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Phase behavior and optical- and mechanical properties of the binary system isotactic polypropylene and the nucleating/clarifying agent 1,2,3-trideoxy-4,6:5,7-bis-*O*-[(4-propylphenyl) methylene]-nonitol

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ABSTRACT

The phase behavior and optical- and selected mechanical properties of the binary system consisting of isotactic polypropylene (i-PP) and a new sorbitol-based nucleating and clarifying agent, 1,2,3-trideoxy-4,6:5,7-bis-*O*-[(4-propylphenyl) methylene]-nonitol (TBPMN), were investigated. Temperature/composition diagrams of the binary were found to be of the simple monotectic type, similar to those of, among others, the previously investigated i-PP/1,3:2,4-bis(3,4-dimethyldibenzylidene)sorbitol (DMDBS). Liquid–liquid phase separation was observed in binaries comprising more than ~5% w/w TBPMN, indicative of enhanced miscibility of the new additive with i-PP when compared with that of DMDBS. At TBPMN contents ≥0.1% w/w the optical properties haze and clarity progressively improved to remarkable levels with increasing concentration of the nucleating agent up to the onset of liquid–liquid phase separation, above which they deteriorated. The enhanced solubility in i-PP of the new clarifying agent on the one hand required uneconomically higher concentrations than previous members of the sorbitol family to be effective, but on the other, the superior optical properties of the system may permit manufacturing of clarified products of increased thickness.

1. Introduction

The ability of sorbitol derivatives such as 1,3:2,4-dibenzylidenesorbitol (DBS, Millad® 3905, Milliken Chemical and Irgaclear® D, Ciba Specialty Chemicals) and 1,3:2,4-bis(3,4-dimethyldibenzylidene)sorbitol (DMDBS, Millad® 3988, Milliken Chemical) to efficiently nucleate the α-crystal form of isotactic polypropylene (i-PP) is well known and has been thoroughly investigated [1–7]. Relatively small amounts of these nucleating agents may also drastically enhance the clarity and reduce haze of artifacts made with this polymer, earning them the connotation "clarifiers". The sorbitol derivatives are – in contrast to many other nucleating agents – designed to dissolve and recrystallize in the molten polymer, permitting the formation of a well-dispersed, large surface area, tri-dimensional nanofibrillar network [8–10]. It has been shown earlier that the nucleating and clarifying abilities of DMDBS, as well as other soluble clarifying agents for i-PP, are strongly dependent on the additive concentration and governed by the phase behavior of the binary system, as well as solidification kinetics [6,11].

Recently, a new member of the sorbitol family, 1,2,3-trideoxy-4,6:5,7-bis-*O*-[(4-propylphenyl)methylene]-nonitol (TBPMN) has been advanced, which is claimed to feature enhanced clarifying ability compared to its predecessors [12]. Another advantage is said to be its increased solubility in i-PP, enabling lower processing temperatures; therewith reducing the problem of the generally poor thermal stability of sorbitol derivatives [13].

In this paper, the phase behavior of i-PP/TBPMN binary is presented and related to its optical and selected mechanical properties, in analogy with previous publications on i-PP/DMDBS [6,14]; salient differences between the two systems are discussed.

2. Experimental

2.1. Materials

The isotactic polypropylene used was Moplen HF 500 N from Basell. The clarifying agent 1,2,3-trideoxy-4,6:5,7-bis-*O*-[(4-propylphenyl)-methylene]-nonitol (TBPMN, CAS Registry Number: 882073-43-0, Fig. 1) was synthesized according to general procedures in Ref. [12].

2.2. Blend preparation

Mixtures of i-PP and TBPMN, comprising up to 10% w/w of the additive, for use in subsequent injection molding were compounded

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in a laboratory co-rotating mini-twin-screw extruder (Technical University Eindhoven, The Netherlands) at 100 rpm during 10 min under a nitrogen blanket at 230 °C. Mixtures for optical studies comprising higher contents of the additive were prepared by dry blending and compression molding at 250 °C. Reference samples of the neat polymer were produced according to corresponding procedures.

2.3. *Thermal analysis*

Thermal analysis was conducted with a differential scanning calorimeter (DSC 822e, Mettler Toledo, Switzerland) calibrated with Indium. DSC thermograms were recorded under nitrogen at standard heating and cooling rates of 10 °C/min; the sample weight was about 10 mg. During each run the sample was kept for 5 min at the highest temperature prior to cooling in order to ensure complete melting of the polymer and to prevent self nucleation. Crystallization and melting temperatures reported here correspond to the peak temperatures in the DSC thermograms. The degree of crystallinity of the polymer was calculated from the enthalpy of fusion, derived from the endothermic peak, adopting a value of 207.1 J/g for 100% crystalline isotactic polypropylene [15].

