

Nano-structuring of isotactic polypropylene in presence of a self-assembling nucleating agent under defined flow conditions

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1. ABSTRACT

Additives play an important role in physical properties of polymers. One of the most frequently used additives for isotactic polypropylene (iPP) is Bis 3,4-dimethylbenzylidene sorbitol (DMDBS). iPP and DMDBS together form a binary mixture with a monotectic phase diagram. Homogeneous dissolution of DMDBS in iPP at reasonable temperatures is possible only in a limited range of low concentrations. Upon cooling, the nucleating agent first crystallizes forming nano-fibrils which are an excellent substrate for heterogeneous crystallization of iPP. Consequence to it, nucleation density is very high thus forming crystals smaller than wavelength of light resulting into a translucent material. In this paper we explore structural development during crystallization of the binary system iPP-DMDBS under defined flow conditions.

2. EXPERIMENTAL SECTION

2.1 Materials

The iPP used in this work is a commercial grade from Borealis named HD120MO ($M_w=365.000$ and $M_w/M_n=5.4$). DMDBS was obtained by Milliken Chemicals (Millad 3988) and used as received.

2.2 Sample preparation

Three different blends containing 0.3, 0.7 and 1 weight % of DMDBS were compounded with iPP for 10 min at 250°C in a co-rotating twin screw extruder under nitrogen atmosphere. After mixing, the extrudate was molded at 230°C in 1mm thick plates, consequently cooled to room temperature. Samples in disk-form were cut from the plates for rheology and X-Rays experiments.

3. RESULTS AND DISCUSSION

3.1 Dynamic Scanning Calorimetry (DSC)

Standard DSC heating/cooling runs with a heating/cooling rate of 10°C/min, reveal that the melting behavior of the polymer is essentially not affected by the presence of DMDBS. All samples show the same melting temperature of the neat iPP, that is 165°C.

As expected, with the addition of nucleating agent, the crystallization temperature is influenced.

DSC cooling thermograms of the neat iPP and its compounds with DMDBS are shown in Figure 1. The neat polymer crystallizes at 113 °C, addition of 0.3% wt of DMDBS shifts the crystallization temperature to 131°C. Further addition of the nucleating agent have minor effects on the crystallization temperature and only decreases the overall crystallization time, defined as:

$$t_c = \frac{T_{onset} - T_{compl}}{\alpha} \quad (1.1)$$

where, T_{onset} is the onset of crystallization temperature, T_{compl} corresponds to the completion of the crystallization and α is the cooling rate.

All samples, but the neat system, show small heat release at temperature well above the crystallization of the polymer, suggesting the crystallization/phase separation of DMDBS.

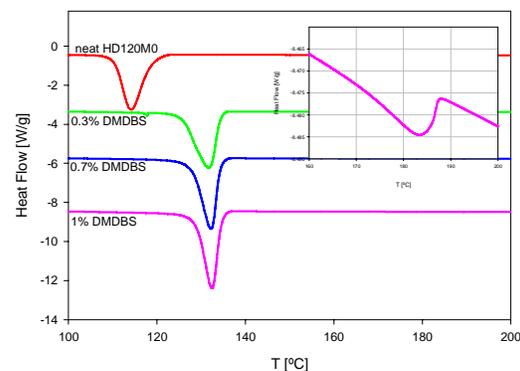


Figure 1: DSC thermograms recorded for the neat polymer and three different compounds with DMDBS. The cooling rate is 10°C/min.

The insert plot is a detail showing the thermal effects of the crystallization of DMDBS in the 1% blend.

The change in relative crystallinity with the temperature can be expressed as:

$$X(T) = \frac{\int_{\tau_{onset}}^{\tau} W(T) dT}{\Delta H_{100\% \text{ cryst}}^{iPP}} \quad (1.2)$$

where, $W(T)$ is the heat flow recorded by the instrument as a function of temperature and $\Delta H_{100\% \text{ cryst}}^{iPP}$ is the latent heat associated to the crystallization of a fully crystalline polypropylene. The final (relative) crystallinity of the samples seems not to depend on the amount of DMDBS. A summary of all the relevant information obtained from the thermograms is given in Table 1.

