Synchrotron X-ray studies on polyamide composites prepared by reactive injection molding

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ABSTRACT: Semicrystalline polyamide 6 (PA6) and composites on its basis are among the most frequently used polymer materials for highly demanding applications. The performance of these composites depends on the crystalline structure of the PA6 matrix in which two crystalline forms most frequently coexist: α- and γ-polymorphs. This work reports on the crystalline structure of a variety of composite materials produced by in-mold reactive polymerization of caprolactam in specially designed semi-automatic equipment for reactive processing of nylons (NYRIM), carried out in the presence of particulate mineral reinforcements (natural organically treated aluminum silicates and synthetic titanosilicates), PA6 oriented monofilaments and textile structures of glass fibers. The morphology and the crystalline structure of all composites were studied by synchrotron X-ray diffraction. Transcrystalline PA6 layer was observed in all fibrous PA6 laminates whose structure fine crystalline structure was accessed.

1 INTRODUCTION

Polymer composites with thermoplastic matrices (TPC) comprising particulate or fibrous reinforcements are being used in steadily increasing number of applications due to their outstanding material performance and manufacturing flexibility (Matabola et al, 2009). Conventional TPCs reinforced by 30–50 wt% of glass, carbon, or other mineral constituents in the form of particles, different fiber types, or structures thereof have received much academic and commercial attention in the past due to their excellent mechanical properties.

TPCs may be produced by either melt-processing or reactive processing. The melt-processing techniques require melting of already existing thermoplastic material in the presence of the reinforcing component. Because of the high melt viscosity of the polymer matrix, elevated processing temperatures and pressures have to be applied to impregnate the reinforcements, especially if they are fibers of textile structures thereof. Nevertheless, proper impregnation at a micro scale in fiber-reinforced TPCs is not easy. Quite often, materials with significant void content are produced that lead to insufficient mechanical properties (Vaxman et al, 1989). In the case of TPCs with particulate and layered inorganic reinforcements, melt processing can result in poor dispersion of the reinforcing component and/or agglomeration with similar negative influence on the mechanical properties (Schaefer & Justice, 2007).

A key for cost-effective preparation of TPCs with optimum impregnation of the reinforcements by the matrix material of the same chemical composition can be the significant decrease of the viscosity of the latter. This is possible in the reactive processing techniques, where the thermoplastic matrix is obtained in situ, through polymerization of low-viscosity monomers or oligomers in the presence of the reinforcements. Among the most commonly used polymerization types is the ring-opening polymerization (ROP) (van Rijswijk & Bersee, 2007). It is based on anionic or cationic reaction mechanisms, in which ring-shaped monomer molecules are opened and transformed into high molecular weight polymers without liberation of by-products. Thus, polyamide 6 (PA6) can be produced through activated anionic ROP (AAROP) of the ε-caprolactam (ECL). The process is carried in a way that the ECL polymerization and PA6 crystallization occur simultaneously at temperatures 40-60°C lower than the melting point of the resulting PA6 (220°C). This drastically reduces the overall production cycle time and increases the energy efficiency of the process.

There exist a number of studies on reactive processing toward PA6 obtained by AAROP (APA6), but only a few of them deal with the preparation of composites (Gong &Yang 2010; Luisier et al, 2003; Cho et al, 1996; van Rijswijk et al, 2005; van Rijswijk et al, 2006; Harkin-Jones & Crawford 1996; Crawford & Harkin-Jones, 1996). Recently, prototype semiautomatic equipment for reaction injection

molding of nylons (NYRIM) was developed in UM-DEP (Dencheva et al, 2012) to prepare APA6-based thermoplastic composites of various types by in situ AAROP of ECL carried out in the presence of the reinforcements. The RIM concept is widely used for the production of polyurethane-based finished parts. To the best of our knowledge, no other studies exist on its application to prepare polyamide composites. Although the AAROP of lactams to neat polyamides is thoroughly documented and well understood, the crystalline structure of anionic PA6 matrices containing particulate, layered or fibrous reinforcements are not sufficiently studies. Therefore, this study reports on the morphology and the crystalline structure of various PA6-based TPCs obtained by the NYRIM technology characterized by synchrotron wide-angle X-ray scattering (WAXS). Applying specific treatment of the WAXS data, a deeper insight on the transcrystallinity and the polymorph transitions in the studied composites during the in-situ matrix creation is pursued.

