and showed that above 10% of rosin the mechanical properties of blends dropped. The goal of this paper is to present the results of optical microscopy accomplished in PP/ROSIN (ester) blends.

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/10 min.

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] = 8.7, softening point [9] = 101.5°C.

Blend Preparation

The blends were prepared by melt mixing in a Haake Rhecord 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, a pressure of 2.5 MPa was applied for 5 minutes and then cooled in air until to 110°C. Finally, the mold was put in another press with water circulation to reach room temperature.

Optical Microscopy Analysis

The optical observations were performed by a Olympus polarizing optical microscope model BX50 equipped with a Linkham TH 600 hot stage. Thin slices were cut from the compression moulded samples, inserted between two microscope cover-glasses, melted and squeezed in order to obtain thin films with homogeneous thickness. The films were put on the hot stage microscope, heated from room temperature up to 200°C at 75°C/min under nitrogen atmosphere and kept for 5 minutes to eliminate the thermal history. Then, the material was cooled to 125°C at the same rate and kept for a time enough to crystallize. Photographs were taken at specified time intervals using polarized and non-polarized light in order to follow the crystallization evolution.

RESULTS AND DISCUSSION

The optical micrograph of PP alone (Fig. 1) crystallized at 125°C shows that small spherulites were formed quickly and contact zone among them is not clear. The melting bulk of mixtures at 200°C was

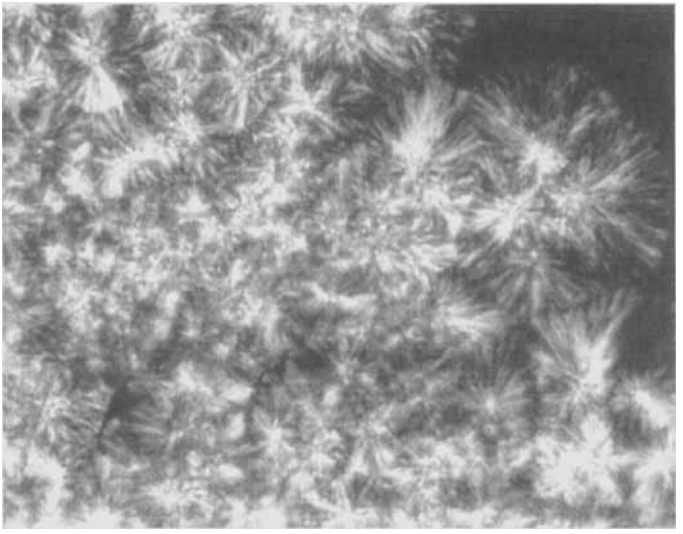

FIGURE 1 Photomicrograph of the 100/0 PP/ROSIN blend, isothermally crystallized for 3 min at 125°C.

heterogeneous. A representative optical micrograph is shown in Figure 2. It was noticed the presence of small dark points as precipitated particles indicating phase separation. In Figure 3 is presented the photomicrograph of 90/10 PP/ROSIN blend crystallized at 125°C. In this mixture the PP birefringent species are larger than PP spherulites without rosin, appeared at longer crystallization time and it can be seen the limit among them. The phase separation was observed by taking pictures with non-polarized light (Fig. 4); the small particles appeared in the intraspherulitic region and non-crystallized portion. In the case of 80/20 PP/ROSIN blend also isothermally crystallized at 125°C the optical micrograph (Fig. 5) reveals spherulites similar in size and shape those found for 90/10 mixture but less birefrigent. The phase separation was enhanced. This is better viewed in the non-polarized photomicrograph of 80/20 blend showed in Figure 6. The rosin phase appeared homogeneously disperse as small and regular spherical domains in both intra and interspherulitic zones. For the 60/40 PP/ROSIN blend, the photomicrograph (Fig. 7) the spherulites present the shape similar those others blends but larger in size. The size of rosin domains showed an increase respect to PP spherulite without rosin.

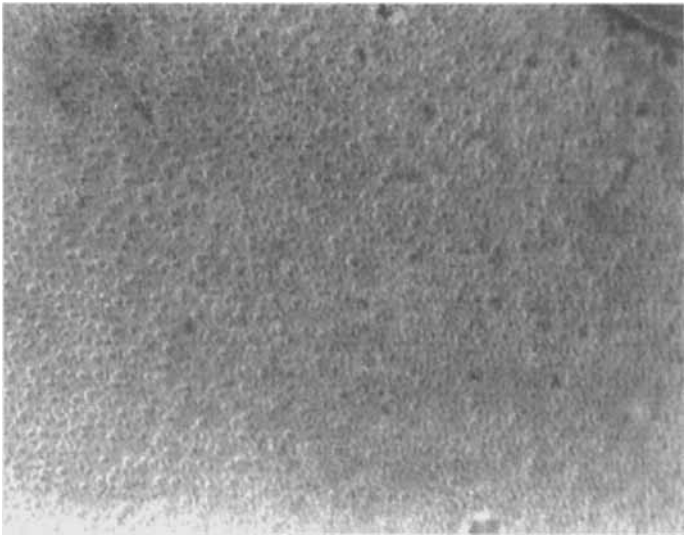

FIGURE 2 Photomicrograph of the 80/20 PP/ROSIN blend, melting bulk at 200°C.