2.4. *Optical microscopy*

Films for optical microscopy were prepared by melt-compression molding previously compounded material between two glass slides at 230 °C, followed by quenching to room temperature. The resulting films were of a thickness of about 0.1 mm. Optical microscopy studies were performed with a Leica DMRX microscope (Leica Microsystems, Germany) equipped with a hot stage (FP82TM, Mettler Toledo). Standard heating and cooling rates of 10 °C/min were adopted.

2.5. *Injection molding*

Circular samples (thickness 1.1 mm, diameter 25.0 mm) for optical characterization were prepared by injection molding previously compounded material using a laboratory mini-injector (DACA Instruments, Santa Barbara CA, USA). The material was molten and kept for 2 min at 240 °C under a nitrogen blanket prior to injection into the mold, which was held at room temperature.

2.6. *Optical characteristics*

The optical characteristics haze and clarity of the injection-molded samples were determined according to ASTM standard D1003 [16] using a Haze-Gard Plus® instrument (BYK Gardner GmbH, Germany). Reported are the averages of measured values for at least three samples.

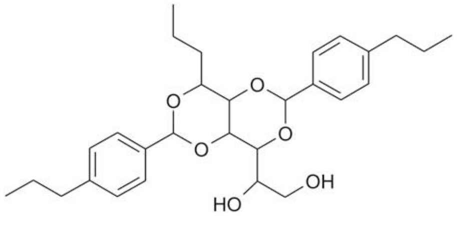

Fig. 1. Chemical structure of 1,2,3-trideoxy-4,6:5,7-bis-*O*-[(4-propylphenyl)-methylene]-nonitol (TBPMN).

2.7. *Small-angle X-ray scattering*

Small-angle X-ray scattering (SAXS) investigations were performed on the Dutch-Belgium beamline (DUBBLE, CRG BM26) at the European Synchrotron Facility (ESRF) in Grenoble, France. SAXS profiles were recorded at a wavelength of 0.95 Å with the detector positioned at 7.5 m from the sample. The experimental data collected were corrected for background scattering, detector response, sample thickness and beam intensity. Lorenz-corrected SAXS profiles were plotted against the scattering vector q, defined as:

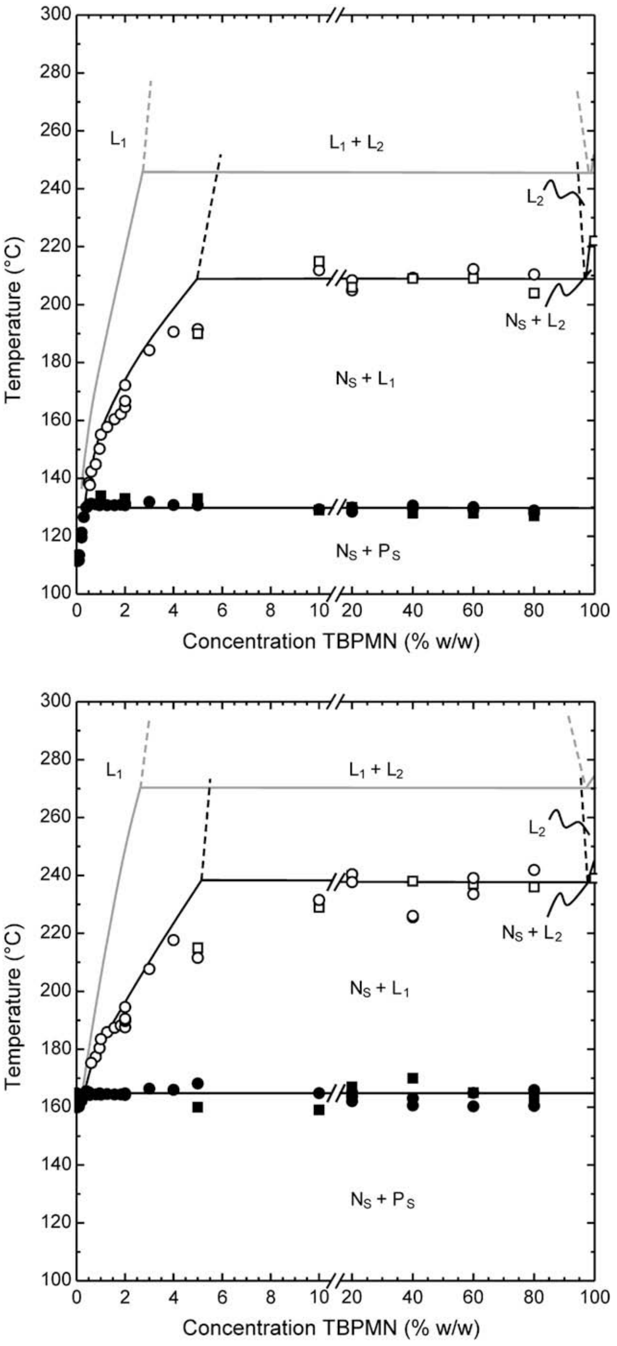

Fig. 2. Crystallization (top) and melting (bottom) temperature/composition diagrams of the binary system i-PP/TBPMN. Data obtained by differential scanning calorimetry (○) and optical microscopy (□) at cooling, resp. heating rates of 10 °C/min. The denotation N refers to TBPMN, P to i-PP, L to liquid, S to solid. The drawn lines are guides to the eye only. Also shown (in grey) are the corresponding schematic diagrams of i-PP/DMDBS (from Ref. [6]).

$$q = \frac{4\pi}{\lambda}\sin\theta \tag{1}$$

where λ is the X-ray wavelength and θ the scattering angle. The q-axis was calibrated using dry rat-tail collagen. The long period D, representing the combined thickness of the crystalline lamellae and the amorphous phase, was determined from the first peak maximum of the Lorenz-corrected scattering profiles as:

$$D = \frac{2\pi}{q_{\max}} \tag{2}$$

The corresponding lamellar thickness l was calculated as the product of the long spacing D and degree of crystallinity χ determined by DSC as:

$$l = \chi \cdot D \tag{3}$$

2.8. Tensile testing

For tensile testing, films with a thickness of 0.5 ± 0.05 mm were prepared by melt-compressing the various compounded blends for 5 min at 230 °C, followed by quenching in a cold press. Mechanical characteristics were investigated using an Instron 5864 tensile tester. The measurements were performed using dumb-bell shaped specimen with a gauge length of 12.7 mm; the rate of extension was 20 mm/min. For each sample at least five specimens were tested and the average values reported here.

3. Results and discussion

3.1. Temperature/composition diagrams

The melting and crystallization behavior of mixtures of i-PP/TBPMN covering the entire composition range was investigated employing differential scanning calorimetry (DSC) and optical microscopy. It was found that the system exhibits a similar, simple monotectic behavior as the binary i-PP/DMDBS [6] with the notable difference that TBPMN displayed enhanced compatibility with the polymer. This is evidenced by the substantially higher additive concentration for the onset of liquid–liquid phase separation of ~5% w/w for the present system, compared with ~2.5% w/w found for that comprising DMDBS (cf. Fig. 2).

DSC analysis revealed that the peak crystallization temperature, T_c, of i-PP was not significantly affected by addition of amounts of clarifying agent ≤0.1% w/w, and remained approximately at the same value as for the neat polymer (~113 °C), or even slightly decreased, as in this concentration range the additive acted simply as a high-melting diluent [6,17,18]. However, addition of quantities of TBPMN exceeding 0.1% w/w caused a rapid increase in the peak crystallization temperature of the polymer until a plateau value of 130 °C was reached at a concentration of about 0.4% w/w. The melting temperature of the polymer was not notably affected by the addition of TBPMN, except at additive concentrations ≤0.2% w/w, for which a slight decrease was detected due to melting temperature depression caused by the (high-melting) "solvent" [17].

Optical microscopy studies confirmed that TBPMN did not act as nucleating agent at low concentrations. As a matter of fact, i-PP/TBPMN mixtures cooled at 10 °C/min containing, for instance, 0.05% w/w of the additive featured spherulites of similar size as the neat i-PP (cf. Fig. 3a,b). Only at contents >0.2% w/w of TBPMN the size of the polymer spherulites was found to drastically decrease (cf. Fig. 3c,d).