2 EXPERIMENTAL

2.1 *Materials*

The ε-caprolactam monomer (ECL) with reduced moisture content suitable for AAROP (AP-Nylon® caprolactam) was delivered by Brüggermann Chemical, Germany. Before use it was kept under vacuum for 1 h at 23ºC. As polymerization activator, Bruggolen C20P® (C20) from Brüggermann Chemical, Germany was used. According to the manufacturers data, C20 contains 80 wt% of blocked diisocyanate in ECL. The supposed chemical structure of C20 is presented in Fig. 1. The initiator sodium dicaprolactamato- bis-(2-methoxyethoxo)-aluminate (80 wt% in toluene, Dilactamate®, DL, Fig. 1) was purchased from Katchem and used without further treatment.

The nanoclay brands employed in this study were Cloisite15® (CL15A) and Cloisite20A® (CL20A) manufactured by Southern Clay Products. They both represent natural montmorillonite (MMT) modified by dimethyl dihydrogenated tallow quaternary ammonium chloride and contain up to 2% of moisture. According to manufacturer's data, CL15A has a slightly higher modifier amount (125 meq/100 g versus 95 meq/100 g of CL20A) resulting in organic contents of 43 and 38%, respectively, measured by TGA. Both nanoclyas were dried for 2 h at 110ºC in an oven and then immediately used. Three titanosilcates (Ti-Si), namely ETS-4, ETS-10 and AM-4 were prepared in a manner well known by art (da Silva, 2013)

The PA6 continuous textile fiber reinforcement monofilament with a diameter of 60 µm (33/1 dtex), a round cross section, and a semi-dull treatment was obtained from ZWCH Stilon, S.A.
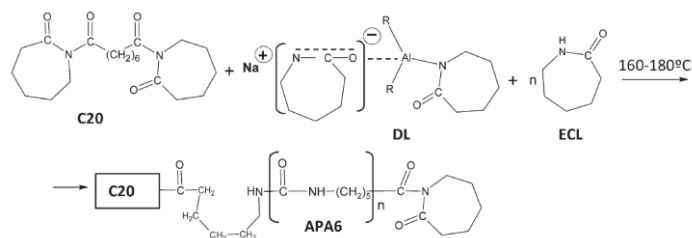

Figure 1 Schematics of the chemical reactions and catalytic system components in AAROP: C20 (activator); DL (initiator), R= $OCH_2CH_2OCH_3$; ECL (monomer) and APA6 (anionic polyamide 6).

The glass fiber reinforcements were supplied by PPG Industries Fiber Glass. Three fabric types of plain-weave E-glass were used with areal densities of 210 (GFL1), 300 (GFL2), and 482 g/m^2 (GFL3) treated with proprietary sizing suitable for polyamide laminates. In some cases, these fabrics were treated with acetone (Sigma-Aldrich, purum grade) for 30 min and dried at room temperature before use to remove the finish.

2.2 *Composite preparation*

The ECL monomer was separated into two equal portions and placed into two heated flasks with magnetic stirrers. To the first of them, 1.5 mmol of DL was added and to the second 0.75 mmol of C20 maintaining the temperature in the 90-110ºC range. In the case of particulate reinforcements (MMT or TiSi), the respected amounts of the inorganic phases were separated into two and added to the two monomer portions. The in-mold AAROP was performed in hydraulically actuated prototype equipment for reactive injection molding of nylons (NYRIM), whose concept and functioning were described in detail elsewhere (Dencheva et al, 2012). The production cycle started by introducing the ECL/C20 and ECL/DL feeds separately into a camera preheated to 110ºC where they were mixed by jet impingement. The resulting initiated and activated molten ECL was then injected into the mold, preheated to the polymerization temperature. In the case of fibrilar reinforcements or textile laminates, the mold already contains the respective amount of PA6 monofilaments or glass fiber textile structures. After elapsing the time for AAROP, the mold cooled down automatically to a preset temperature of ca. 65ºC at a rate of 25ºC/min and opened ejecting the molded composite plate (80×80×3 mm). In this study the AAROP was performed in the range of 165ºC, setting the reaction time at 15 min. Two sets of samples were produced for each PA6 monofilament- or glass textile-reinforced TPCs: with the as-obtained commercial fibers bearing their original proprietary sizing and after removing of any non-chemically bonded finish on the fiber surface by immersion in acetone

