TEMPERATURE EXPERIMENTS FOR IMPROVED ACCURACY IN THE
CALCULATION OF POLYAMIDE-11 CRYSTALLINITY
BY X-RAY DIFFRACTION

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ABSTRACT

The calculation of the crystalline index (CI) of polymeric materials by X-ray diffraction (XRD) may be rendered difficult by the number of overlapping crystalline phases and amorphous halos that contribute to the diffraction pattern. Rilsan® Polyamide-11 (PA-11), produced by Arkema Inc., is a semi-crystalline polymer with an eleven-carbon repeat unit belonging to the general class of Nylon polymers. This material presents the peculiarity of having a smectic phase along with three crystalline phases. Samples from melt-extruded Rilsan® PA-11 oil pipeline liners that had been subjected to various aging conditions were analyzed by XRD. From wide-angle X-ray scattering (WAXS) patterns their CI was calculated, which were compared to values obtained from differential scanning calorimetry (DSC) measurements. Severe overlaps among the crystalline, amorphous and smectic phases of Rilsan® PA-11 were observed, which were further convoluted by the amorphous phases of additives in the polymer matrix. Initial attempts to calculate CI reliably from XRD data were therefore unsuccessful. Subsequently, hot stage XRD was used to perform peak decomposition on three temperature patterns (90ºC, 150ºC, and 180ºC). A linear evolution for smectic and amorphous peak positions was seen in this temperature range. Extrapolation of peak positions to room temperature conditions helped to refine the experimental patterns and greatly increased the accuracy of the crystalline index calculation by XRD, which is seen by comparison with DSC data.

INTRODUCTION

Rilsan® PA-11 is a semi-crystalline polymer with an eleven-carbon repeating unit belonging to the family of Nylon polymers. It is a high-performance polymer used in a variety of applications such as airbrake tubing for semi-tractor trailers, coatings, and liners for high temperature crude oil and gas pipelines. Several studies completed on PA-11 have elucidated many of the crystalline forms of this polymer and have found that its X-ray patterns resemble those of Nylon 6,6 [1]. Indeed, Slichter reported that the reflections of PA-11 could be indexed using the triclinic structure described by Bunn and Garner for Nylon 6,6. Slichter [1, 2] also discussed the possibility for the polymer chains to pack parallel or anti-parallel to each other in ordered arrays. Kawaguchi and co-workers [3] reported that anti-parallel chain packing could be described with a triclinic cell as observed by Little [4], or by a monoclinic cell as they observed it. They also stressed that it would be unlikely statistically to create only parallel chain arrangements from either melt or solution, and that a combination of parallel and anti-parallel chain organization is more probable in PA-11 lamellar structure.

Newman and co-workers [5] reported that the triclinic α-form transforms reversibly to the pseudo-hexagonal δ-form at 95ºC, which is known as the Brill transition temperature, following a change in thermal expansion coefficient in the [010] direction. A disordered pseudo-hexagonal
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form, called the $\delta'$-form, can be obtained upon quenching or slow cooling the polymer from the melt state [4], which has a smectic-like order [6]. Finally, Kawaguchi et al. [3] discussed the existence of a $\gamma$-form of PA-11, similar to that which exists for Nylon-6.

Because of its effects on mechanical properties, crystallinity of polymers is a subject of substantial importance, and literature exists regarding the calculation of the degree of crystallinity or crystalline index [7-9]. Our interest was primarily to develop a procedure for the decomposition of the X-ray patterns and for the calculation of CI from XRD data. Further, we were interested to compare CI from XRD and DCS measurements to determine whether the two methods could be used interchangeably.

**EXPERIMENTAL**

All samples used in this study came from pipe liners constructed from a commercial grade of Rilsan® PA-11 containing additives. Samples were shaved from the liners in serpentine form using a lathe and then were cut further into small squares with scissors. Samples were measured on a zero background holder for all room temperature experiments, or on a copper sample holder when the hot stage was used. All samples were analyzed using a Rigaku Ultima II diffractometer with fixed slit optics, at 40 kV and 40 mA, in reflection mode. Divergent and receiving Soller slits of 5° were used, and the scans were acquired from 10° to 60° 2θ, with a step scan of 0.02° 2θ and a count time of 3 seconds. The CI by XRD was calculated from the ratio of the areas of the peaks of the crystalline phases to the sum of the areas of the crystalline peaks and the amorphous profile using Equation (1) [7]:

$$ CI = 100 \times \frac{\sum A_{\text{crystal}}}{\sum A_{\text{crystal}} + \sum A_{\text{amorphous}}} $$  

Peak fitting and peak integration were performed with the program SHADOW [10].

Thermal analyses of the samples were performed using a TA2940 –DSC instrument at a heating rate of 10°C/min between -50°C and 250°C, under nitrogen atmosphere. The glass transition temperature and the heat capacity were obtained using the half-height tangent method. The enthalpy of fusion was obtained by integrating the fusion peak. The corrected enthalpy of fusion ($\Delta H_m^c$) was obtained using Equation (2), and the CI, $\chi_c$, was calculated with Equation (3):

$$ \Delta H_m^c = \Delta H_m \times \frac{100}{100 - \text{additive (}%)} $$  

$$ \chi_c = \frac{\Delta H_m^c}{\Delta H_m^0} \times 100 $$

Here, $\Delta H_m$ (J.g$^{-1}$) refers to the enthalpy of fusion of the sample and $\Delta H_m^0$ (J.g$^{-1}$) is the enthalpy of fusion of perfectly crystalline PA-11 ($\Delta H_m^0 = 189.05$ J.g$^{-1}$ after [11]).

