Advances in Materials Research, *Vol. 2, No. 2 (2013) 111-118*
DOI: http://dx.doi.org/10.12989/amr.2013.2.2.111

A study of plastic plateau disappearance in stress-strain curve of annealed polypropylene films during stretching

Caihong Lei*, Shuqiu Wu, Ruijie Xu, Yunqi Xu and Xinlong Peng

School of Materials and Energy, Guangdong University of Technology, Guangzhou 510006, China

(Received Jun3 21, 2012, Revised January 03, 2013, Accepted April 8, 2013)

Abstract. The changes of plastic plateau in the stress-strain curves of annealed polypropylene (PP) films during stretching under room temperature were followed and the corresponding melting properties and microstructure were characterized by differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). It was found that during stretching the plastic plateau disappeared progressively with the increase of drawing ratio. At the same time, the endotherm plateau in DSC curves also disappeared progressively. The presence of the plastic plateau was attributed to the stretching of unstable crystalline part which was formed by tie chains around initial row-nucleated lamellae structure during annealing. During stretching, the unstable part was stretched and converted to bridges connecting separated lamellae. There was direct relationship between the disappearance of plastic plateau and pore formation.

Keywords: polypropylene; row-nucleated lamellae structure; melt-stretching mechanism; micropores; hard elastomer

1. Introduction

Polypropylene (PP) is a well-known semi-crystalline polymer and it has been used for the fabrication of microporous membranes based on melt-stretching mechanism. During the fabrication process, there are three main consecutive stages: (1) production of the precursor film with row-nucleated lamellar structure by crystallization under shear or elongation field, (2) annealing of the film to remove imperfections in crystalline phase and to thicken the lamellae, and (3) stretching at low and high temperatures to create and enlarge pores, respectively.

Obtaining a precursor film with uniform row-nucleated lamellar structure is the most important step in the fabrication of microporous membrane. Both raw material physical properties and processing conditions have shown important influence on the row-nucleated lamellar structure. Sadeghi *et al*. (2007b) found that the resin with a higher molecular weight had a tendency to form a planar crystalline morphology as the draw ratio increased. Air cooling, the temperatures of chill rolls and thermal-setting rolls and draw ratio were the main factors to control the crystal structure in the processing of precursor film, which can be found in the work given by Tabatabaei *et al*. (2009).

Annealing is able to eliminate some drawbacks in the initial lamellae structure. After annealing, lamellae are rearranged and the row-nucleated lamellar structure with thicker lamellae and

*Corresponding author, Professor, E-mail: Lch528@gdut.edu.cn

http://www.techno-press.org/?journal=amr&subpage=7 ISSN: 2234-0912 (Print), 2234-179X (Online)

narrower thickness distribution can be obtained.

In the third stage, the lamellae are separated by cold stretching and at the same time pores are created. The later hot-stretching enlarges the pores. Sadeghi *et al*. (2007a) found that during hot stretching, some lamellae melted and formed a 'bridge' structure through re-crystallization in the micropores. The lamellae thickness was reduced when a large number of 'bridge' structures were created.

It has been well known that annealing stage is of great importance for the fabrication of microporous membrane. Lei *et al*. (2012) found that compared with that of precursor film, the significant change after annealing was that a low temperature melting plateau endotherm appeared in the differential scanning calorimetry curves. During stretching under room temperature, the plateau disappeared progressively and there was a direct relationship between the plateau disappearance and void formation during stretching.

Sadeghi *et al*. (2007a) compared the stress-strain curves of precursor and annealed film and the difference after annealing was that a plastic shoulder and later strain-hardening appeared after the initial elastic region. Many investigations have shown that the shoulder was related to the lamellae separation and pore formation. However, up to now, no work has reported its changes during stretching and its direct relationship with pore structure.

In this article, the stress-strain curves of PP film which has been stretched to different ratio under room temperature were followed. The corresponding melting curves and microstructure were tested using differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). Before stretching, the PP precursor film has been annealed under 145°C for 30 min. Finally, the relationship between the plastic plateau and pore formation was discussed.