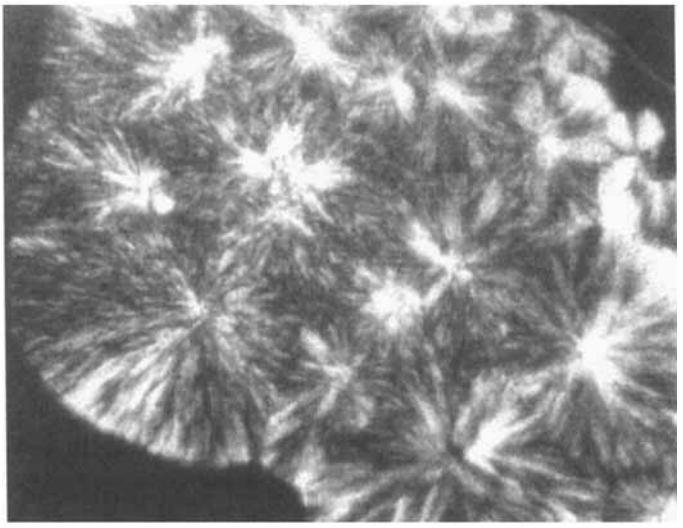

FIGURE 3 Photomicrograph of the 90/10 PP/ROSIN blend, isothermally crystallized for 7 min at 125°C.

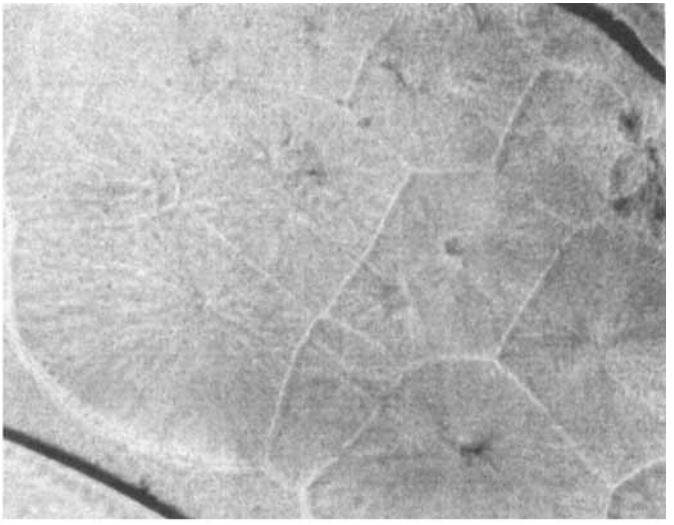

FIGURE 4 Photomicrograph of the 90/10 PP/ROSIN blend, isothermally crystallized for 7 min at 125°C (non-polarized light).

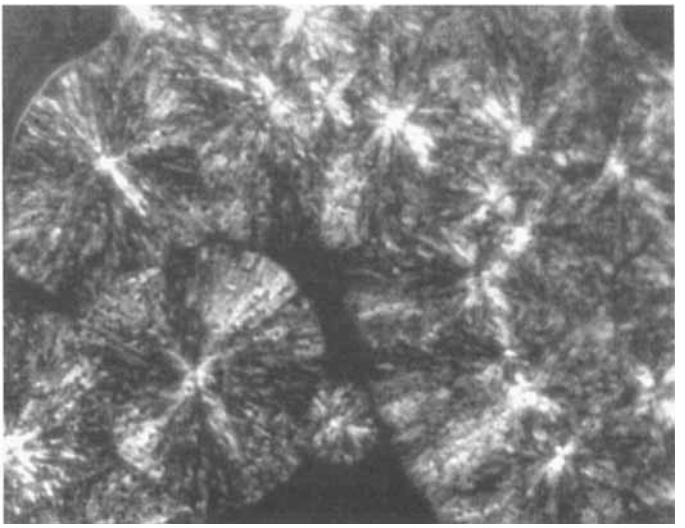

FIGURE 5 Photomicrograph of the 80/20 PP/ROSIN blend, isothermally crystallized for 6 min at 125°C.

