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# Mechanical Properties of Sorbitol-Clarified Isotactic Polypropylene: Influence of Additive Concentration on Polymer Structure and Yield Behavior

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ABSTRACT: The solid-state structure and yield behavior of isotactic polypropylene (*i*-PP) containing the nucleating/clarifying agent 1,3:2,4-bis(3,4-dimethylbenzylidene)sorbitol (DMDBS) was investigated in the additive concentration range 0–1 wt %. The raise of the crystallization temperature of *i*-PP caused by addition of 0.2 wt % and more of the additive led to an increase in the polymer lamellar thickness, which, in turn, resulted in an increase of the yield stress at constant aging time. Both the strain-rate dependence of the yield stress and the rate of increase of the yield stress upon physical aging of compression-molded samples were not influenced by the addition of DMDBS. Analysis of the experimental data by means of the Eyring theory for thermally activated processes resulted in an average shear activation volume of 2.21 nm$^3$. The dependence of the yield stress on the additive concentration was in gratifying agreement with the previously reported monotectic phase behavior of the *i*-PP/DMDBS system.

## 1. Introduction

The crystallization behavior of isotactic polypropylene (*i*-PP) and manipulation thereof by the use of appropriate nucleating or clarifying agents have received and continue to attract both scientific and industrial interest. Considerable efforts have been directed to the search for substances capable of increasing the relatively slow rate of nucleation of *i*-PP.[1,2] Most searches for potential nucleating agents involve their classification and comparison to other substances in terms of their influence on the crystallization temperature of the polymer.[3] Among the most efficient nucleating agents for *i*-PP are organophosphates,[4] the recently disclosed trisamide derivatives,[5] and certain sorbitol derivatives, such as 1,3:2,4-bis(3,4-dimethylbenzylidene)sorbitol (DMDBS).[6] The latter additives are capable of efficiently nucleating the α-form of *i*-PP at relatively low concentrations, typically around 0.25 wt %. Certain sorbitol-based nucleating agents also render the polymer highly transparent, thus acting as so-called clarifying agents.[7] This beneficial improvement of the optical properties is commonly attributed to a drastic reduction of the spherulite size of *i*-PP,[8] resulting from the enhanced rate of nucleation, which is usually associated with an increase in the crystallization temperature.[9] Previously, we advanced a monotectic phase behavior of the quasi-binary system *i*-PP/DMDBS[10] to provide a rationale for the strong additive-concentration dependence of the conspicuous clarifying phenomenon.

Remarkably, the influence of nucleating/clarifying agents on the polymer solid-state structure and its relationship with the mechanical properties have received only modest attention and, in particular, its additive concentration dependence [see e.g. refs 11–15]. It has been argued that changes in the mechanical characteristics of the nucleated polymer are due to an increase in the crystallinity[8,15] or a reduction of the average spherulite size of the polymer,[2,16] both of which are demonstrated here to be doubtful for the present quasi-binary system.

The present study explores the effect of DMDBS on the solid-state structure—analyzed by small- and wide-angle X-ray scattering and thermal analysis—and the mechanical properties of *i*-PP, in particular its yield behavior.

## 2. Experimental Section

**Materials.** The isotactic polypropylene (*i*-PP) grade used throughout this study was Montell FL-F20 ($M_n = 5.5 \times 10^4$ g/mol, $M_w = 3.8 \times 10^5$ g/mol), which contained the antioxidant Irganox 1010, and was provided in powder form. The nucleating/clarifying agent 1,3:2,4-bis(3,4-dimethylbenzylidene)sorbitol (DMDBS, Millad 3988, Milliken Chemical, Belgium) was used as received.

**Sample Preparation.** Various dry-blended mixtures of *i*-PP and DMDBS with additive contents ranging from 0.1 to 1.0 wt % were compounded in a co-rotating mini-twin-screw extruder (Technical University Eindhoven, The Netherlands) at 240 °C under a nitrogen blanket during 5 min, after which the mixtures were discharged. Samples for mechanical testing were prepared by melt-compression molding plaques of 0.5 or 1.0 mm thickness at 240 °C for 10 min and subsequent quenching in a cold press. The thus-obtained samples were thereafter stored at room temperature (aged) for different periods of time prior to further investigation.