for 30 min and subsequent drying for 2 h at 60ºC. Table 1 summarizes the description and designations of the TPC prepared. The APA6 sample represents neat matrix material prepared by AAROP under the same processing conditions as the respective composites.

Table 1. Description of the APA6-based composite materials of this study

Composite type	Designation	Reinforcement amount wt %
Neat anionic PA6	APA6	-
MMT clay hybrids	PA6-CL15	0.5; 1.0; 2.0; 3.0
	PA6-CL20	0.5; 1.0; 2.0; 3.0
Ti-Si hybrids	ETS4	0.5; 1.0; 3.0
	ETS-10	0.5; 1.0; 3.0
	AM-4	0.5; 1.0; 3.0
APA6 single-polymer composites	SPC	10; 15; 20
Glass fiber laminates	GFL1	
	GFL2	20
	GFL3	

CL = Cloisite, organically treated montmorillonite clay
SPC = Single polymer composites, with and without fiber treatmen;
Ti-Si = titanosilicate phase
GFL1-3 = glass fiber textile structures with low, medium and high densities

2.3 Characterization techniques

The degree of AAROP conversion was determined as a relation of the mass of the sample after and before Soxhlet extraction with methanol for 8 h until constant weight. Values of 97-99% were reached. In all composites no inhibition of the polymerization process was observed. The average viscometric molecular weight M_v of the neat APA6 prepared by the NYRIM technology was determined by intrinsic viscosity measurements in 97% sulfuric acid at a concentration of 0.2 g/dL with a suspended level Ubbelohde viscometer thermostatted at 25ºC. Using the Mark-Houwink equation with K = 10^{-3} and α = 0.7 for PA6 (Ivanova et al, 1978) values in the range of 42,000-45,400 were obtained.

The wide-angle X-ray scattering patterns (WAXS) in this study were registered at the Soft Condensed Matter Beamline (A2) of HASYLAB, Hamburg, Germany using synchrotron radiation with wavelength fixed to 0.15 nm. The sample-to-detector distance was set at 90 mm, the diffraction patterns being registered by means of a MAR two-dimensional detector of Rayonix. The samples were studied in transmission mode with an exposure time of 25 s. A specially designed sample holder was used allowing for controlled heating–cooling cycles in the 30-300ºC range. An Imago multichannel processor and program controller of JUMO GmbH were used to regulate the sample temperature in heating and cooling. The difference between the read-out and real temperature was found to be 3-4ºC at the heating rate of 20ºC/min applied in this study. Corrections for background scattering, irradiated volume, and beam intensity were performed for each 2D pattern. To separate the WAXS contributions of the isotropic matrix and the oriented fibers and to study the transcrystallinity, the 2D WAXS patterns were processed with POLAR 2.7.1 X-ray software.

