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Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem

Study of the morphology, thermal and mechanical properties of irradiated isotactic polypropylene films

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ARTICLE INFO

Keywords:

Polypropylene film
Gamma radiation
Uniaxial stretching
SEM
DSC

ABSTRACT

Thin films of isotactic polypropylene (iPP) are of great economical importance and their production is quite challenging due to the need of very fast uniaxial or biaxial expansion. During the expansion, critical problems usually arise, like structure disruption, shear thinning, causing material, energy and time losses. This work aims to study the surface morphology and compare the thermal, mechanical properties of PP films irradiated by gamma ray in an acetylene atmosphere after uniaxial expansion. PP films were made by compression molding at 190 °C with cooling in water at room temperature and irradiated by gamma ray, at (5, 12.5 and 20 kGy) under acetylene atmosphere. After irradiation the samples were submitted to thermal treatment at 90 °C for 1 h and then stretched out at 170 °C using an Instron machine. The surface of PP films, pristine and modified, (i.e., irradiated), was studied using optical microscopy (OM) and scanning electron microscopy (SEM). The changes in morphology, crystallinity and tensile parameters, like yield stress, rupture stress and elongation strain of the PP with irradiation dose were investigated. The results showed some evidences of gel formation due to crosslinking and/or long chain branching induced by radiation.

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1. Introduction

The use of traditional polypropylene resins in blown film processes has been prevented due to their poor melt strength and bubble instability. To overcome these deficiencies it is necessary to improve the melt strength since it is apparent that opportunities exist for a high melt strength polypropylene resin in blown film.

Previous efforts to improve the melt strength of polypropylene resins focused on introduction of long chain branching (Spadaro and Valenza, 2000; Lugão et al., 2002, 2003, 2007; Auhl et al., 2004), to increase the network entanglement level. In order to understand the influence of the level of network entanglement on the physical and chemical properties of iPP and high melt strength polypropylene (HMS-PP) films several studies have been reported. The main technique of investigation has been the atomic force microscopy (AFM) of thin films obtained under various experimental conditions, as temperature and mechanical processing varied (Auriemma and De Rosa, 2006; Boger et al., 2009; Kailas et al., 2007; Schönherr et al., 2003; Coulon et al., 1998; Zia et al., 2008; Koike and Cakmak, 2006; Snétivy et al., 1993; Wawkuszewski et al., 1995; Chang et al., 2002; Nie et al., 1999; Zhang et al., 2007; Zuo et al., 2007). One way to verify the

efficiency of the entanglement network in the melt is by stretching the PP film at temperatures higher than the melting temperature. In this work differential scanning calorimetry (DSC) was used to determine the crystallinity. Optical microscopy (OM) and scanning electron microscopy (SEM) were used to image the surface morphology of an uniaxially oriented polypropylene film that was gamma irradiated in a crosslinking-promoting atmosphere of acetylene and stretched at 170 °C in sequence.

2. Experimental

The commercial iPP was supplied by BRASKEM with 1.5 dg min^{-1} melt flow index (ASTM D 1238) obtained using a Ceast apparatus operating at 230 °C with a charge of 2.16 kg. The films were made by compression molding at 190 °C (10 min without pressure and 5 min under a pressure of 8 MPa) and cooled in water bath at room temperature. The irradiation of the films was performed under acetylene atmosphere in a ^{60}Co gamma source under a dose rate of 10 kGy h^{-1} with doses of 5, 12.5 and 20 kGy monitored by a Harwell Red Perspex 4034 dosimeter. After irradiation the film samples were submitted to a thermal treatment at 90 °C for 1 h. The film stretching was performed at 170 °C in an Instron machine with a strain rate of 0.17 s^{-1} . The thermal properties of the PP films were obtained using DSC (Mettler Toledo DSC822^c). The DSC thermograms are obtained before and after stretching of the film. Samples at around 3 mg

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were submitted to temperature program of 25–280 °C at a heating rate of 10 °C min⁻¹. Crystallinity was calculated as the ratio of melting enthalpy of the samples determined from the first run, and the melting enthalpy of a perfect PP crystal (209 kJ kg⁻¹), (Brandrup et al., 1999), under nitrogen atmosphere. The samples were observed by optical microscopy (Olympus PME3) and scanning electron microscopy (EDAX Philips XR-30). For the SEM analysis, surface Au deposition was used to improve electrical conductivity.

