Crystal Structure and Texture Refinement of Polymers from Diffraction Images

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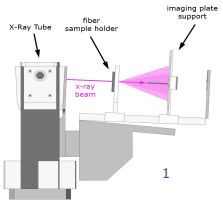
Introduction

An exact refinement of the crystal structure of polymers has always been a difficult task, mainly due to the partial amorphous nature of these materials. Fiber specimens usually possess a high degree of cristallinity induced by to mechanical drawing; the x-ray crystal structure refinement, on the other hand, is complicated by the presence of a strong preferred orientation.
In this work we present an integrated methodology that allows to analyze diffraction patterns to extract structural, microstructural and texture information from fiber specimen. Diffraction data from two different polymers, **isotactic polipropilene** and **Nylon-6** has been collected using a laboratory imaging plate system. The images have been processed with the **Maud** software (Material Analysis Using Diffraction - http://www.ing.unitn.it/~luttero/maud/) and a structure refinement approach including a Rietveld Texture Analysis was performed for each polymer. A combined profile / energy cost function approach has been incorporated , as well as the use of structural rigid-body fragments, to help the refinement strategy to converge. From the texture point of view, the standard function method for quantitative texture analysis has been developed and successfully applied to these systems, allowing to determine with high precision the spread of the single polymers chains in the fibers.



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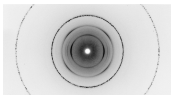
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Schematic view of the trasmission x-ray equipment used for collecting the fiber diffraction images (1) and an example of a typical ring pattern (2)

Experimental setup

Measurement were carried out using an x-ray diffractometer in both transmission and reflection geometry. A non-monochromatized copper radiation of 1.5406 Å wavelenght was used. Samples consisting of a single fiber were placed in ortohogonal position with respect to the beam, using an apposite attachment (3); diffraction data were collected using a phosphor-coated imaging plate placed 90 mm behind the sample, also orthogonal to the beam. Exposure time were approximately 60 minutes for each sample.
The imaging plates were successively digitally acquired using a Denoptix phosphor scanner system (4).


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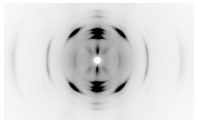
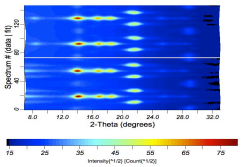
Analysis and results

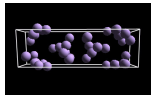
All the data analysis were performed with the use of the MAUD Rietveld software, that allows for simultaneous refinement of structural, microstructural and preferred orientation data. The image obtained from the imaging plate scanner system were integrated in azimuthal increments of 5° obtaining a total of 72 diffraction spectra, analyzed simultaneously. As for the Rietveld refinement procedure, initially only the intensity scale, center of image and backgrounds parameter were refined, successively adding crystallite size and microstrain and, at last, all the texture and atomic structure parameters.

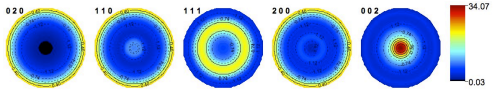
Isotactic polypropylene





The α_1 iPP structure (C2/c), as indexed by Natta and Corradini and found in the Cambridge Structural Database, provided a good starting point for the refinement, but additional adjustment had to be made to obtain a good fit.
The structure consists of an helicoidal chain, aligned along the z crystallographic axis, repeated 4 times following the space group rules. To obtain a consistent structural refinement, the polymer chain was fixed in a rigid-body structural fragment, whose coordinates (center of mass and orientation angles) were used as parameters of the least squares algorithm. Only at the end of the fitting cycle all the atom coordinates were freed and refined simultaneously.

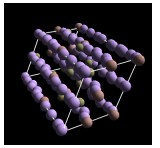


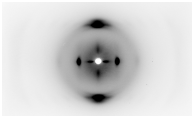


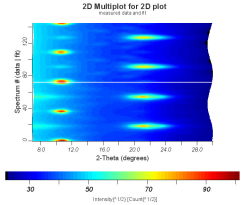
The preferred orientation distribution for the fiber specimen was very simple as expected, and could be modeled satisfactorily using only a single standard function component in a direction aligned along the fiber axis. A second component however, was added to fit some secondary texture pattern, slightly improving the refinement.

Nylon-6

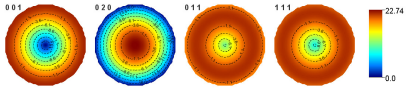
A complete structure refinement of the α form of Nylon-6 was not found in the literature, as only the main structural chain is known with a good approximation, the correct reciprocal chain alignment and orientation being ambiguous.
The crystal cell and the main polymer chain, as found in the CSD, were used to build a trial cell that was then refined using a rigid-body fragmen strategy to obtain the correct relative positioning and orientation of the chains inside the cell.







As in the case of polypropylene, a single texture component was sufficient to describe the preferred orientation distribution with a good approximation. Sample pole figures are reported, reconstructed from the calculated ODF.



Conclusions

The two-dimensional imaging plate detector system combined with the use of the Maud software allows, with a single analysis, to extract precise information of structure, microstructure and anisotropic nature of the samples. The transmission setup proved to be an excellent tool for studying fiber samples, and with the use of imaging plates technology demonstrated to be a relatively inexpensive though powerful tool for polymer characterization.