STRETCHING HIGH MELT STRENGTH POLYPROPYLENE (HMSPP)

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Abstract – The use of traditional polypropylene resins in blow film processes has been prevented due to their poor melt strength and bubble instability. To overcome these deficiencies is necessary to improve the melt strength since it is known that opportunities exist for the use of a high melt strength polypropylene resin in blown film process.
This work aims to study the HMSPP films obtained by gamma radiation under acetylene, after uniaxial expantion. The thin films were stretched at 170 °C using an Instron machine. Film surface morphology and the thermal properties at HMSPP stretched were analised using atomic force microscopy (AFM), scanning electron microscopy (SEM) and differential scanning calorimetry (DSC).
The results showed some evidences of fibrillar structures containing crystallites and gel formation. Preferred orientations of crystals that develop stretching polypropylene samples are observed

Introduction

The use of traditional polypropylene resins in blown film processes has been prevented due to their poor melt strength and bubble instability. Improvement of the melt strength by radiation processing is an opportunity for a high melt strength polypropylene resin use (application) in blown film (Oliani et al, 2010).

The primary process in the interaction of radiation with polymers is the formation of excited species leading to the breakdown of chemical bonds and to free radicals formation. The produced radicals can react, resulting in crosslinking or chain scission (Zhang et al, 1999, Stojanovic et al, 2005).

Isotactic polypropylene (iPP) undergoes crosslinking and extensive main chain scissions when submitted to irradiation. Particularly in presence of acetylene, the simultaneous irradiation of PP is able to control chain scission and to produce grafting in radiation induced long-chain branching. The grafted PP further reacts with PP radicals resulting in branching and crosslinking (Yoshiga et al, 2009, Cheng et al, 2010).

The PP grade having low MFI values tends to have longer molecular chains and higher average molecular weight which form more molecular entanglements in the polymer melt. These polymers with a greater degree of molecular entanglements tend to have a higher resistance to extensional deformation yielding a higher melt strength (Muke et al, 2001).

In recent study, were investigated the deformation induced changes in the structure of iPP films during uniaxial stretching at three different temperatures (room temperature, 60 and 160 °C). The role of chain entanglement in the interlamellar amorphous region plays an important role affecting the structure. At low temperatures, as the chain mobility is relatively low, tie chains from entanglements may initiate the fragmentation of lamellar crystals upon stretching, forming oriented mesomorphic iPP phase with extended-chain conformation. At high temperatures, as the chain mobility is relatively high, tensile deformation can lead to chain disentanglement allowing the formation of more folded-chain crystals from coiled segments (Zuo et al, 2007).

In important study of microstructure of iPP (Dasari, 2003), the evolution during tensile deformation was examined by atomic force microscopy (AFM) and scanning electron microscopy (SEM), as a function of strain rate. Although both AFM and SEM are similar in lateral resolution, AFM has superior vertical resolution, and provides quantitative evaluation of surface topographical characteristics. The excellent resolution of AFM to describe surface topography has opened new opportunities to study surface deformation in polymeric materials (Dasari et al, 2003, Dvir et al, 2006, Koike and Cakmak, 2006, Hosier et al, 2004).

Many authors have investigated the structure and morphological properties of stretched polypropylene films (Tabatabaei et al, 2009) and the influence of molecular orientation on the crosslinking behavior iPP exposed to gamma radiation (Oliani et al, 2010, Suljovrujic, 2009).

It is considered a nanogel or a microgel an internally cross-linked macromolecule. This approach is basead on the fact that, in principle, all the chain segments of a nanogel or microgel are linked together, thus being a part of one macromolecule. It also reflects the fact that such entities can be synthesized either by intramolecular cross-linking of single linear macromolecules or in a single polymerization event (e.g., initiated by one radical) that in the absence of cross-linking would lead to the formation of a single linear polymer chain (Ulanski and Rosiak, 2004).

The purpose of the present study is to evaluate the influence of the stretching on the pristine and irradiated PP.

Experimental

Materials and Methods

The commercial iPP film was supplied by BRASKEM. The MFI is 1.5 dg min^{-1} (ASTM D 1238-4), obtained using a Ceast apparatus operating at 230 ºC with a charge of 2.16 Kg. The irradiation of the films was performed under acetylene atmosphere in a ^{60}Co gamma source and dose rate of 10 kGy h^{-1}. The irradiation doses were 5, 12.5 and 20 kGy monitored by a Harwell Red Perspex 4034 dosimeter. After irradiation the film samples were submitted to thermal treatment at 90 °C for 1 h (Oliani et al, 2010).