3. Results and discussion

Fig. 1 shows the stress–strain curves for the pristine and modified (irradiated) PP films that were stretched at 170 °C with a strain rate of 0.17 s⁻¹ up to the rupture.

Each curve represents an average of five experiments. The load–extension curves follow the typical ductile deformation behavior – a yield point followed by a smooth strain hardening – well known for semi-crystalline polymers in tensile experiments, with exception of 20 kGy irradiated film that broke at strain equal to one. In our case, it was supposed that there was no crystalline phase because the tensile test was performed at 170 °C, so we postulate that the yielding can be attributed to the entanglement of the polymer chains. However, at 170 °C there

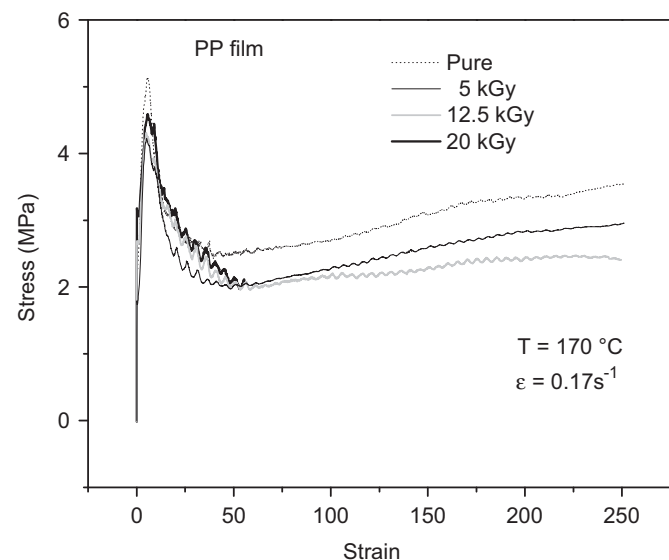


Fig. 1. Stress–strain curves for the PP film stretched up to rupture at 170 °C with a strain rate of 0.17 s⁻¹ ($l_0 = 50$ mm).

was a possibility of some remaining crystallinity, therefore the yield can also be caused by non-melted crystals. The higher value to the pristine PP film was attributed to the greater molecular weight compared to the modified (irradiated) PP films that have been submitted to scission, branching and crosslinking. The lower yield stress for the 5 and 12.5 kGy irradiated films was a consequence of the prevalence of the chain scission over the branching and crosslinking at low doses (Lugão et al., 2002). For the 20 kGy sample the yield stress increase and the elongation at rupture diminished due to the high level of crosslinking.

OM and SEM results are shown in Figs. 2 and 3. All the irradiated and stretched samples present lines in the stretching direction signalized by the arrows. The polymer films that have been submitted to mechanical testing were characterized by a micrometer-scale fiber-like network structure, which reflects the stretching process at 170 °C. According to Koike and Cakmak (2006), stretching polypropylene in the solid state invariably leads to formation of fibrillar texture. This micro-structure can be seen in the micrographs presented in Figs. 2 and 3, as streaks aligned in the stretching direction represented by the arrows. This was confirmed by observations of samples that have been heavily deformed (Fig. 3-a3) where the fibrils are detached from the bulk. In Fig. 2 for the 20 kGy sample we can observe coarse streaks which have been reported by Chang et al. (2002), to reflect the difficulty to align the branched and/or crosslinked chains. The stretching temperature of 170 °C was higher than the melting temperature of the crystalline phase of a 90% isotactic polypropylene. At this temperature the enhanced chain mobility due to the absence of crystals or the melting of remaining crystals can significantly weaken the amorphous entanglement network. As a result, the tensile deformation would lead to chain disentanglement which favors the creation of the fiber-like network structure. In spite of this fibrils are observed (set of tie chains) that join adjacent fibers (Wawkuschewski et al., 1995) and suffer rupture in a cavitation process which only occurs under tensile loading (Thomas et al., 2007). This process can liberate a lot of chains that may crystallize during the cooling to the room temperature. The crystallization begins with lamellae formation followed by organization that creates the spherulites similar to those observed by Kajioka et al. (2008), in isotactic poly(butene-1). The observed elongated features (see Fig. 3-a1 and -a2) can be assigned to edge-on oriented lamellae, as described by Schönherr et al. (2003), in low-crystallinity polypropylene and Kailas et al. (2007), in nano droplets of low molecular weight isotactic polypropylene using AFM.

