10th International Research/Expert Conference
"Trends in the Development of Machinery and Associated Technology"
TMT 2006, Barcelona-Lloret de Mar, Spain, 11-15 September, 2006

STRUCTURE AND PROPERTIES OF CAST FILMS PRODUCED FROM β-NUCLEATED POLYPROPYLENES

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ABSTRACT
The effect of β-nucleation on structure and properties of cast films manufactured from various isotactic polypropylenes has been studied. Two commercial-available polypropylenes – homopolymer (PP) and random copolymer (rPP) – were modified by 0.03 wt.% of specific β-nucleating agent based on N,N´-dicyclohexylnaphthalene-2,6-dicarboxamide. Cast films were prepared from both starting and nucleated polypropylenes using an extrusion line consisting of a Brabender single-screw extruder, slit die and water-cooled chill-rolls. Supermolecular structure of the films was evaluated using wide-angle X-ray scattering; tensile testing was used for the preliminary measurement of mechanical properties. A significant effect of the nucleation and solidification temperature on structure and consequent properties of the films was found in both PP and rPP and is discussed in this work.
Keywords: isotactic polypropylene, cast film, crystallinity, beta-phase, mechanical properties

1. INTRODUCTION
In today's period, conventional materials, such as metals, wood, glass and natural fibers are replaced by polymeric materials. Even recently as compared to conventional materials, they have found their way from the research lab to virtually any industrial application, ranging from medical to automotive, and from building industry to production of children toys. Similarly, isotactic polypropylene has become one of the most commonly used thermoplastics. This fact rises from its versatility. The polymer exhibits excellent chemical resistance, low density, high tensile strength, and relatively high melting point. According to crystallization conditions, isotactic polypropylene can crystallize into several crystalline forms (α, β, γ and smectic) [1-4]. From the application point of view, predominant α-phase and, presently, β-phase are the most important [5-7]. Recently, there have appeared interesting film applications based on the use of β-nucleated polypropylene. This approach allows manufacturing sheets with enhanced thermoforming ability (with extended processing window) or using specific drawing condition to produce microporous film with breathable features [5, 6]. The microvoiding is caused by β-to-α phase transformation during drawing. It can also results in a significant density reduction of the final film and even in a production of films with high levels of vapour transmission or breathability. Another interesting film product based on β-phase polypropylene application is biaxial-oriented film with a high degree of surface roughening which is important when the film is used as a dielectric capacitor [7]. The roughened surface after drawing improves the impregnation properties of insulating oils.
In this context, the aim of this work is to produce cast films from β-polypropylene at different processing conditions and to evaluate their structure with a particular interest directed towards an optimisation of β-phase content in cast films. Indeed, an integral part of the work is a basic assessment of their mechanical properties. For these purposes, cast films are prepared from commercially available isotactic polypropylenes Mosten 58412 homopolymer and from Mosten GB 802 random copolymer modified by a β-nucleating agent NJ Star NU 100 in the concentration of 0.03

wt. % of the nucleator. An investigation of prepared films is carried out using wide-angle X-ray scattering and tensile testing.

2. EXPERIMENTAL

2.1. Materials

Two commercially available isotactic polypropylenes produced by Chemopetrol, Litvínov, Czech Republic were used in this work: homopolymer Mosten 58412 and random copolymer Mosten GB 802. Generally, the content of β-modification in iPP articles processed under common conditions is insignificant; therefore, to enhance the content of β-modification, NJ Star NU100 nucleating agent produced by RVI International was used. Previous studies have confirmed its high nucleating activity; the addition of 0.03 wt.% nucleating agent led to β-modification content rise to 90 % [8]. A Brabender DSK 42/6D twin-screw extruder was used for the preparation and homogenization of blends containing PP Mosten 58412 and GB 802, respectively, 0.03 wt.% of NU100 and 0.30 wt.% of paraffin oil (for better dispersion of the nucleating agent).