One important difference between the present nucleating agent and DMDBS is that the fibrils formed upon recrystallization of molten mixtures containing the latter additive was of a substantial width and could readily be observed in the optical microscope, already at concentrations of 1% w/w. By stark contrast, TBPMN fibrils were much finer and difficult to detect even at concentrations as high as 4% w/w in mixtures with i-PP prepared in an identical manner. In Fig. 4 are presented a set of comparative micrographs of additive fibrils formed in samples containing 2% w/w of DMDBS (Fig. 4a) and TBPMN (Fig. 4b). The finer morphology of the TBPMN fibrils is indicative of a reduced lateral growth rate of the present additive, likely due to its more complex substituents. The polymer spherulite sizes in samples containing the minimum concentration of TBPMN for optimum haze (~0.6% w/w; see below) after cooling at 10 °C/min were similar to those found in samples containing the corresponding concentration of DMDBS (~0.3% w/w) processed in the same way.

3.2. Optical properties

The optical characteristics clarity and haze [16,19] of injection-molded i-PP/TBPMN samples were determined in the additive concentration range between 0 and 5% w/w. These characteristics were found to improve at additive contents exceeding ~0.2% w/w reaching an optimum between ~0.6 and ~4% w/w (Fig. 5). The minimum value of haze that was achieved by addition of TBPMN was around 10%, which is significantly lower than the levels

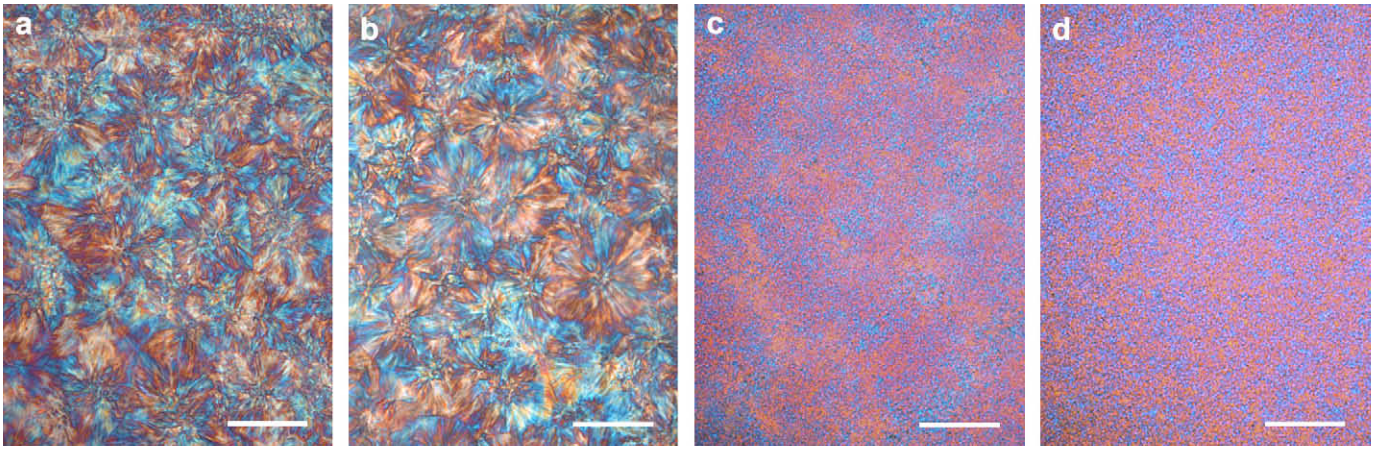

Fig. 3. Optical micrographs of compression-molded films of i-PP/TBPMN mixtures containing (a) 0% w/w, (b) 0.05% w/w, (c) 0.5% w/w (d) 4% w/w of the nucleating-, clarifying agent TBPMN. All samples were cooled at 10 °C/min. Images taken with crossed polarizers and ¼ λ plate; scale bars 50 μm.