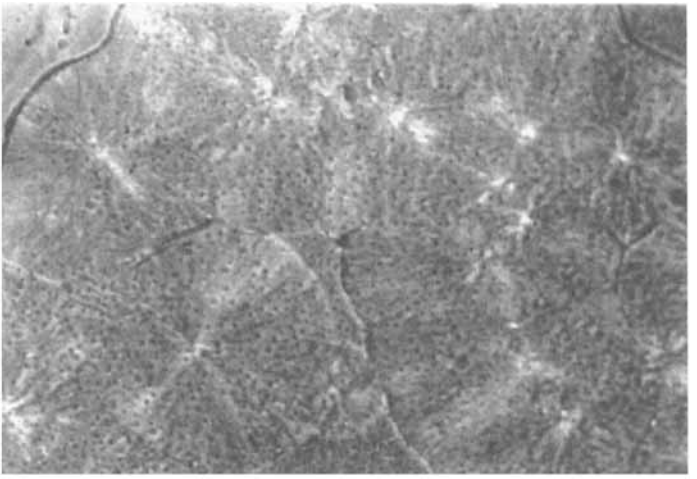

FIGURE 6 Photomicrograph of the 80/20 PP/ROSIN blend, isothermally crystallized for 6 min at 125°C (non-polarized light).

The spherulite radius increased linearly with time crystallization for all compositions at temperature investigated. The isothermal radial growth rate, G, shown in Figure 8 was measured from the slope of the

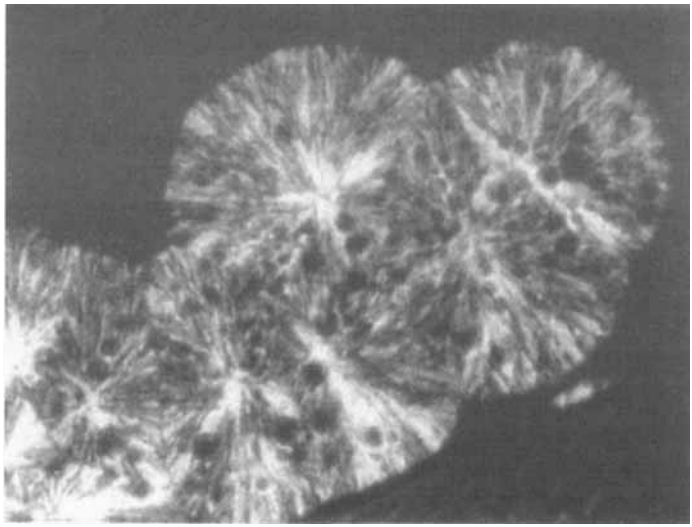

FIGURE 7 Photomicrograph of the 60/40 PP/ROSIN blend, isothermally crystallized for 7 min at 125°C.

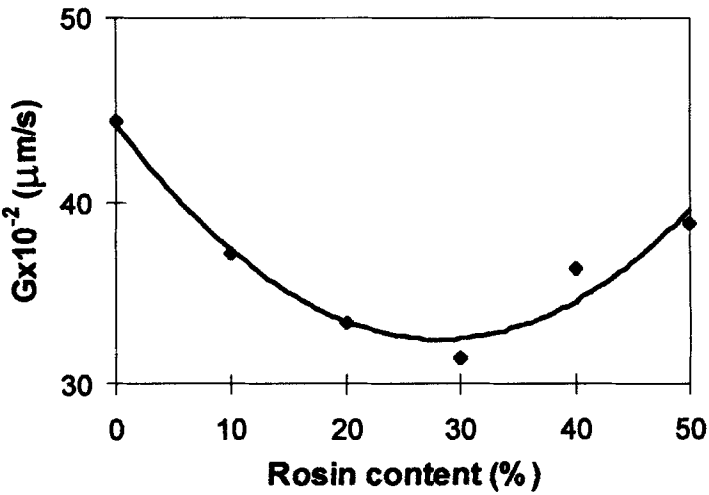

FIGURE 8 Spherulite radial growth rate (G) of PP/ROSIN blends.

radius *versus* time curves of blends. It was noticed that a decrease of G values occurred up to 30% of rosin. Above this amount, a slight increase of G values occurred. This means that the crystallization

raised the concentration of the non-crystallizable component in the melt and induced demixing.

CONCLUSION

The isothermal crystallization of blends of polypropylene (PP) and glycerol ester of hydrogenated rosin (ester gum), at 125°C, formed a phase separation system in the melt state and after crystallization. The radial growth rate and size of PP spherulites changed with rosin content. The rosin-separated domains were observed in the intraspherulitic and interspherulitic regions. The size of rosin phase increased when the blends were enriched by the oligomer. It was observed a decrease of spherulite radial growth rate up to 30% of rosin and above this amount an increase occurred.

Acknowledgements

The authors thank to Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES, Brazil) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Brazil) for support this research.

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