3 RESULTS AND DISCUSSION

3.1 WAXS studies on APA6/Cloisite hybrids

Figure 2 shows the low s-values region of WAXS patterns of PA6/o-MMT composites, in which the CL20A and CL15A vary in a broad range. To enable comparison, the WAXS profile of the neat PA6 is also presented (curves 1a and 1b).
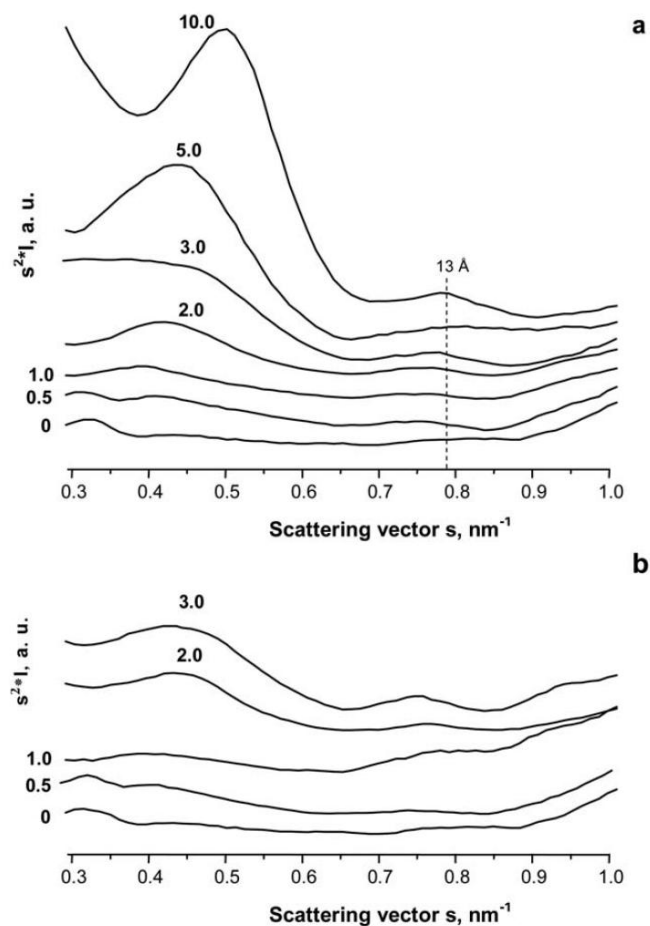

Figure 2. WAXS patterns of PA6/MMT composites (low s-values region) containing different amounts of: (a) CL20A and (b) CL15A. The numbers to curves correspond to the MMT concentrations in wt % in respect to APA6. The Lorentz-corrected patterns are shifted along the y-axis for clearness.

It can be seen that irrespective of the Cloisite brand, the hybrids with 0.5% (curves 2a and 2b) and 1.0 % of clay (3a and 3b) do not display basal reflection and can be therefore considered fully exfoliated nanostructured polymer composites (NPC).

As expected, increasing the MMT content led to aggregation and formation of intercalated PA6/MMT composites. Thus, the composites with 2 and 3% CL20A show a weak reflection with d001 of 20-29 Å corresponding to basal long spacings of silicate layers with different stages of intercalation (Fig. 2a). This reflection is somewhat more intense in the systems containing CL15A (Fig. 2b). AAROP of ECL in the presence of 5 and 10% of CL20A produced composite materials with increasing aggregation of clay layers showing gallery heights of 23 Å and 20 Å, respectively. In these two profiles, the d001 reflection of the pristine MMT at ca. 13 Å is also observed (Fig. 2a).

The WAXS profiles in Figure 2 allow the conclusion that exfoliated NPCs via AAROP can readily be produced with clay concentrations below 2 wt %. Intermediate amounts of 2 and 3% lead to intercalated PA6/MMT materials, whereas clay loads of 5 and 10% CL20A resulted in pronounced aggregation of the MMT component.

3.2 *WAXS studies on APA6/Ti-Si hybrids*

Titanosilicate materials are normally synthesized in aqueous media at elevated temperatures and pressures. When crystallizing, they arrest in their porous or lamellar structure various amounts of water molecules which upon heating are lost thus causing significant change or even collapse of the structure. That is why only thermally stable titanosilicates were synthesized and used in the NYRIM process for PA6 modification, namely the ETS-4, ETS-10 (porous phases) and AM-4 (platelets). APA6/Ti-Si composites prepared with the NYRIM technology display um relatively high WAXS crystallinity of 45-50%, whereas composites obtained by bulk polymerization show lower crystallinities of ca. 40%. The crystallinity of the NYRIM samples does not change significantly with annealing temperatures in the range of 160-200ºC, however the polymorph content ratio α/γ can alter significantly – from 3.7 for neat APA6 to 7.8 or even 8.5 for APA6/ETS-10 composites with 1% of Ti-Si. Figure 3 shows one of the WAXS patterns from which the above information was extracted. It can be seen also that the APA6 composites containing ETS-4 and ETS-10 clearly show some of the reflections of the pure titanoslicates meaning that the in-mold AAROP does not change the crystalline structure of the Ti-Si reinforcing phases. At the same time, GTS-1 reinforced composite does not display the typical 001 reflection of the pure phase at $2\theta = 12º$. This fact indicates profound alterations during the AAROP taking place at ca. 170ºC. Therefore, such materials are less appropriate for use as PA6 reinforcement.

