# STUDY OF THE MORPHOLOGY OF HMS-PP (High Melt Strength Polypropylene) FILMS

**W.L. Oliani[a], L.F.C.P. Lima[a], D.F. Parra[a], D.B. Dias[b] and A.B. Lugão[a]**

**Nuclear and Energy Research Institute – IPEN-CNEN/SP**
**a. Chemical and Environmental Center (CQMA)**
**b. Radiation Technological Center (CTR)**
**Av. Professor Lineu Prestes, 2242, 05508-000, Sao Paulo, SP, Brazil**

## Abstract

The High Melt Strength Polypropylene (HMS-PP) can be considered a fast growing grade of isotactic PP (iPP) due to its superior processing characteristics. HMS-PP has much greater strain hardening than conventional PP grades, therefore it can be applied for production of thin films. Thin films of PP 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, a lot of problems usually arise, causing material, energy and time losses. This work aims to study the surface morphology of HMS-PP films after uniaxial expansion. The experiment was conducted by PP compression molding at 190 $^{o}$C with cooling in water at room temperature followed by gamma irradiation (5, 12.5 and 20 kGy) under acetylene. After irradiation the samples were submitted to thermal treatment at 90 $^{o}$C during 1 hour and then stretched out at 170 $^{o}$C in an Instron machine. The surface of PP films, pure and modified, was studied using optical microscopy (OM) and scanning electron microscopy (SEM). The changes in morphology of the PP with irradiation dose were investigated. The results showed some evidences of gel formation increase due to physical or chemical crosslinking induced by radiation.

Key words: Polypropylene film, gamma radiation, uniaxial stretching, HMS-PP

## Introduction

The use of traditional polypropylene resins in blown film processes has been prevented due to their poor melt strength and bubble instability. To surmount 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; Lugão et al, 2003; Auhl et al, 2004; Lugão et al, 2007), to look at an increase of the entanglement network. In order to understand the influence of the entanglement network on the physical and chemical properties of iPP and HMS-PP several studies have been reported. The main technique of investigation has been the atomic force microscopy (AFM) of thin films obtained under a large number of experimental conditions, as temperature and mechanical mode processing (Auriemma and De Rosa, 2006; Kailas et al, 2007; Schönherr et al, 2003; Coulon et al, 1998; Zia et al, 2008: Koike et al, 2006; Snétivy et al, 1993; Wawkuschewski 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 HMS-PP at temperatures higher than the crystalline phase melting temperature. In this work optical microscopy (OM) and scanning electron microscopy (SEM) were used to image the surface morphology of an uniaxially-oriented polypropylene film stretched at 170 $^{o}$C.

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## Experimental

The commercial iPP was supplied by BRASKEM and its melt flow index (ASTM D 1238) obtained in an apparatus CEAST at 230 $^{o}$C with a charge of 2.16 kg was 1.5 dg.min$^{-1}$. The films were obtained by compression molding at 190 $^{o}$C (10 minutes without pressure and 5 minutes under a pressure of 8 MPa) with cooling in water bath at room temperature. The irradiation was performed under acetylene atmosphere in a $^{60}$Co source with doses of 5, 12.5 and 20 kGy monitored by a Harwell Red Perspex 4034 dosimeter with dose rate of 10 kGy.h$^{-1}$. After irradiation the samples were submitted to a thermal treatment at 90 $^{o}$C during one hour. The film stretching was performed at 170 $^{o}$C in an Instron Machine with a deformation rate of 500 mm.min$^{-1}$. The samples were observed by Optical Microscopy (OM) (Olympus PME3) and Scanning Electron Microscopy (SEM) (EDAX Philips XR-30). To the SEM observation a film surface Au deposition was done to improve electrical conductivity.