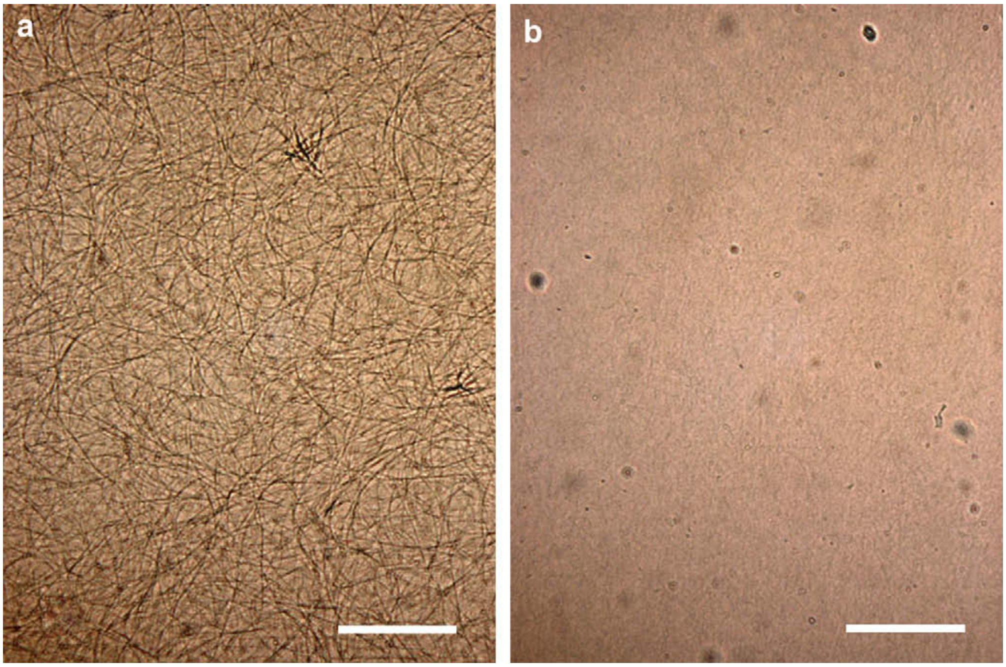

Fig. 4. Optical micrographs of compression-molded films of (a) i-PP/DMDBS and (b) i-PP/TBPMN comprising 2% w/w of the respective additive. The images were taken at 150 °C, i.e. *above* the crystallization temperature of i-PP, after cooling the samples from the molten state at 10 °C/min. The images reveal the substantially coarser fibrillar structure of solid DMDBS when compared to that of TBPMN. Scale bars 50 μm.

reached with DMDBS (∼15%; cf. Ref. [5]). Initial, variable-temperature small-angle light scattering studies (SALS; to be published elsewhere) revealed a lower level of scattering due to solidified TBPMN in the polymer *melt* than recorded for corresponding samples of i-PP/DMDBS. This may be associated with the above-mentioned finer fibrillar structure of the former additive, or/and enhanced refractive index matching between the components, and might account for the reduced minimum haze achieved with this clarifier; this considering the fact that the polymer spherulite size was found to be comparable for i-PP nucleated by DMDBS or TBPMN.

Noteworthy is that haze remained at this low value at significantly higher additive contents, and only significantly increased at compositions comprising ∼5% w/w of TBPMN, i.e. at the onset of liquid–liquid phase separation in the binary, which is reassuringly consistent with previous studies on other i-PP/(soluble) clarifier systems [6,11,20].

3.3. Mechanical properties

The yield behavior of compression-molded i-PP films comprising TBPMN was investigated for blends comprising from 0 to 1% w/w of the additive. The results are presented in Fig. 6, which reveal that an increase in yield stress was detected at concentrations of the clarifying agent equal to or higher than 0.1% w/w. A similar increase was reported for systems of i-PP comprising DMDBS, and has been demonstrated to be directly related to the increased crystallization temperature and concomitant increase in lamellar thickness of i-PP [21,22]. A slight decrease in yield stress was found for samples

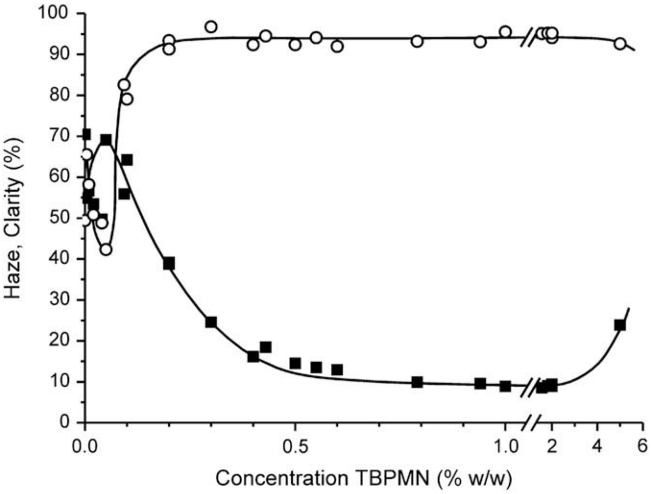

Fig. 5. Haze (■) and clarity (○) of injection-molded samples of i-PP/TBPMN as function of the additive content. The drawn lines are guides to the eye only.