Table 1, summarizes the crystallinities of the PP films, pristine and modified (irradiated), before and after stretching process. The crystallinity values of the PP films before stretching were lower than the respective ones after stretching. On the stretched condition the irradiated films crystallinity was at around 30%

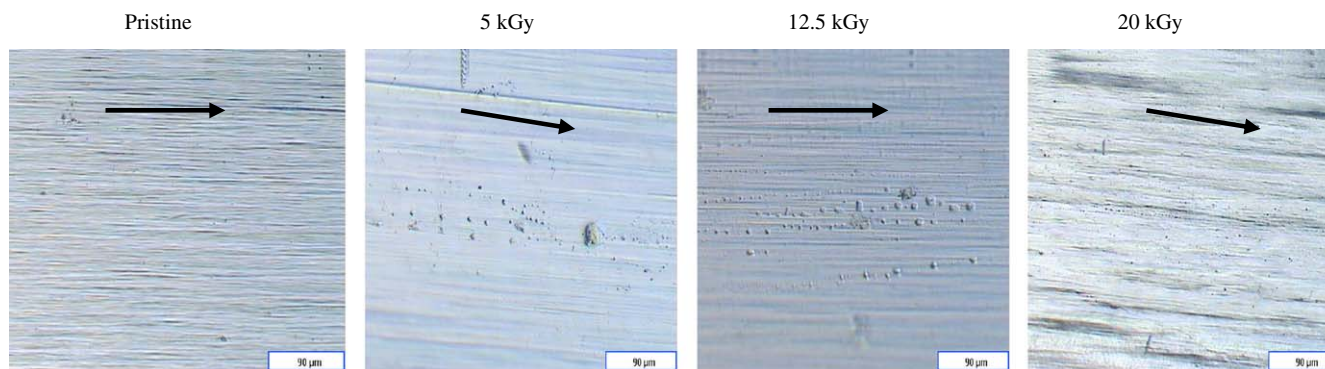


Fig. 2. Optical microscopy micrographs of irradiated and stretched samples 90 µm.