2. Experimental

2.1 Materials

A 2.0 g /10 min PP (230°C, 2.16 Kg) from Yangzi petrochemical company, China, was used. Its peak melting point (T_m) and crystallization temperature (T_c), obtained from differential scanning calorimetry (DSC, PerkinElmer DSC 7, Massachusetts, United States) at a rate of 10°C/min, were 167.7°C and 115.1°C, respectively.

2.2 Preparation of stretched PP film

Firstly, the precursor film was prepared. It was made by cast extrusion through a *T*-slit die followed by stretching and thermal-setting. During extrusion, the uniaxial (machine direction, MD) stretching was applied to PP melt, which resulted in the oriented crystalline structure. The die temperature was set at 210°C and a draw ratio of 125 was applied. The films were produced under chill roll temperature of 80°C and then annealed at 145°C for 30 min.

The annealed film was stretched under room temperature using Hualong WDW-10C machine. The drawing ratios for sample A, B, C, D, E and F were 2.5%, 6%, 15%, 25%, 60% and 100%, respectively. Samples were chosen according to the stress-strain curve of annealed PP film shown in Fig. 1. Sample A represented the film before yielding point. Sample B was around the yielding point. Sample C and D were in the plastic region, especially sample D was near the strain-hardening zone. Sample E was within the strain-hardening region. Sample F represented the film after its second yielding point.

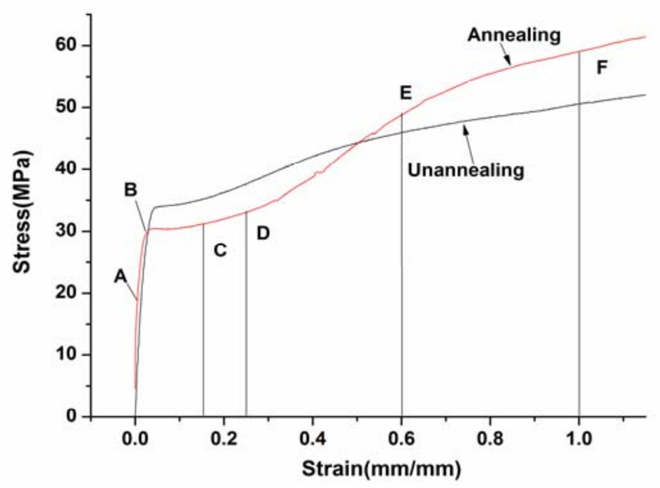

Fig. 1 Sample designation in the stress-strain curve of annealed PP film

2.3 Characterization

The stress-strain curve of stretched PP film was tested using Hualong WDW-10C machine. The initial length of test samples was 50mm and the strain rate was 50mm/min.

A PerkinElmer DSC 7 was used to measure the melting curves of precursor film, annealed film and stretched samples at a heating rate of 10℃/min. Surface morphology was characterized by scanning electron microscopy (SEM; LEO SUPRA 55, Carl Zeiss, Germany). For FTIR measurements, a Nicolet Magna 860 FTIR instrument from Thermo Electron Corp. (DTGS detector, resolution 2 cm^{-1}, accumulation of 128 scans) was used. The beam was polarized by means of a Spectra-Tech zinc selenide wire grid polarizer from Thermo Electron Corp. For PP, absorption at the wavenumber of 998cm^{-1} was chosen to characterize the orientation of crystalline phase (c-axis). The dichroic ratio was defined as the ratio of the absorption parallel and perpendicular to the machine direction. Then the Herman orientation function at 998cm^{-1} can be calculated (Sadeghi *et al*. 2007a).

3. Results and discussion

In Fig. 1, it could be seen that compared with that of precursor film, the significant differences in the stress-strain curve of annealed film were the appearance of plastic plateau after the initial elastic region and apparent strain-hardening behavior. To investigate the plateau change during stretching under room temperature and its direct relationship with pore structure, samples with different drawing ratio were chosen and their stress-strain curves were tested.