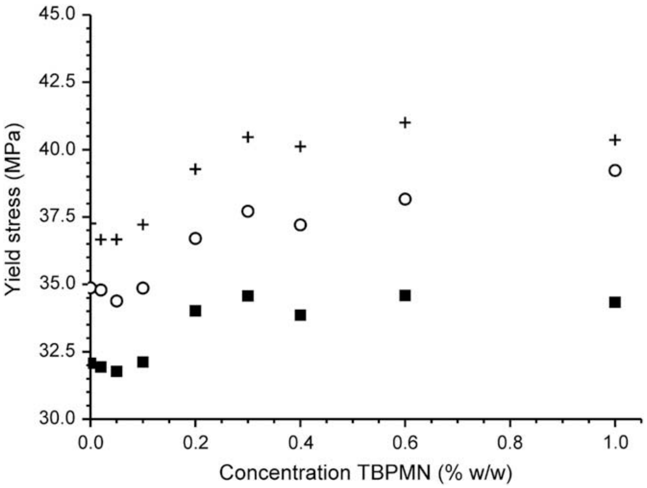

Fig. 6. Yield stress vs. additive concentration of compression-molded i-PP/TBPMN films after aging for 1 h (■), 24 h (○) and 1 week (+).

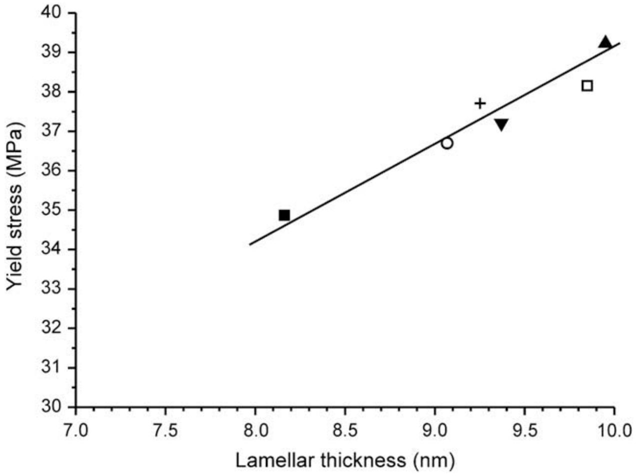

Fig. 7. Yield stress vs. lamellar thickness of i-PP of i-PP/TBPMN films containing (■) 0% w/w, (○) 0.2% w/w, (+) 0.3% w/w, (▼) 0.4% w/w, (□) 0.6% w/w, (▲) 1.0% w/w TBPMN. The samples were aged for 24 h. The drawn line is a guide to the eye only.

containing less than 0.1% w/w TBPMN. This is in gratifying accord with the finding that the nucleating agent does not enhance the crystallization of the polymer at such low additive concentrations, as it in these compositions merely acts as a diluent. For blend films comprising between 0.1 and 0.5% w/w of TBPMN the yield stress gradually reached a relatively constant value. The rate of "aging", i.e. the increase in yield stress with time, of i-PP was found to be unaltered by the presence of the nucleating agent (cf. Fig. 6).

These results of the tensile tests are in general accord with the temperature-composition diagrams presented above. The increased crystallization temperature of the polymer – due to nucleation by TBPMN – decreased the supercooling required for crystallization of i-PP, which in turn is directly correlated to the increased lamellar thickness for the polymer [23]. Indeed a plot of the yield stress vs. i-PP lamellar thickness for a spectrum of nucleated samples revealed a fairly linear relationship (Fig. 7), as commonly observed for semi-crystalline polymers above their glass transition temperature, T_g [24].

4. Conclusions

The binary system comprising i-PP and the nucleating/clarifying agent TBPMN was established to be of the simple monotectic type, similar to that reported for i-PP/DMDBS [6], as well as other recently developed, soluble clarifiers [11,20]. Compared to the earlier generations of sorbitol-based clarifying agents, TBPMN displayed enhanced miscibility with i-PP, and a finer fibrillar structure, which lead to reduced light scattering by the nucleating agent and, consequently, improved haze and clarity characteristics of this polymer/additive system. Furthermore, the increased solubility of this additive allows processing at lower temperatures, permitting reduction of the rate of decomposition of the nucleating agent – even though in and by itself it is not more thermally stable than other sorbitols such as DMDBS. Finally, again due to its enhanced compatibility with i-PP, larger contents of the clarifying agent can be employed, which – although possibly economically unattractive – might render optical properties of the system to be less sensitive to solidification kinetics. That latter feature, in combination with the lower values of haze achieved, may facilitate production of, among other things, clarified objects of increased dimension – an outstanding issue for many of the present clarifying agents [25].

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