**Uniaxial Tensile Testing.** Mechanical testing was performed with an Instron 4411 tensile testing machine equipped with pneumatic clamps. All tests were performed at room temperature on dumbbell-shaped specimens of a width of 2

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mm. The clamp distance was 20 mm, and the gauge length was 12.7 mm. Samples were subjected to uniaxial tensile deformation at extension speeds varying from 20 to 200 mm/min, which corresponded to strain rates ranging from approximately 0.025 to 0.25 $s^{-1}$. All reported values for the yield stress refer to the average of three measurements.

**Thermal Analysis.** Thermal analysis was conducted with a Netzsch differential scanning calorimeter (DSC, model 200) with samples of 5−10 mg at a standard heating or cooling rate of 10 °C/min under nitrogen. Prior to the recording of cooling and heating thermograms, the samples were held at 240 °C for 5 min to erase their thermal history and prevent self-seeding of *i*-PP. Crystallization temperatures reported hereafter refer to peak temperatures in the corresponding thermograms. Indium was used to calibrate the temperature and the heat flow.

**X-ray Scattering.** X-ray investigations were performed at the DUBBLE (Dutch-Belgium) beamline[17] at the ESRF Grenoble, France, at wavelengths ranging from 1.0 to 1.27 Å. Small-angle X-ray scattering (SAXS) data were collected with either a gas quadrant chamber[18] or a gas multiwire proportional 2D chamber detector. Wide-angle X-ray diffraction (WAXD) data were collected with a microstrip gas chamber detector.[19] The raw data were corrected for absorption, detector sensitivity, and background scattering. The $q$-axis (SAXS) was calibrated with dry rat tail collagen and silver behenate and the $2\theta$ values (WAXD) with silicon and polyethylene standards. Long periods were determined from the maximum in plots of $Iq^2$ vs $q$ (Lorentz-corrected intensities); multiplication of the latter values with the WAXD crystallinity was taken to be the average lamellar thicknesses.[20,21]

## 3. Results

**3.1. Yield Behavior.** *3.1.1. Influence of Aging Time.* It is well-known that the mechanical properties of isotactic polypropylene (*i*-PP) change dramatically after melt-compression molding due to secondary crystallization and physical aging, also at room temperature.[22] Hence, to determine the influence of the clarifying agent on the mechanical properties of *i*-PP, the effect of aging on the yield stress was investigated. Typical results are presented in Figure 1a for reference, neat *i*-PP. The yield stress was found to increase predominantly within the first 24 h after compression molding and quenching the *i*-PP plaques to room temperature. Subsequently, the yield stress increased at a substantially lower, approximately constant rate. Interestingly, the rate of aging was found to be hardly influenced by the incorporated nucleating agent (Figure 1b). By contrast, the absolute level of the yield stress (at constant aging time) was observed to increase upon addition of DMDBS at additive concentrations exceeding 0.2 wt %, while a small but conspicuous decrease was noted for plaques comprising 0.1 wt %, which will be discussed in a following section.

*3.1.2. Influence of DMDBS Content.* In view of the above results, the following studies on the yielding behavior were conducted with sorbitol-nucleated *i*-PP samples aged at room temperature for a period of time of 1 year.