2.2. Preparation of cast films

Films with 100μm thickness were cast with a Brabender single-screw extruder equipped with a slit die from the prepared blends at extrusion temperature of 220 °C. Temperatures of the extrusion barrel were 160, 190, 200 and 220 °C. Feeding zone was cooled by cold water and chill roll temperatures was set to 30 °C, 60 °C and 90 °C, respectively.

2.3. Assessment of cast film

To evaluate crystallinity and β-phase content, wide angle X-ray scattering (WAXS) was performed using an URD 6 diffractometer equipped with CuK_α working in the reflection mode. Radial scans of intensity vs. diffraction angle, 2θ, were recorded in the range of 10 ° to 30 º by steps of 0.03 º and length of step scan 5 s. Rectangular specimens for WAXS (10x30 mm) were cut out from the central part of the film. Total integral intensities I and integral intensities diffracted by crystalline part I_c were used for the determination of crystallinity $X_c = (I_c/I)*100$. The fraction of β-phase (K-value) was calculated using the following relation proposed by Turner-Jones et al. [2]

$$K = \frac{I_{300}^{\beta}}{I_{100}^{\alpha} + I_{040}^{\alpha} + I_{130}^{\alpha} + I_{300}^{\beta}} \qquad (1)$$

where $I_{300}^{\beta}, I_{100}^{\alpha}, I_{040}^{\alpha}, I_{130}^{\alpha}$ correspond to the diffraction intensities of crystalline lattices of β-phase and α-phase respectively. Tensile properties of the films were examined using a Zwick tensile testing machine in accordance to ISO 527. Five dog-bone specimens, which were cut out from the central part of individual cast films (in extrusion direction), were tested by elongation speed of 200 mm/min and average value was calculated.

2. RESULTS AND DISCUSSION

First of all the structure of cast films was evaluated. Relevant WAXS spectra are shown in *Figure 1*. From a comparison of left and right figures it is evident that solidification at 90 °C (setting of chill-roll) led to rather higher crystallinity of the films (indicaded by sharp diffraction maxima) while the spectra of the films cooled at 30 °C show high amorphous halo and their structure can be clearly assigned to smectic arrangement. *Figure 1* (on the right) illustrates also the spectra of the films solidified at 60 °C and it is evident that their structure does not show smectic arrangement and consists of regular crystalline structure. In the case of polymorphic composition, it is clear that the most significant β-diffraction peak is visible in the film made from nucleated homopolymer (β-PP) and cooled at 90 °C. This peak is also visible in the film produced from random PP with nucleating agent at 90 °C. In the film solidified at 30 °C, the content of β-phase is virtually insignificant in all films. What is also particularly interesting is that the β-diffraction peak (even in β-PP) is not virtually evident in the films cooled at 60 °C although they possess significant crystalline structures.