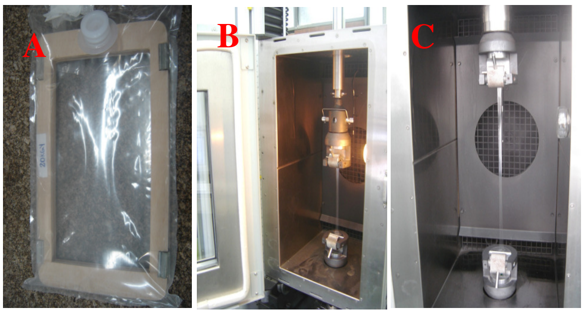

Figure 1 – (A) Film PP under bag device, (B and C) Instron machine with film stretched.

Stress Strain

The samples were manufactured at dimensions according to ASTM D 882-09. The film stretching was performed at 170 °C in an Instron machine with a strain rate of 0.17 s^{-1}.
The Fig. 1 A, shows the device in which the films were irradiated under acetylene atmosphere in a **^{60}Co** gamma source. Fig. 1 (B and C) show the PP film stretched in Instron machine at 170 °C.

Atomic Force Microscopy (AFM)

The atomic force microscopy measurements were performed with a scanning probe microscope Nanoscope III A, Digital Instruments (Veeco), equipped with Multi-Mode heads. The probe used for the images acquisition were commercial mode by Si, with resonant frequence of about 250 KHz. The images were obtained using 512 x 512 pixes. Experiments were performed in tapping mode with a E scanner.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was done using an EDAX PHILIPS XL 30. The nonconducting materials, like most of polymers, need to be coated using a metal including silver, gold or gold-palladium, or carbon to their outer surfaces be conductive. In this work, very thick coating of gold is sputter-coated onto the samples.

Thermal Analysis

Thermal properties of specimens were analyzed using a differential scanning calorimeter (DSC) 822, Mettler Toledo. The thermal behavior of films was obtained by heating from 25 to 280°C at a heating rate of 10°C min^{-1} under nitrogen atmosphere; holding for 5 min at 280°C, then cooled to 25 °C and reheating to 280°C at 10°C min^{-1}, according to ASTM D 3418-08. The crystallinity was calculated according to the equation:

$$X_C(\%) = \frac{\Delta H_f \times 100}{\Delta H_0}$$

Where:
ΔH_f = melting enthalpy of the sample, ΔH_0 = melting enthalpy of the 100% crystalline PP which is assumed to be 209 kJ kg^{-1} (Brandrup et al, 1999; Stojanovic et al, 2005).

Results and Discussion

Stress Strain

The Fig. 2 shows the stress-strain curves for the pristine and modified PP films.

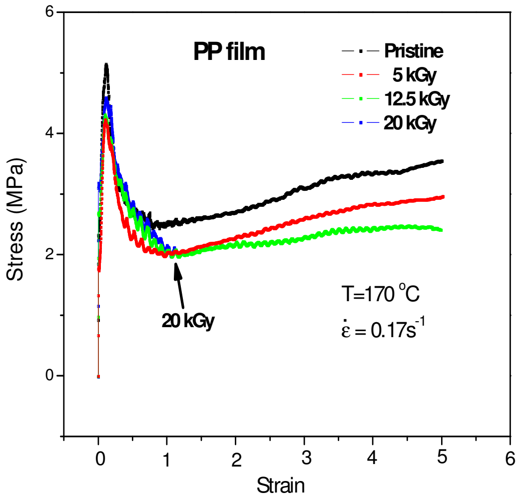

Figure 2 – Stress-strain curves for the PP film stretched up to rupture at 170ºC with a strain rate of $0.17s^{-1}$ (l_o=50mm).

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 170ºC, so we postulate that the yielding can be attributed to the entanglement of the polymer chains. However, at 170ºC there 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, compared to pristine, was a consequence of the prevalence of the chain scission over the branching and crosslinking at low doses (Lugao et al, 2002). For the 20 kGy sample the yield stress increases and the elongation at rupture diminished due to the high level of crosslinking.

Atomic Force Microscopy (AFM)

Fig. 3 shows a representative image for the surface morphology of polypropylene films, obtained by AFM.