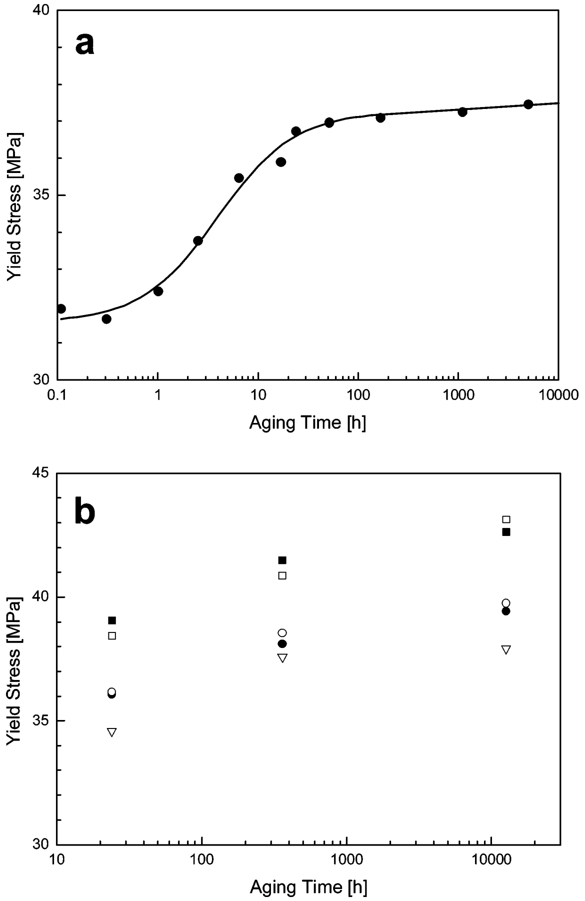

**Figure 1.** Yield stress as a function of aging time for compression-molded plaques of (a) neat *i*-PP and (b) *i*-PP containing different amounts of DMDBS (wt %): 0.0 (●), 0.1 (▽), 0.2 (○), 0.5 (□), and 1.0 (■). Note: the slight differences in the yield stress for neat *i*-PP in the figures arise from slightly different samples thicknesses used (~400 μm for (a) and 500 μm for (b)) and, therewith, cooling rate.

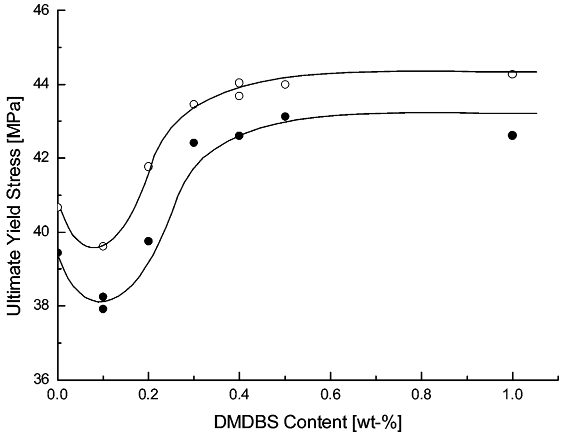

**Figure 2.** Yield stress vs additive concentration of compression-molded *i*-PP/DMDBS samples of 0.5 mm (●) and 1.0 mm (○) thickness. The samples were aged for 1 year to allow virtually time-independent measurements.

Figure 2 collects the values of the yield stress, determined at a strain rate of ~0.025 $s^{-1}$ (20 mm/min), of *i*-PP plaques as a function of the DMDBS content. In the additive concentration range between 0.2 and 0.5 wt %, a substantial increase in the yield stress was observed. This finding coincides with the previously reported increase of the crystallization temperature of about 18 °C at a cooling rate of 10 °C/min in that same concentration regime.[10] At additive concentrations exceeding 0.5 wt %, the yield stress was found to remain almost constant, accompanied by a constant crystallization temperature.[10] Melt-compression-molded plaques containing 2 wt % DMDBS or more displayed a marble-like texture owing to the occurrence of liquid−liquid phase separation at elevated temperatures in this composition regime. As expected, the yield stress of these samples continuously decreased with increasing additive concentration due to a reduced fraction of load-