Fig. 2 gives the stress-strain curves of stretched PP films. Similar to that in annealed film, an apparent plastic plateau was still observed in sample A and B, but it became weak for sample C. For sample D, which was in the transition zone from plastic to strain-hardening region, the plateau almost disappeared. In sample E and F, the plateau vanished completely. During stretching under room temperature, the plastic plateau disappeared progressively.

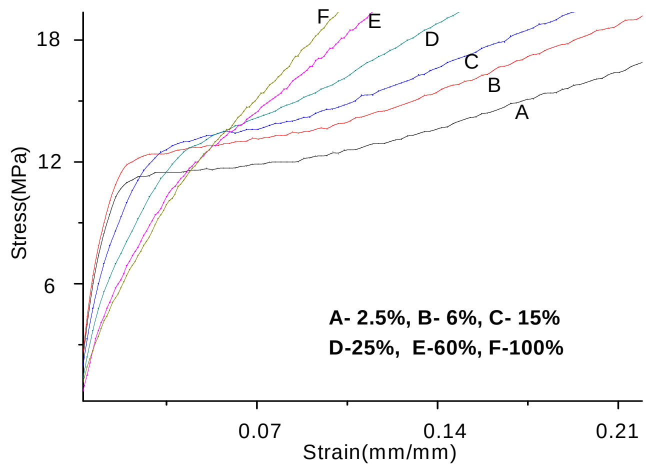

Fig. 2 Stress-strain curves for PP films with different drawing ratios

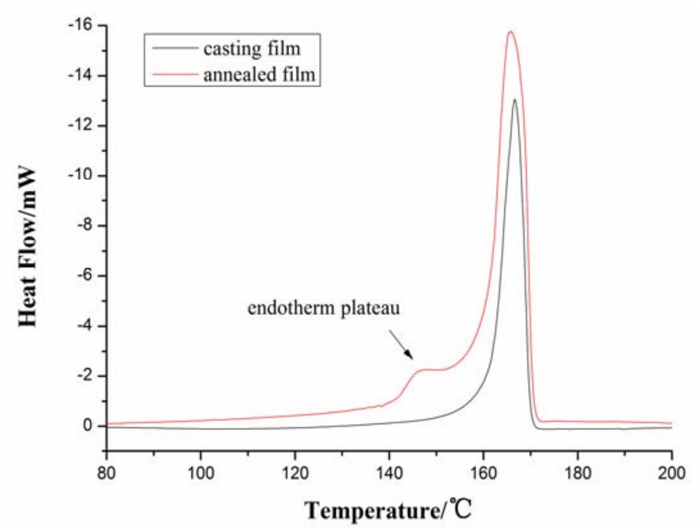

Fig. 3 DSC curves of PP film before and after annealing

Fig. 3 gives the DSC curves of PP film before and after annealing. It was apparent that after annealing, the melting peak area increased, indicating the occurrence of crystallization behavior during annealing. The other change was that an endotherm plateau appeared before the main melting peak. Fig. 4 gives the DSC curves of PP samples with different drawing ratios. With the increase of drawing ratio from sample A to F, the low-temperature endotherm plateau formed during annealing disappeared progressively and it could not be seen in sample D, E and F. In our previous work (Lei *et al*. 2012), the low-temperature endotherm plateau in the DSC curve was believed to come from the crystallization of some chains situated between the row-nucleated lamellae structure. The DSC curves in Fig. 4 indicated that the grown crystals around initial lamellae during annealing were unstable and could disappear during stretching. We believe there must be some relationship between the disappearance of plastic region and melting plateau endotherm.