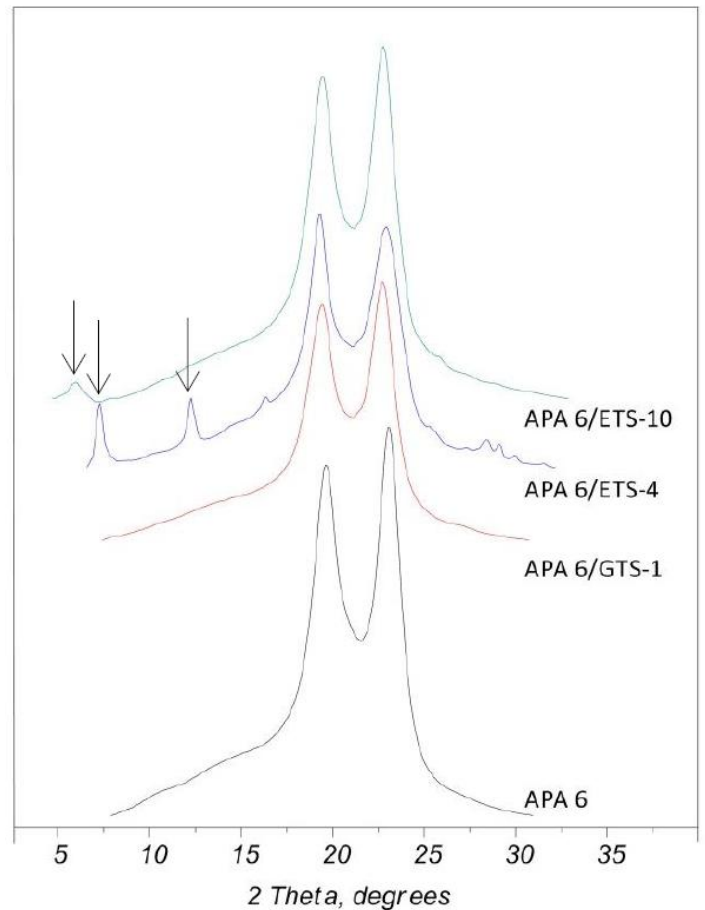
Figure 3. WAXS patterns of PA6/Ti-Si composites obtained by NYRIM process. The arrows indicate the reflections of the respective titaosilicate phase.