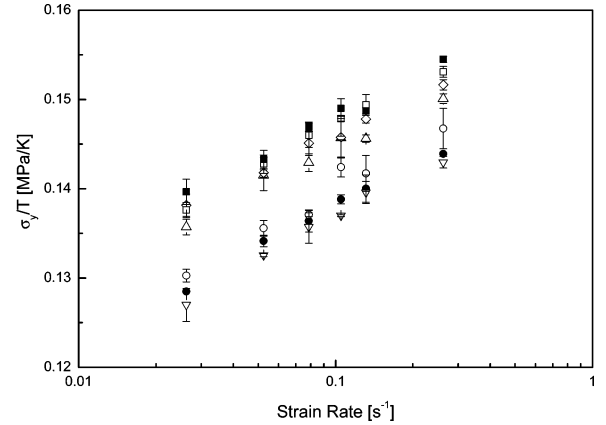

**Figure 3.** Strain-rate dependence of the yield stress/temperature $\sigma_y/T$ (Eyring plot) for *i*-PP/DMDBS samples aged for 360 h; DMDBS content, wt %: reference 0.0 (●), 0.1 (▽), 0.2 (○), 0.3 (△), 0.4 (◇), 0.5 (□), and 1.0 (■). Sample thickness was 500 $\mu$m.

bearing matrix material (not shown). Clearly, the sorbitol network did not contribute to the mechanical properties of the polymer plaques, which can easily be understood in view of the brittle nature of these molecular crystals.

As noted above and illustrated in Figure 2, an initial *decrease* in the yield stress was observed for mixtures containing only 0.1 wt % DMDBS. This finding can readily be understood in terms of the previously reported monotectic phase behavior of this pseudobinary system[10] and is associated with the slight decrease in melting point and crystallization temperature (~110 °C) of the polymer due to the presence of the dissolved additive, which at this concentration does not act as a nucleating agent but rather as a low molecular weight diluent.

*3.1.3. Influence of Strain Rate.* The influence of the strain rate on the yield stress, $\sigma_y$, was determined on samples aged for 360 h. The data obtained were analyzed and presented in the customary way on the basis of the Eyring viscosity theory.[23-26] Accordingly, $\sigma_y$ is given by

$$\sigma_y = \tau_0\sqrt{3}\ln(2A\sqrt{3}) + \tau_0\sqrt{3}\ln\dot{\epsilon} \tag{1}$$

where $\dot{\epsilon}$ is the strain rate and $A$ and $\tau_0$ are material constants (at a constant temperature) related to the activation energy, $\Delta H$, and the (shear) activation volume, $V^*$, for the thermally- and stress-activated segmental motion:

$$A = A_0 \exp\left(\frac{\Delta H}{RT}\right), \quad \tau_0 = \frac{RT}{V^*} \tag{2}$$

Here, $A_0$ is a preexponential factor involving the fundamental vibration frequencies of the system, $R$ the universal gas constant, and $T$ the absolute temperature. Combination of eqs 1 and 2 yields

$$\frac{\sigma_y}{T} = \frac{R\sqrt{3}}{V^*}\left[\frac{\Delta H}{RT} + \ln\dot{\epsilon} + \ln(2\sqrt{3}A_0)\right] \tag{3}$$

From the latter (Eyring) equation, it can easily be seen that the activation volume, $V^*$, is inversely proportional to the slope of a plot of the yield stress normalized to the temperature vs the logarithm of the strain rate.

Figure 3 shows the Eyring plot (strain-rate dependence of the yield stress) of *i*-PP/DMDBS plaques comprising 0.0−1.0 wt % of the additive. From the virtually equal slopes in this figure, it is evident that the activation volume did not change significantly due to the presence of DMDBS. Fitting eq 3 to the experimental data resulted in values of the activation volumes, $V^*$, ranging from 1.98 to 2.44 nm$^3$, essentially independent of the additive concentration. The average shear activation volume value of 2.21 nm$^3$ is in good agreement with the previously reported values for the tensile activation volume of 4.16−4.51 nm$^3$ for *i*-PP,[25] taking into account a difference of $\sqrt{3}$ between the shear and tensile activation volumes.[26]