	T_c^1 [°C]	t_c^2 [s]	T_{ps}^3 [°C]	X^4 [%]
HD120MO	113	123.5		0.46
0.3% DMDBS	131	68.5	144	0.52
0.7% DMDBS	132	53.6	174	0.52
1% DMDBS	132	47.3	183	0.50

Table 1: Summary of the relevant information extracted from DSC cooling runs.

- ¹ crystallization temperature of the polymer
- ² crystallization time according to (1.1)
- ³ temperature of crystallization for DMDBS
- ⁴ (final) relative crystallinity ($=X(T_{room})$)

Ultimately, making only use of calorimetric data it is possible to depict the crystallization phase diagram at least in the range of concentration investigated.

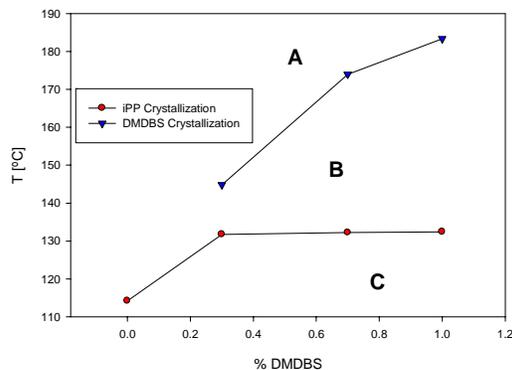


Figure 2: Phase diagram of the system iPP-DMDBS obtained from cooling runs at 10°C/min. Different regions can be

distinguished: A) liquid homogeneous solution; B) DMDBS crystallized in the molten polymer matrix; C) both iPP and DMDBS are solid.

3.2 Rheology

Many authors [1] have reported that crystallization of DMDBS prior to the polymer crystallization (transition from region A to region B in Figure 2) confers to the system a gel like behavior. This behavior is suitable for rheological investigations.

Phase separation of the DMDBS from the molten polymer can be readily tracked by following the changes occurring in the storage modulus during temperature sweep experiments.

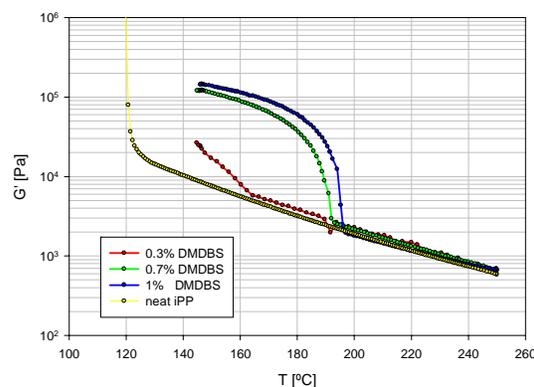


Figure 3: Storage modulus ($\omega = 5 \text{ s}^{-1}$) as function of temperature in cooling ramp experiments with $\alpha = 5 \text{ °C/min}$.

Prior to crystallization, the neat iPP shows a simple thermorheological behavior. Samples containing DMDBS show complex temperature dependence. With crystallization of DMDBS, as the sol-gel transition occurs, a sharp upturn in the storage modulus. The upturn temperature increases with the amount of DMDBS.

The presence of phase separated, fibrillar, structures changes the rheological frequency dependent response of the system, as shown in Figure 4.

The system shows a slower relaxation dynamics and furthermore a plateau appears in the low frequency region.

3.3 Small Angle X-Rays scattering (SAXS)

The combined effect of DMDBS phase separation, flow and temperature on the morphology development during crystallization was followed by means of time resolved SAXS. This gives an opportunity to follow density

fluctuations on the nanoscale due to any structure formation.