## Results and Discussion

All the irradiated and stretched samples present lines in the stretching direction signalized by the arrows (Figures 1 and 2). The polymer films that have been

INSERT FIGURES 1 AND 2

submitted to mechanical testing are characterized by a micrometer-scale fiber like network structure, which reflects the stretching process at 170 $^{o}$C. According to Koike and Cakmak ( 2006), stretching polypropylene in the solid state invariably leads to formation of fibrilar texture. This micro-structure can be seen in the micrographs presented in Figures 1 and 2, as streaks aligned in the stretching direction represented by the arrows. This is confirmed by observations of samples that have been heavily deformed (Figure 2-a3) where the fibrils are detached from the bulk. In the Figure 1 (HMS 20 kGy) we can observe coarse streaks which have been reported by Chang et al (2002) and reflect the difficulty to align the branched and/or crosslinked chains. The stretching temperature of 170 $^{o}$C is higher than the melting temperature of the crystalline phase of a 90% isotacticity polypropylene. At this temperature the enhanced chain mobility due to the absence of 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 there are fibrils (set of tie chains) that join adjacent fibers (Wawkuschewski et al, 1995) and suffer rupture in a cavitational 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. This crystallization begins with lamellae formation that subsequent organization creates the spherulites as observed by Kajioka et al (2008) in isotactic poly(butene-1). The observed

elongated features (see Figure 2-a1 and 2-a2) can be assigned to edge-on oriented lamellae, how as been observed by Schönherr et al (2003) in low-crystallinity polypropylene and Kailas et al (2007) in nanodroplets of low molecular weight isotatic polypropylene using AFM.

**Conclusion**

The stretching process at high temperature (170 $^{o}$C) creates a micrometer-scale fiber like network structure in the iPP and HMS-PP 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 during cooling to room temperature the observed 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. In a nanometer-scale the entanglement consisting of branched and crosslinked chains in the amorphous phase is the primary cause of this phenomenon.

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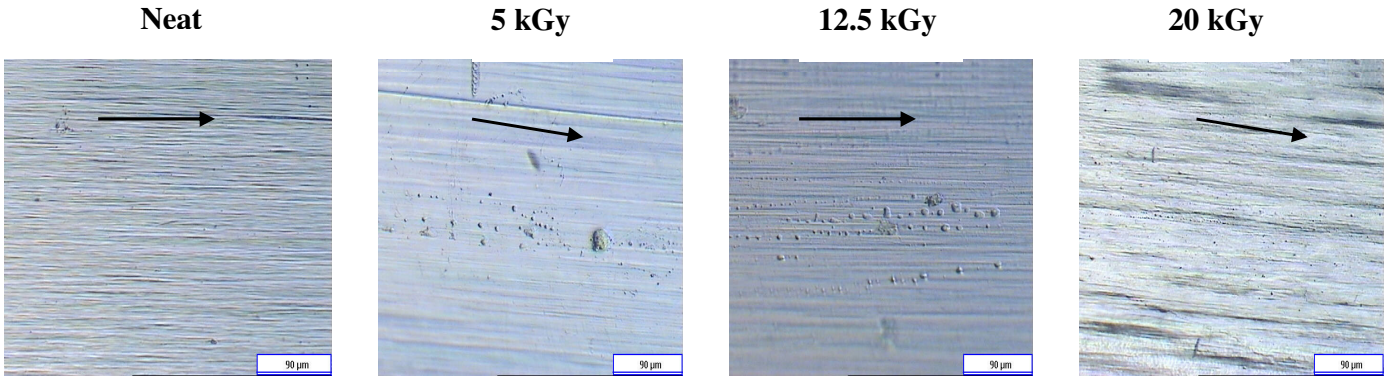
**Captions to figures.**