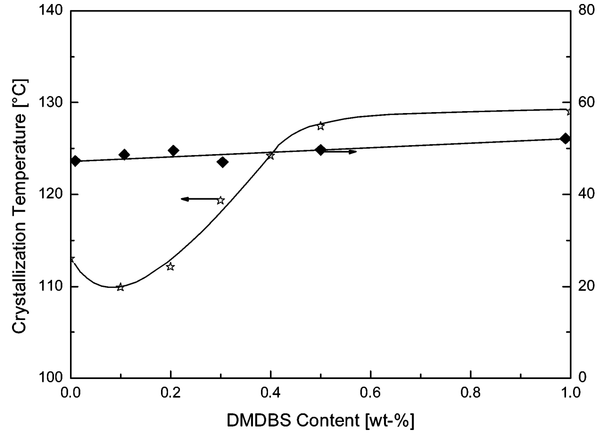

**Figure 4.** Peak crystallization temperature (☆) and crystallinity (◆) of *i*-PP, determined by differential scanning calorimetry, as a function of the concentration of *i*-PP/DMDBS mixtures.

To summarize this part of the work, the principal influence of the presence of the nucleating/clarifying agent DMDBS on the mechanical properties of *i*-PP is an increase in the yield stress. By contrast, the aging process itself and the strain-rate dependence of the yield stress at constant aging times were not profoundly affected by the additive. Somewhat surprisingly, the Young's modulus (typically ~600 MPa) was found to be hardly affected by the added DMDBS, which is contradictory to the previously reported increases of the latter characteristic (e.g. refs 2, 8, and 13). This apparently contradicting result may be due to the relatively thin samples used throughout this study. For thicker samples, higher polymer crystallinities might be obtained due to the lower cooling rate within the bulk of the samples, which could have resulted in the higher reported values for the Young's modulus.

**3.2. Nonisothermal Crystallization.** The nonisothermal crystallization behavior of the *i*-PP/DMDBS system was investigated by means of differential scanning calorimetry (DSC) with samples of different additive content, as described in the Experimental Section. Figure 4 shows the peak-crystallization temperatures of *i*-PP, $T_c$ (which, strictly speaking, correspond to the crystallization temperature of the *i*-PP/DMDBS eutectic), recorded at a cooling rate of 10 °C/min as a function of additive concentration. It can clearly be seen, and was already alluded to in the previous section, that the values of $T_c$ displayed a very similar concentration dependence as the yield stress, suggestive of a strong correlation between them.

Also shown in Figure 4 are the values of the crystallinity of *i*-PP, derived from melting endotherms of the various samples assuming a melting enthalpy of 209 J/g

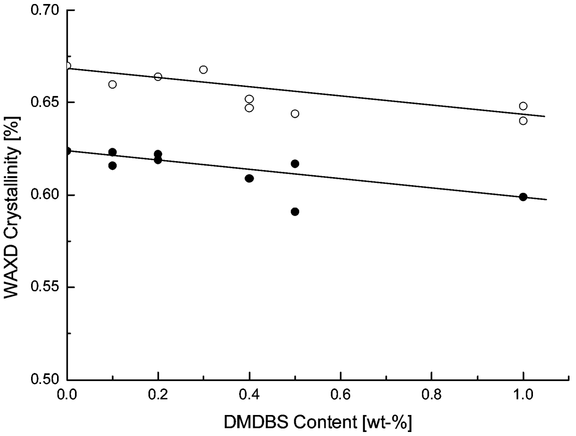

**Figure 5.** WAXD crystallinity of *i*-PP as a function of DMDBS content; sample thickness 0.5 mm (●) and 1.0 mm (○).

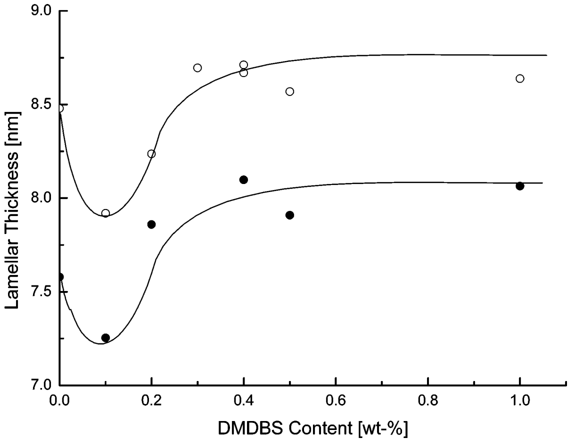

**Figure 6.** (a) Polymer lamellar thickness vs additive concentration in compression-molded *i*-PP/DMDBS plaques (aged for 1 year) of 0.5 mm (●) and 1.0 mm (○) thickness.