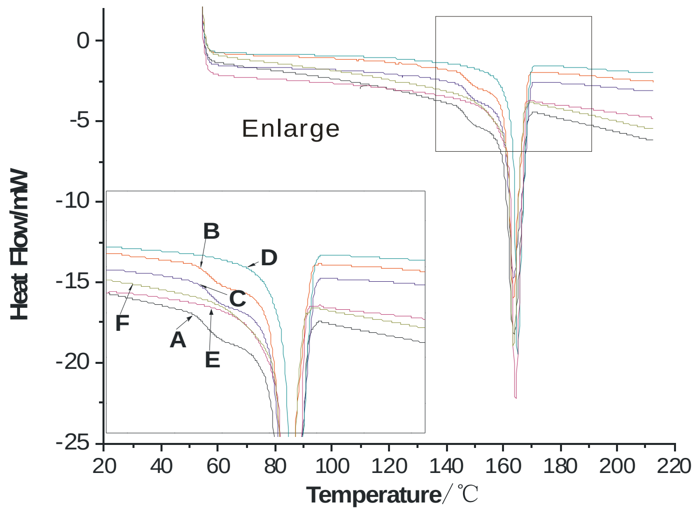

Fig. 4 DSC curves of PP films with different drawing ratios

Fig. 5 gives SEM results for stretched PP films with different drawing ratios. On the surface of sample A and B, no voids could be observed. For sample C, some chains were pulled out and standing near the lamellae. For sample D, the pulled out chains connected and formed bridges between the lamellae. In sample E, the connecting-bridge structure became more apparent and some scission of bridges and deformation of lamellar crystal were also observed. With further drawing to sample F, serious lamellae deformation, bridges scission and pores disappearance were observed. It was well known that the deformation of lamellar crystal was due to the interaction between lamellae by connecting-bridges. Some weak bridges were broken during stretching and the direct results were that the number of bridges was reduced and the pore size was decreased.

It could be seen that the disappearance of plastic plateau was directly related to the disappearance of low temperature endotherm plateau and the appearance of pore structure. For sample D, the plastic plateau and the endotherm plateau almost disappeared. On its surface, connecting bridges were observed. Within the plastic region in the stress-strain curve, the unstable crystalline part formed during annealing was slowly pulled away from the fold-chain lamellae and converted to connecting-bridges. In the strain-hardening region, the unstable part completely disappeared, and the lamellae interacted with each other through the bridges. Therefore, the presence of the plastic region could be attributed to the conversion of unstable crystalline part. It has been well known that during annealing, other than crystallization occurrence, the orientation or chain relaxation may also happen. To investigate the influence of orientation on the stress-strain curves, the orientation degree of films before and after annealing was tested using polarized FTIR. It was found that after annealing, the crystalline orientation degree was increased from 0.52 to 0.61. So small increase of orientation degree could not lead to the apparent changes of stress-strain curves of films before and after annealing in Fig. 1. Also the increase of orientation degree could not explain the decrease of first yielding point after annealing in Fig. 1. Based on the relationship between the mechanical properties and the fraction of tie chains proposed by Nitta and Takayanagi (2000), the decrease of first yielding point was due to that some tie chains were involved in the crystallization process during annealing and less tie chains were remained.