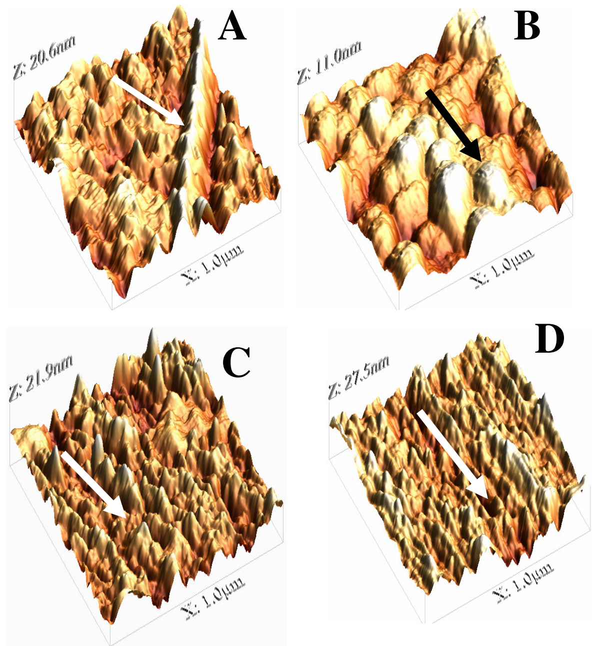

Figure 3 – Atomic force microscopy images 3D of pristine and irradiated stretched samples (A) iPP Pristine, (B) HMSPP 5 kGy, (C) HMSPP 12.5 kGy and (D) HMSPP 20 kGy.

In all images the stretching direction is indicated by an arrow. When PP film is stretching performed at 170ºC a significant change in the surface of the material takes place. It is observed the formation of microfibrillar structures of HMSPP aligned by stretching.

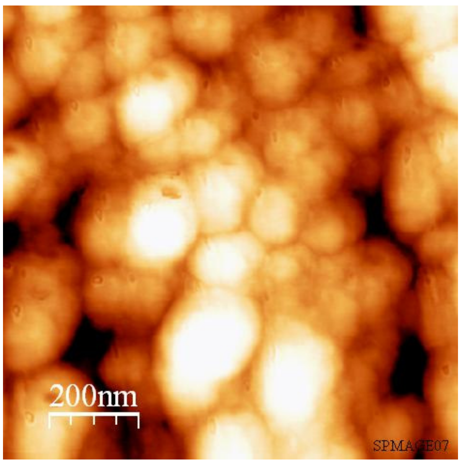

Figure 4 - Atomic force microscopy image stretched sample HMSPP 5 kGy.

The Fig. 4 shows some fibrils with an average diameter of 180 nm that are uniformly distributed at the surface of the 5 kGy. In this case, the number of fibrils by micrometer (approximately, 7) is the lower of the irradiated samples, which are 12 and 13, for 12.5 kGy and 20 kGy samples respectively.

Scanning Electron Microscopy (SEM)

The SEM results are shown in Fig.5 in irradiated and stretched samples presents lines in the stretching direction signalized by the arrows.

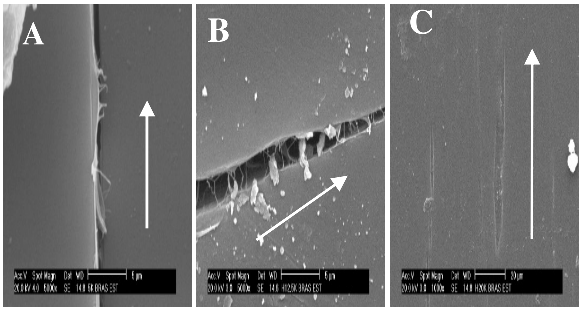

Figure 5 – (A) HMSPP 5 kGy film magnified 5 µm, (B) HMSPP 12.5 kGy film, magnified 5 µm and (C) HMSPP 20 kGy film, magnified 20 µm.

A fibrillar structure oriented along the stretching direction is also the dominating morphological feature in these images Fig. 5, indicates surface regions with microfibrils parallel and perpendicular to the stretching direction.

Thermal Analysis

The crystallinity (%) was determinated from the second melting event the differential scanning calorimetry (DSC). Table 1, summarizes the results of the pristine and modified (irradiated) films, before and after stretching.

Table 1 – Crystallinity (%) of PP films before and after stretching.

	Crystallinity (%) (± 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

The crystallinity increases after stretching. On the stretched condition the irradiated films crystallinity was at around 30% 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 and the improvement of fibril diameter (Fig.4), 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.

Conclusions

The stretching process at high temperature (170 ^{o}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.

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.

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