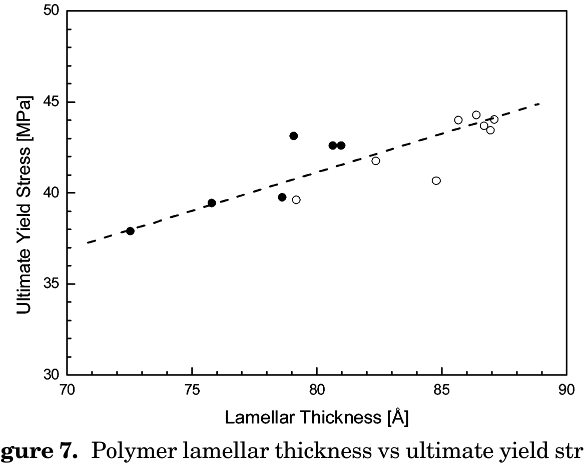

**Figure 7.** Polymer lamellar thickness vs ultimate yield stress of compression-molded *i*-PP/DMDBS plaques (aged for 1 year) of 0.5 mm (●) and 1.0 mm (○) thickness. The dashed line is a guide to the eye only.

for the 100% crystalline sample.[27] The polymer crystallinity determined in this manner was not significantly affected by the additive.

**3.3. X-ray Scattering.** *3.3.1. Crystallinity.* Wide-angle X-ray diffraction (WAXD) also was used to determine the crystallinities of the various samples, according to standard procedures (see e.g. ref 28), the results of which are presented in Figure 5. The thicker samples, which experienced a lower cooling rate, displayed higher crystalline contents, and as is commonly observed, all values exceeded those obtained by thermal analysis. However, unlike the latter, the WAXD crystallinity values were found to slightly decrease with increasing additive concentration. It should be noted that DSC and WAXD techniques are differently sensitive to (dis)order and crystal size, which influences the crystallinity values obtained.

*3.3.2. Lamellar Thickness.* Small-angle X-ray scattering (SAXS) was used to study the influence of the DMDBS concentration on the average lamellar thickness of *i*-PP. The latter data are presented in Figure 6 as a function of additive content for melt-compression-molded plaques of 0.5 and 1.0 mm thickness. Clearly, the thicker specimen were characterized by a larger average lamellar thickness, which can be readily understood as a direct consequence of differences in the cooling kinetics. In Figure 7, finally, the yield stress of the *i*-PP/DMDBS samples is plotted against the polymer lamellar thickness, yielding a simple, approximately linear correlation.

## 4. Discussion

The above-reported values of the yield stress, the polymer lamellar thickness, and crystallization temperature (respectively Figures 2, 4, and 6) all displayed a very similar, highly characteristic, nonlinear additive concentration dependence. Initially, a decrease in these three values was observed for mixtures containing 0.1 wt % of DMDBS, indicative of the adverse effect of the presence of DMDBS at such low concentrations,[10,29] followed by a substantial increase in the concentration regime between 0.2 and 0.5 wt %, to “saturate” toward higher concentrations (1.0 wt %). Clearly, the DMDBS-concentration-dependent mechanical properties directly reflect the monotectic phase behavior of the pseudobinary *i*-PP/DMDBS, which, as previously shown, also governs its optical properties.[10]

This consistent set of data unambiguously demonstrates that the principal consequence of adding the nucleating/clarifying agent DMDBS to *i*-PP at concentrations exceeding the eutectic is an increase of the crystallization temperature of the polymer, resulting in an increase of the polymer lamellar thickness and therewith directly associated increased yield stress. This conclusion is contrary to the general notion that the change in mechanical properties of *i*-PP caused by nucleating agents is related to a reduction of the spherulite size and/or changes in the crystallinity.

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