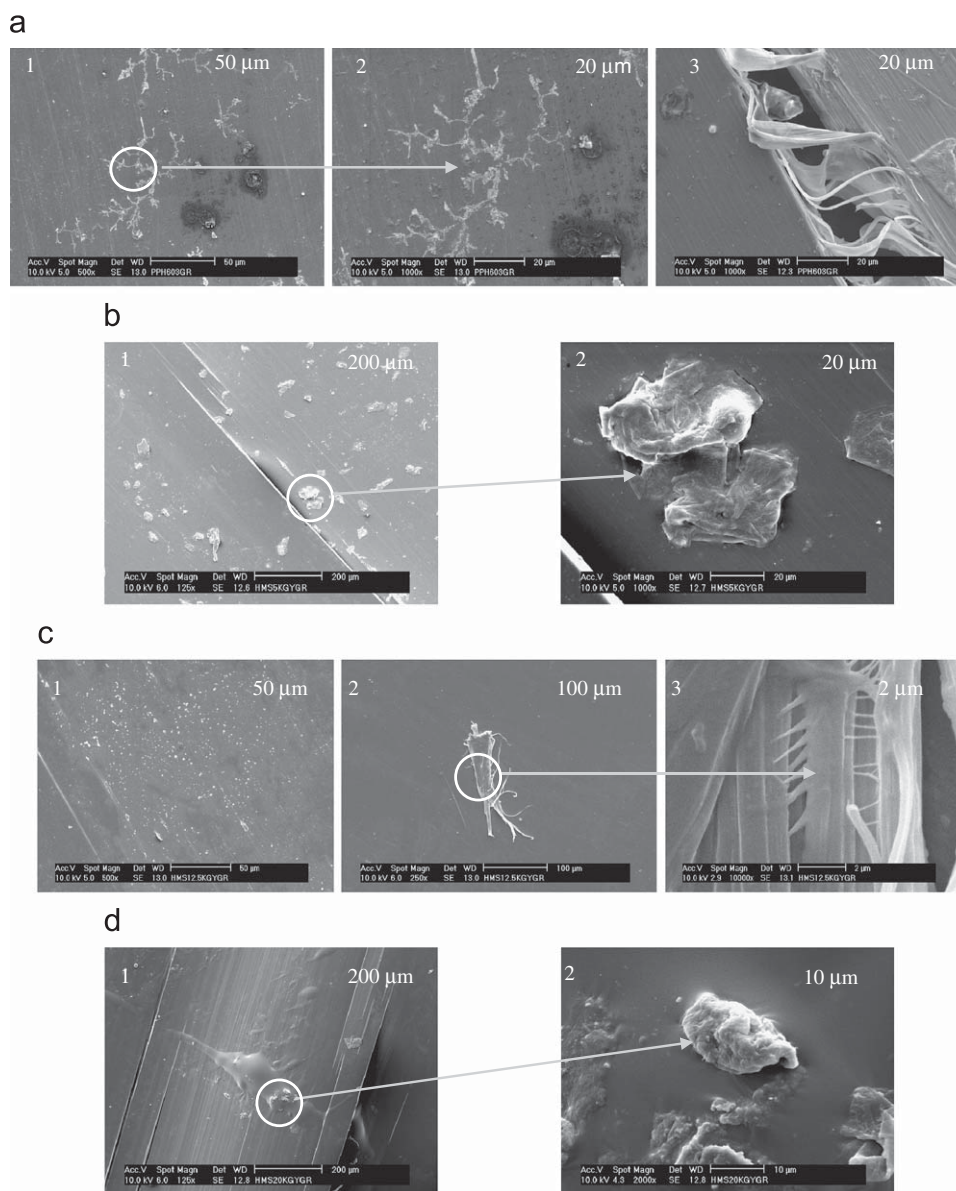


Fig. 3. Scanning electron microscopy micrographs of irradiated and stretched samples: (a) neat, (b) 5 kGy, (c) 12.5 kGy and (d) 20 kGy.

Table 1

Crystallinity (%) of PP films before and after stretching.

	Crystallinity (%) ($\pm 5\%$)			
	Pristine PP	5 kGy	12.5 kGy	20 kGy
Before stretching	33.3	35.3	39.9	33.8
After stretching	38.3	51.9	50.9	48.9

higher than that of the pristine film. This difference is almost certainly due to the scission of soft segment chains that underwent stress-induced crystallization. Moreover there was a contribution to the crystallinity that came from the creation of the fiber-like structure due to the stretching process at high temperature. The lower irradiation doses also favor the crystallization due to the reduction of molecular size by chain scission, but for 20 kGy crosslinking clearly dominated the overall process, and the crystallinity was lower in both cases, before and after stretching.

4. Conclusion

The stretching process at high temperature (170 °C) creates a micrometer-scale fiber-like network structure in the pristine iPP and irradiated iPP films. This structure consists of microfibrils parallel and perpendicular to the stretching direction. The predominant location of crazes between fibrils suggests that craze development is strongly influenced by fibril orientation.

In the iPP thin film crystallization under cooling to room temperature, microcrystals showed a preferential growth in edge-on orientation.

The film irradiated with the higher dose, 20 kGy, presents coarse streaks which reveal the difficulty to align fibrils in the stretching direction. On a nanometer scale the entanglement involving crosslinked and/or branched chains in the amorphous phase is the primary cause of this phenomenon.

The increase of the crystallinity of the irradiated and stretched films is due to the crystallization of the soft and tie segment chains of the amorphous phase that suffered scission process.

Acknowledgement

The authors thank Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Financiadora de Estudos e Projetos (FINEP) and EMBRARAD/CBE.

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