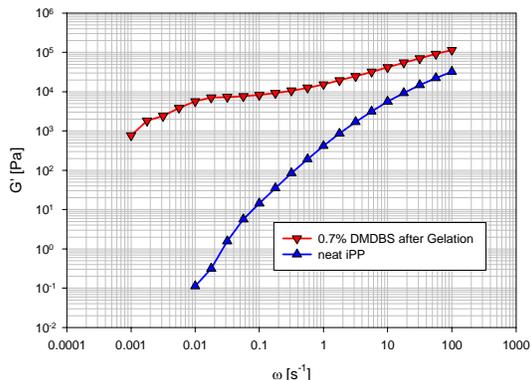


Figure 4: Frequency sweep at 190°C for the neat polymer and a mixture containing 0.7% DMDBS annealed at 190°C for 30min. Strain is 5%.

The thermo-mechanical history experienced by the samples during short term shearing is shown in Figure 5. Flow is applied on the system, either in the homogeneous melt state (above the crystallization temperature of DMDBS), or in the phase separated melt state (after crystallization of DMDBS). Resultant morphology shows strong dependence on the flow conditions.

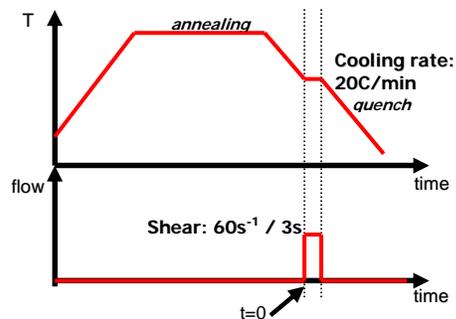


Figure 5: Thermal and mechanical history experienced by the samples.

All samples containing DMDBS, sheared in the homogeneous solution state didn't show any signal in the SAXS detector, which corresponds to the absence of any long range order.

On the other hand, application of shear flow at temperatures such that DMDBS is already phase separated, induces ordering of the fibrils parallel to the flow direction causing a streak of intensity in the equatorial region of the SAXS pattern (see Figure 6).

As shown in the previously discussed rheological experiments, morphology developed at high

temperatures is retained for long times and doesn't relax on the experimental time scale.

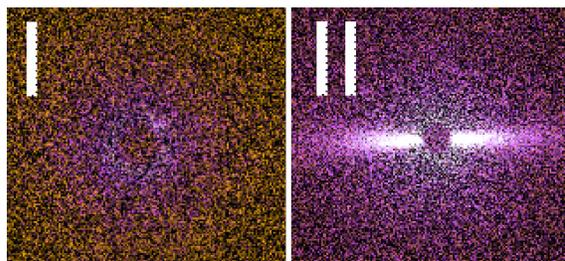


Figure 6: SAXS patterns of systems containing 1wt% DMDBS at the shear moment, I) $T_{\text{shear}}=210^{\circ}\text{C}$ and II) $T_{\text{shear}}=188^{\circ}\text{C}$

Consequence to it, Figure 7 shows that before crystallization intensity in the equatorial region remains higher than the other regions in the SAXS pattern.

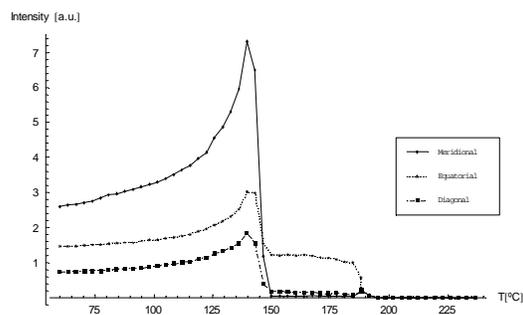


Figure 7: Integrated SAXS intensities as a function of temperature/time when shearing a compound containing 1% DMDBS at 188°C.

After application of shear flow the system is quenched to room temperature. Because of nucleation, strong density fluctuations appear at temperatures depending only on the amount of DMDBS (c.a. 150°C in Figure 7). Crystallization rapidly decreases the density fluctuations.

SAXS patterns of the crystallized compounds reveal different morphologies according to the temperature at which shear flow was applied.

When shear flow is applied to homogeneous solutions isotropic scattering pattern is obtained (pattern A of Figure 8), fingerprint of a randomly distributed lamellar morphology. Whereas shear flow applied after phase separation of DMDBS leads to anisotropic scattering pattern with a clear separation between intensity in the equatorial and meridian direction (pattern B of Figure 8). These patterns are typical of system with high lamellar orientation.