**RESULTS AND DISCUSSION**

**Crystalline sample of Rilsan PA-11**

The diffraction pattern of a highly crystalline sample, denoted as Rilsan® PA-11 #3, is shown in Figure 1. This material was prepared by aging a sample for 20 days at 140°C in the absence of oxygen. Miller indices have been reported in Figure 1, and this pattern is typical of the triclinic
α-form of PA-11. Based on the breadth of the (001) reflection it is possible to calculate the thickness of the lamellae using the Scherrer equation [12]. A value of 63 Å was found for this sample, which corresponds to the extension of four chains of PA-11 (several authors have reported a c-axis value between 14.1 Å and 15.2 Å [1, 5, 6, 13]).

The peak positions of the α-form obtained from our decomposition are reported in Table 1 and show good agreement with data from the literature. The smectic phase had to be included in the peak decomposition procedure in order to achieve good fits.

<table>
<thead>
<tr>
<th>Material</th>
<th>Phase</th>
<th>(001)</th>
<th>(200)</th>
<th>(010) + (210)</th>
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</thead>
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<tr>
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<td>20.5</td>
<td>23.1</td>
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<td>Rilsan® PA-11 [15]</td>
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<tr>
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</tbody>
</table>

Table 1. Experimental peak positions in Rilsan PA-11 #3 compared to data from the literature.

Temperature experiments to improve peak decomposition procedure

Strong peak overlaps in the region between 14° and 28° 2θ made initial attempts to produce repeatable peak decomposition challenging, especially in defining reliable peak positions of the smectic phase and the amorphous halo. Temperature scans on a Rilsan® PA-11 sample formulated without additives were acquired at temperatures ranging from 30°C to 200°C, which are shown in Figure 2. The last scan shown was recorded after the sample was slowly cooled to 30°C. The initial low temperature scans (30°C to 50°C) indicate a mixture of α-phase and δ'-phase, with the smectic phase being dominant. At 90°C the transition to a single sharp peak around 21° 2θ demonstrates that the α-phase was transformed into the high-temperature δ-phase. This phase is observed up to 180°C, and then vanishes in the melt at 200°C. After slow cooling and once the temperature is decreased back to 30°C it is expected that a pattern dominated by the two peaks of the α-phase in the region 20° to 24° 2θ emerges, as is seen in Figure 2. An interesting point is that the peak position of the (001) reflection does not change when temperature is increased from 30°C to 180°C, whereas the peaks around 20° 2θ of the α-phase and especially of the δ-phase beyond 90°C are shifted progressively to higher d-spacings with...
temperature. This observation could be an indirect indication that the thermal expansion in Rilsan® PA-11 is not isotropic along the c-axis and the a- and b-axes perpendicular to it, which has been reported previously by Newman et al. [5], who found different thermal expansion coefficients for the [100] and [010] directions below the transition temperature of 95°C.

Figure 2. Temperature scans on a pure (without additives) Rilsan® PA-11 sample.

Because of the polymorphism of polyamide 11, only one crystalline peak needs to be fit at 180°C, 130°C, and even 90°C, instead of two at room temperature, and the amorphous profile is more apparent in the raw signal at high temperature than it is at room temperature, making the decomposition easier. The smectic phase was included in our procedure because evidence of its presence at high temperature (180°C to 190°C) has been reported by some authors [6, 16]. Figure 3 shows the peak fitting procedure with the δ-phase, the smectic phase and the amorphous phase for the scan at 180°C. The same procedure was applied for the patterns recorded at 150°C and 90°C. The peak positions obtained for the amorphous and the smectic phases were then plotted against the temperature, as shown in Figure 4.
A linear trend was observed for both the amorphous and smectic phases. Extrapolation of the best-fit line to 30°C gave the following peak positions: 19.4° 2θ for the amorphous phase and 20.6° 2θ for the smectic phase. It should be noted that the peak position of the smectic phase calculated by this procedure corresponds to previously reported observations from several authors [6, 15-17].

Comparison of CI values obtained by XRD and DSC

The procedure presented in the previous section was applied to the seven samples of Rilsan PA-11 comprising this study. An example of the procedure as applied to one of these samples is presented in Figure 5.

Values for CI as calculated from the XRD and DSC methods are reported in Table 2. Although the values are comparable there is no clear correlation in these data. That is, neither method consistently gives a higher or lower CI than the other. Murthy et al. [18] reported the same result in a study of the CI of poly-chlorotrifluoroethylene. They commented on the possible sources of error in the various measurements. For example, changes in the crystallinity of the sample during heating will affect the DSC measurement. In our study, many samples contained an additive that
contributed to the amorphous signal. Even though this contribution to the X-ray pattern is small, fitting errors around 7 - 8° 2θ may lead to small errors in the final calculated CI, probably less than 1% absolute. Errors in the CI calculation from DSC relate to inaccuracies in the estimation of the additive content in the polymer matrix and the potential impact of the additives on the overall crystallinity of Rilsan® PA-11.

<table>
<thead>
<tr>
<th>Rilsan® PA-11</th>
<th>#1-1</th>
<th>#1-2</th>
<th>#1-8</th>
<th>#1-9</th>
<th>#1-10</th>
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<td>32</td>
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<td>25</td>
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<tr>
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<td>31</td>
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<td>30</td>
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</tr>
</tbody>
</table>

Table 2. XRD and DSC determination of the crystalline index in Rilsan® PA-11 samples.

In conclusion, the development of a procedure based on elevated temperature experiments to extrapolate peak positions to room temperature have shown to be of interest in the case of PA-11. This method could be used for determining CI in other polymers, particularly for systems with severe peak overlaps. Additionally, the comparisons made in this study of CI from XRD and DSC measurements were encouraging.

ACKNOWLEDGMENTS

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REFERENCES