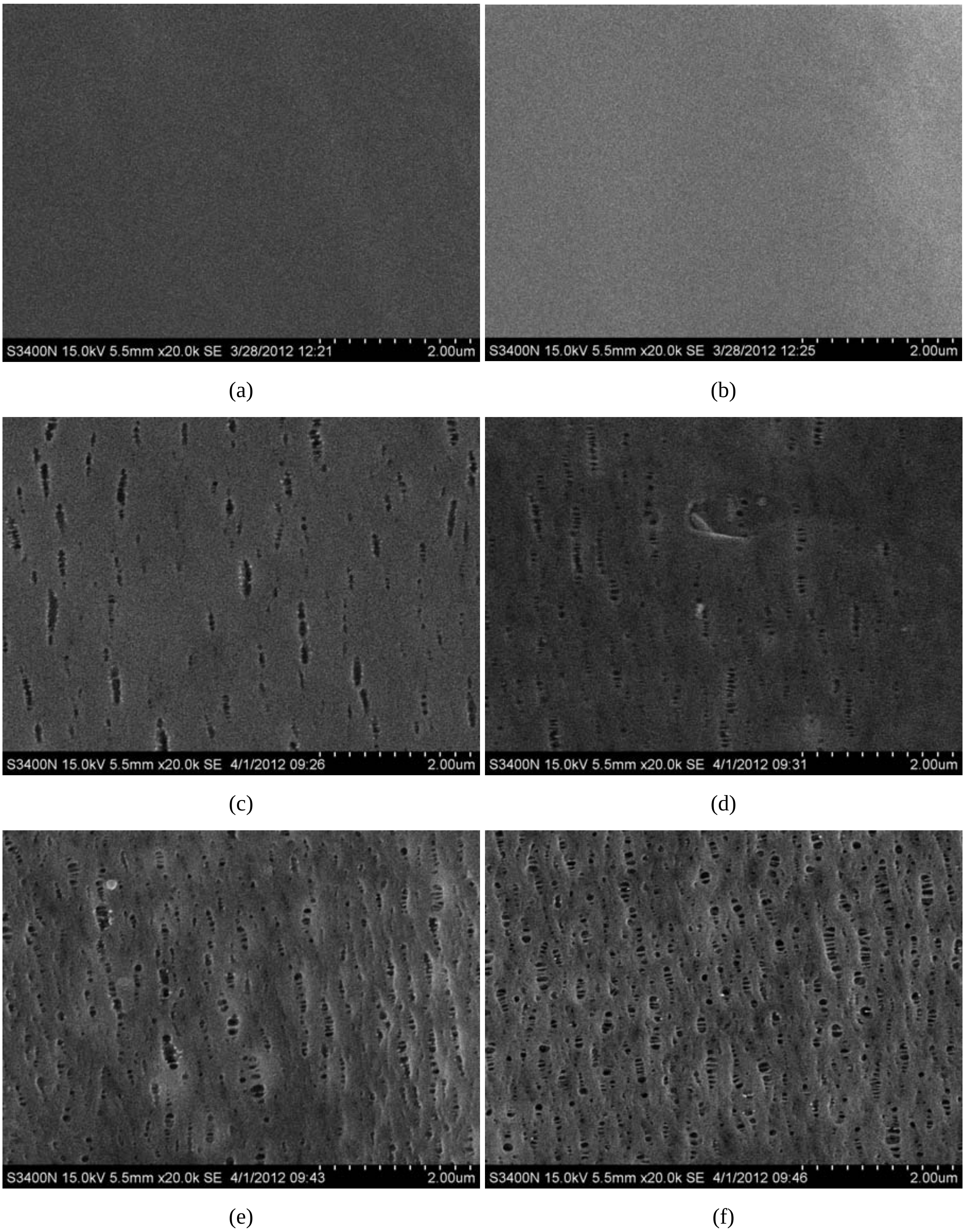

Fig. 5 SEM for PP films with different drawing ratios

Based on the above results, the pore and bridge-formation process during stretching under room temperature was illustrated in Fig. 6. For the precursor film, besides row-nucleated lamellae structure, tie chains, amorphous chains and chain entanglements existed among the interlamellar region. After annealing, some tie chains and amorphous chains would crystallize and formed the unstable crystalline part. Rastogi *et al*. (2005) had discussed that the entanglements in the amorphous regions limited the drawability in the solid state. Feng *et al*. (2007) also proved that during stretching under room temperature, the local entanglement stress concentration would be stronger than that for lamellae fragmentation. For the annealed film, the weakest part during stretching was the formed crystals around initial lamellae. During stretching within the plastic region, these unstable parts were gradually pulled out and converted into connecting bridges. At the same time, pores were formed. During stretching, the unstable crystalline part was like a buffer zone which prevented the increase of stress, explaining the existence of plastic plateau in the stress-strain curve of annealed PP films. During the strain-hardening stage, some scission of formed bridges occurred and the load was transferred to the residual tie chains which were not included in the crystallization process during annealing. The stretched residual tie chains crystallized locally. Local crystallization created more apparent bridges between the crystal blocks. Noether (1978) proved that the bridge between lamellae was crystalline and the stabilization of micropores structure was due to the crystallization of interlamellar bridges. The interaction between the lamellae became stronger through bridges. Further stretching induced bridges fracture and severe lamellae deformation. At the same time, pores were closed.