3.3 *WAXS studies on GFL*

To study the influence of the type and amount of the textile reinforcement on the crystalline structure of the APA6 matrix, synchrotron WAXS studies were performed with the GF APA6 laminates. Figure 4 displays the WAXS patterns of the as prepared GFLs at 30ºC (A) and after melting of the matrix and its recrystallization (B). In all the as-prepared GFL materials, as well as in the neat APA6 matrix obtained under the same NYRIM conditions, the overall crystallinity index changes in the 46-49% range. The α/γ ratio in these composites displays little sensitivity to the presence and type of glass fiber reinforcements, being in the range of the experimental error. Hence, it may be supposed that the type of the glass fiber fabric do not influence the PA6 polymorph content in the as-prepared samples. The presence of GF in the as-prepared GFL (Fig. 4A) does not result in significant changes in α/γ values therefore no steric hindrance effects are present and the just formed PA6 macromolecules when crystallizing can assume the conformation necessary for the formation of the α-polymorph.
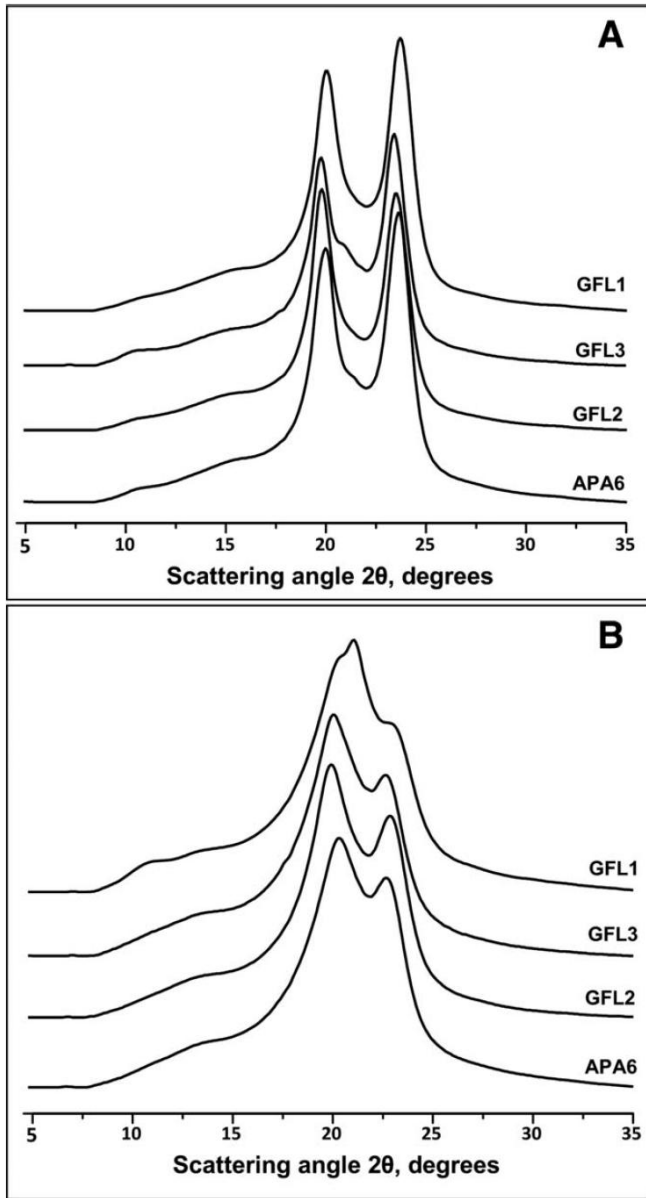
Figure 4. WAXS patterns of APA6/GFL of (A) as-prepared composites and (B) after melting at 260ºC and recrystallization of the matrix

If the GFL is subjected to melting/recrystallization (Fig. 4B), the variations of the α/γ ratio become statistically significant showing an increase of the γ-PA6 polymorph proportional to the fabrics density that increases from GFL1 to GFL3.

3.4 WAXS studies in PA6 single polymer composites (SPC)

Figure 5 presents the WAXS patterns of the SPC sample (as-prepared, at 30ºC and after melting at 260ºC and recrystallization) with 20% of reinforcing PA6 fibers treated with acetone prior to AAROP in the NYRIM equipment. The two-dimensional WAXS pattern of the as-prepared SPC (the inset on the left side) shows the co-existence of two isotropic Debye rings and two oriented ark-like reflections on the equator oriented parallel to the direction of the fiber axis.
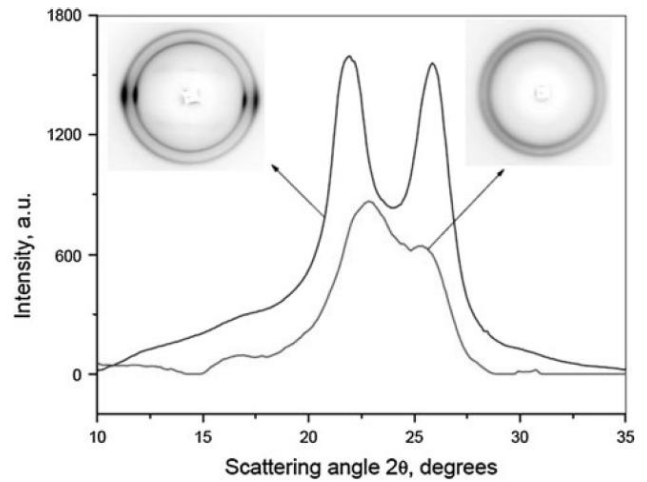

Figure 5. WAXS patterns of SPC sample with 20% PA6 mono-filaments, acetone treated. Left inset: as prepared sample at 30ºC; Right inset: sample after melting at 260ºC and cooling to 30ºC. The insets show the 2D WAXS patterns from which the linear profiles were obtained after radial integration. Fiber orientation is vertical.