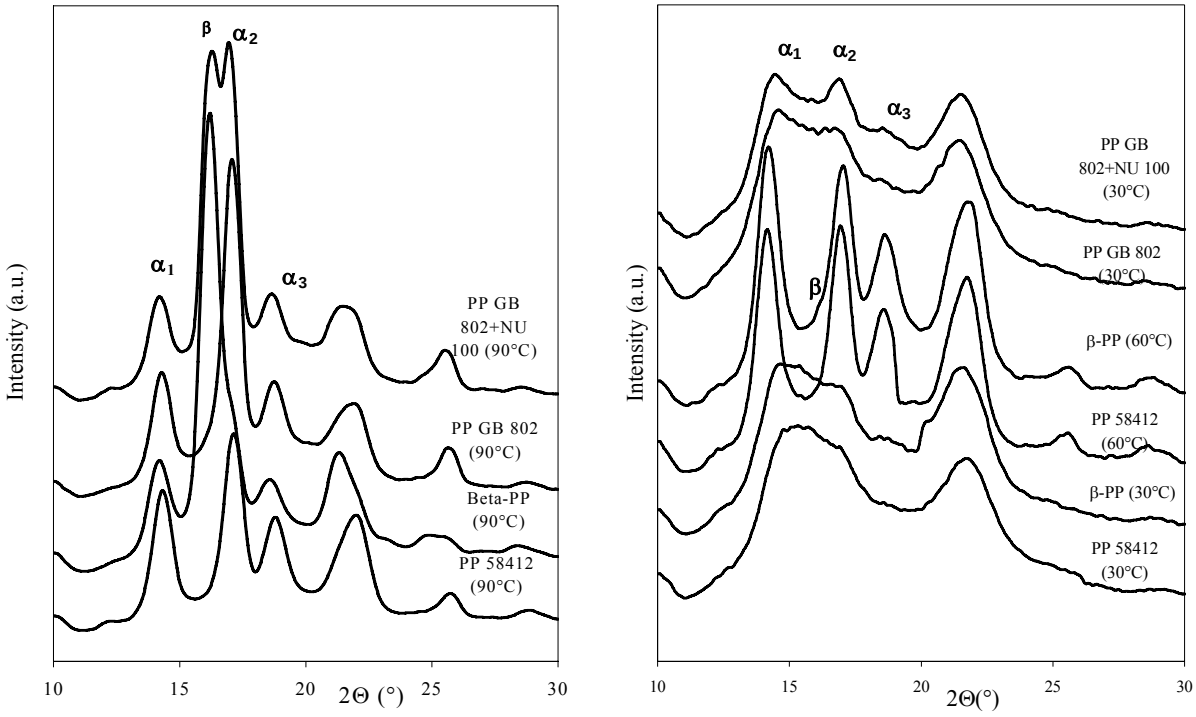

Figure 1. WAXS spectra of cast films solidified at various chill roll temperatures (left: 90 °C, right: 30 and 60 °C).

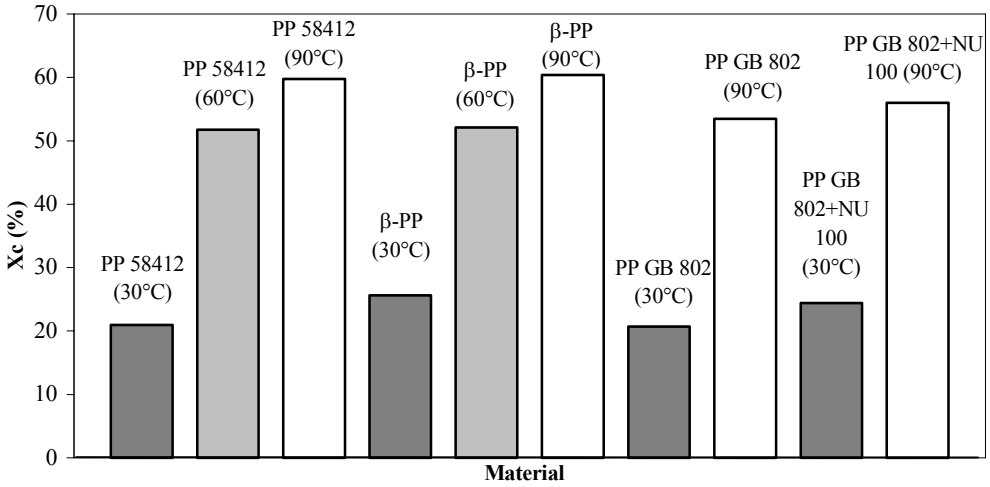

Figure 2. Crystallinity of cast films solidified at various temperatures

Figure 2 shows crystallinity values of the cast films produced from different materials at various chill roll temperatures. It is evident that with increasing chill roll temperature the percent of crystallinity increases. The highest crystallinity is indicated the film produced from β-PP at 90 °C chill-roll temperature. The films cooled at 30 °C chill-roll temperature have particularly low crystallinity, approx. 20 %. Also in this case, the values of crystallinity are slightly enhanced by the nucleator addition. The variations of β-phase content (k-value) are mentioned in *Figure 3*. Only three β-nucleated cast films contain β-phase within their crystalline portion. The highest k-value was detected in β-PP (approx. 60 %) solidified at 90 °C; when the chill-roll temperature was lowered to 60 °C, the cast films made from this material contained less than 10 % of β-phase (k-value < 0.10). The film manufactured from random PP with nucleating agent at a 90 °C chill-roll temperature had approx. 40