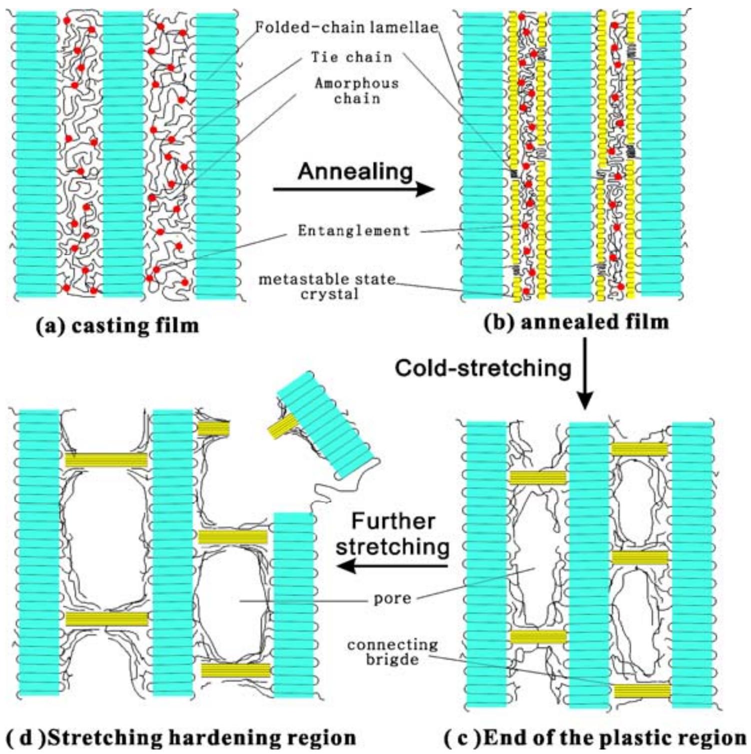

Fig. 6 Proposed pore-creation process during stretching of annealed PP film

4. Conclusions

The direct correlation among the plastic plateau in stress-strain curve, endotherm plateau in DSC melting curve and bridge formation was built up. The existence of the plastic plateau was attributed to the stretching of unstable crystalline part formed during annealing. The disappearance of the plastic plateau coincided with the disappearance of unstable crystalline part and the appearance of connecting-bridges and pore structures.

Acknowledgements

The authors would like to thank National Science Foundation of China under Grant No. 51003017 for financial support.

References

Feng, Z, Keum, J.K. and Chen, X.M. (2007), "The role of interlamellar chain entanglement in deformation-induced structure changes during uniaxial stretching of isotactic polypropylene", *Polym. J.*, **48**(27), 6867-6880.

Lei, C.H., Huang, W.L., Xu, R.J. and Xu, Y.Q. (2012), "The correlation between the lower temperature melting plateau endotherm and the stretching-induced pore formation in annealed polypropylene films", *J. Plast Film Sheet.*, **28**(2), 151-164.

Nitta, K.H. and Takayanagi, M. (2000), "Tensile yield of isotactic polypropylene in terms of a lamellar-cluster model", *J. Polym. Sci. Part B: Polym. Phys.*, **38**(8), 1037-1044.

Noether, H.D. and Hay, I.L. (1978), "Small-angle X-ray diffraction studies and morphology of microporous materials and their 'hard' elastic precursors", *J. Appl. Cryst.*, **11**, 546-547.

Rastogi, S., Lippits, D.R., Peters, G.W.M., Graf, R., Yao, Y. and Spiess, H.W. (2005), "Heterogeneity in polymer melts from melting of polymer crystals", *Nat. Mater.*, **4**, 635- 641.

Sadeghi, F., Ajji, A. and Carreau, P.J. (2007a), "Analysis of microporous membranes obtained from polypropylene films by stretching", *J. Membr. Sci.*, **292**(1-2), 62-71.

Sadeghi, F., Ajji, A. and Carreau, P.J. (2007b), "Analysis of row nucleated lamellar structure of polypropylene obtained from cast film: Effect of melt rheology and process conditions", *Polym. Eng. Sci.*, **47**(7), 1170-1178.

Tabatabaei, S.H., Carreau, P.J. and Ajji, A. (2009), "Effect of processing on the crystalline orientation morphology and mechanical properties of polypropylene cast films and microporous membrane formation", *Polym. J.*, **50**(17), 4228-4240.

CC