The Debye rings should be associated with the isotropic matrix of anionic PA6 obtained during AAROP. The equatorial arcs belong to the oriented PA6 material of the reinforcing textile fiber and to the transcrystalline layer (TCL) on the top of it made of matrix PA6. The linear WAXS profile of the SPC is obtained after a conventional radial integration of the 2D pattern. The two peaks at $2\theta=20.0º$ and $23.6º$ are of the α-PA6 crystalline phase, which is the predominant one in the as-prepared SPC. Melting the composite at 260ºC and its recrystallization (the right inset) produce completely isotropized PA6 without oriented equatorial reflections in the WAXS image.

A more in-depth structural characterization is possible after separation of the isotropic scattering of the APA6 matrix from the oriented scattering of the reinforcing fiber coated with TCL. The separation procedure was reported earlier (Somani et al, 2000). The contribution from all oriented (with varying degree of orientation) scatterers is computed by subtracting the azimuthally independent component from the total scattered intensity. To perform the said subtraction, commercial X-ray software was used.

The linear WAXS profiles of the fiber material after the said separation and radial integration are presented in Figure 6. Four crystalline peaks were necessary to fit the profile of the oriented WAXS meaning that two types of oriented monoclinic α-PA6 crystallites with similar but distinguishable d-spacings coexist in this SPC sample thus proving the existence of TCL from oriented matrix material upon the PA6 fiber.

The more intense reflections at $2\theta=21.6º$ and $25.7º$ (line-patterned peaks) were attributed to the oriented

PA6 of the reinforcing fiber. The dark-shaded less intense peaks at 2θ = 20.3º and 23.8º were supposed to originate from the TCL on the top of the fiber. The direction of chain orientation in TCL most probably coincides with that in the oriented textile reinforcing fiber. No peaks for γ-PA6 phase were found in the oriented WAXS of the as-prepared sample irradiated at 30ºC.
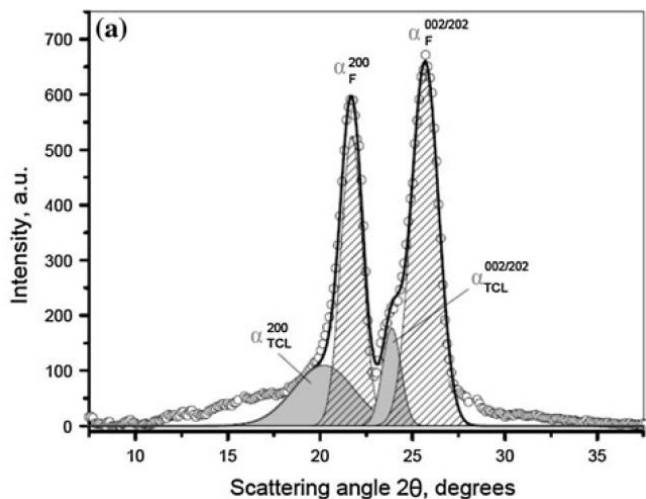

Figure 6. WAXS profile deconvolution by peak-fitting for the oriented part of the WAXS scattering. Sample: SPC with 20 wt% of monofilaments treated with acetone. Indices F and TCL denote fiber and transcrystalline layer.

4 CONCLUSIONS

The NYRIM equipment based on in mold activated anionic polymerization of caprolactam can produce different thermoplastic polyamide-based composite materials with all types of reinforcements: particulate, lamellar, porous, fibrilar and textile structures. In all cases synchrotron WAXS studies can be used for in-depth structural characterization of both matrix and reinforcement structure leading to better understanding f the structure-properties relationship.

5 AKNOWLEDGEMENTS

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