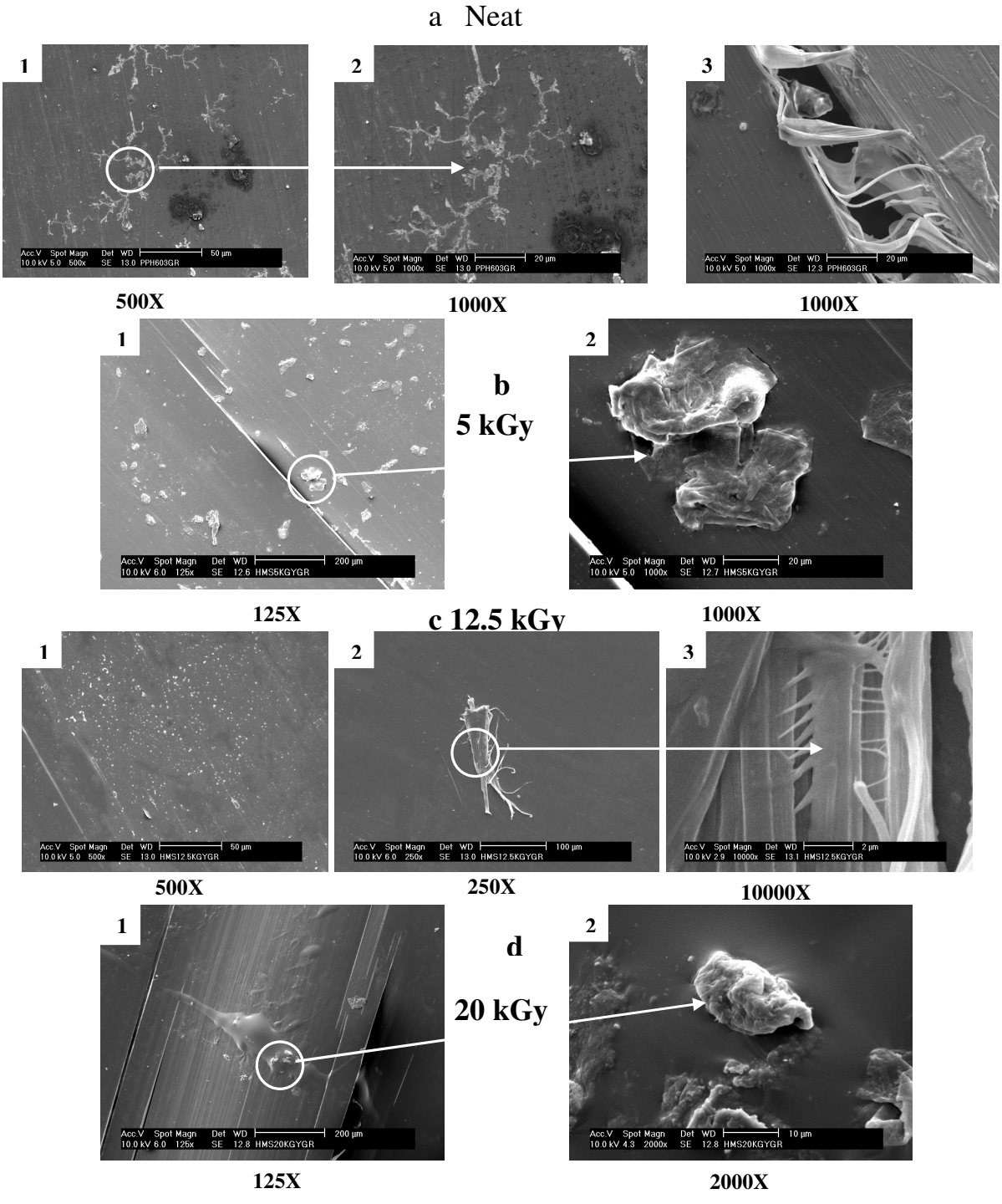
**Figure 1: Optical microscopy micrographs of irradiated and stretched samples (400X).**

**Figure 2: Scanning electron microscopy micrographs of irradiated and stretched samples: a) neat, b) 5 kGy, c) 12.5 kGy and d) 20 kGy.**

Figure 1



# Figure 2


a Neat
1
2
3
500X
1000X
1000X
1
b
5 kGy
2
125X
1000X
c 12.5 kGy
1
2
3
500X
250X
10000X
1
d
20 kGy
2
125X
2000X