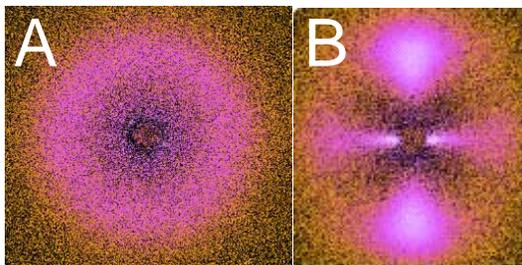


Figure 8: Samples of SAXS patterns for A) crystallization after shearing the system in the homogeneous solution state and B) after shearing a phase separated system.

The patterns recorded at room temperature of all the samples investigated in this work together with the position of the system in the phase diagram when shear flow is applied are shown in Figure 9.

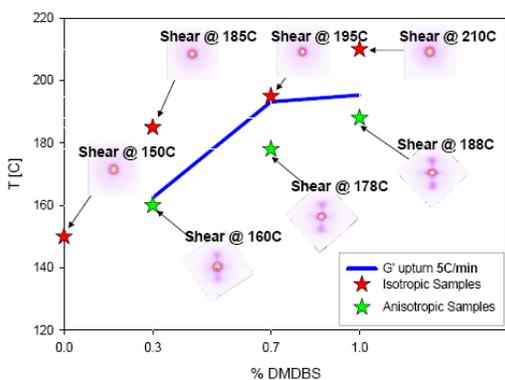


Figure 9: Phase diagram and room temperature SAXS patterns for all the samples investigated. The phase separation line corresponds to the upturn of the storage modulus observed in rheological experiments.

Finally, according to the intensity distribution in the SAXS patterns we can assess a degree of lamellar orientation as the ratio between the intensity scattered by the lamellae having normal parallel to the flow direction and the total intensity scattered by the polymer [2]:

$$\Phi = \frac{I_{\text{oriented}}^{\text{polymer}}}{I_{\text{tot}}^{\text{polymer}}} = \frac{I_{\text{lobes}} + I_{\text{streaks}} - I_{\text{DMDBS}}}{I_{\text{tot}} - I_{\text{DMDBS}}} \quad (1.3)$$

Calculated values of Φ as a function of temperature for the three amounts of DMDBS are shown in Figure 10.

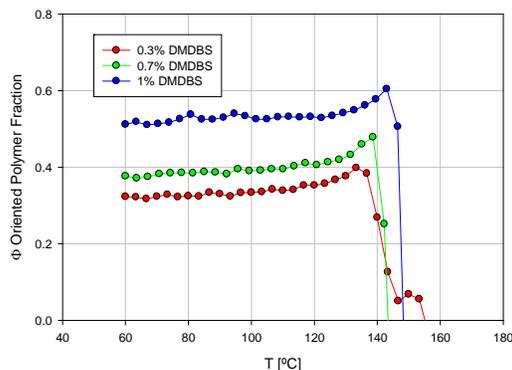


Figure 10: Fraction of oriented polymer lamellae according to (1.3) for different amounts of DMDBS

4. CONCLUSIONS

DMDBS crystallizes at temperatures higher than the polymer forming nano-fibrils. This morphology assures a high surface to volume ratio. When combined with a strong molecular match DMDBS serves a good substrate for the heterogeneous nucleation of iPP molecules. Polymer lamellae preferentially grow on top of the DMDBS fibrils. Since the crystallized fibrils have much longer relaxation times than the polymer melt they can be oriented easily. A result of it, once phase separation has occurred and DMDBS network is formed the application of shear produces high degrees of lamellar orientation.

5. REFERENCES

- [1] M. Kristiansen, M. Werner, T. Tervoort, P. Smith, M. Blomenhofer, H.W. Schmidt, *Macromolecules* 2003, 36, 5150-5156
- [2] Aurora Nogales and Geoffrey R. Mitchell *Polymer*, 46 (15), 2005, 5615-5620