% of β-phase. Thus, it can be stated out that the k-value favourably increases with increasing chill-roll temperature, particularly in the case of homopolymers.

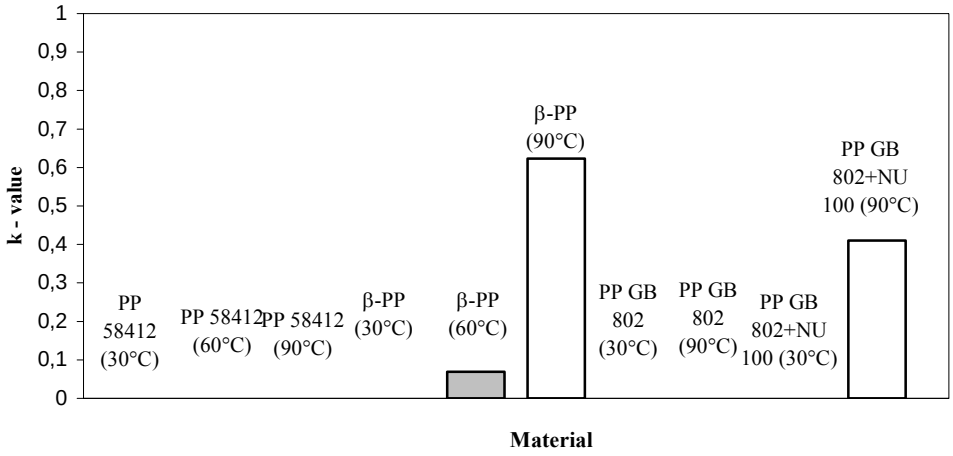

Figure 3. k-value (β-phase content) of cast films solidified at various temperatures

Preliminary evaluation of tensile properties was performed and it can be briefly summed up as follows. Enormous differences in elongation at break values between neat PP 58412 (90 °C) and nucleated β-PP (90 °C) were indicated. This confirms significantly higher drawability of β-PP as compared to neat PP 58412. Generally, the break strain decreases at all cast films with increasing chill roll temperature. Random PPs show slightly higher elongation at break as compared to homopolymers. As for yield stress values, we can say that tensile yield stress increases with increasing chill roll temperature. The highest tensile yield stress has neat PP 58412 (90 °C), however comparable with β-PP film. The films manufactured from random PP possess significantly lower tensile strength as compared to homopolymers.

3. CONCLUSIONS

This work deals with the preparation and assessment of cast film manufactured from both neat and nucleated polypropylenes – homopolymer and random copolymer. From wide-angle X-ray scattering it is evident that the solidification at 90 °C led to rather high crystallinity of the films while the spectra of the films cooled at 30 °C show high amorphous halo. The films solidified at 60 °C consist of regular crystalline structure. The highest content of β-phase was in the film made from β-nucleated homopolymer solidified at 90 °C. Random polypropylenes show lower crystallinity and β-phase content as compared to homopolymers. For the enhancement of β-phase content, high chill-roll temperature is desirable. The effect of nucleation and chill-roll temperature on mechanical properties is briefly discussed for both hopomolymer and random copolymer PP.

4. REFERENCES

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5. ACKNOWLEDGEMENTS

The authors kindly acknowledge the support provided from the Ministry of Education, Youth and Sport of the Czech Republic (project MSM7088352101).