Crystal Structure and Texture Refinement of Polymers from Diffraction Images

Mauro Bortolotti, Luca Lutterotti, Luca Fambri, Department of Materials Engineering and Industrial Technologies, University of Trento. E-mail: mauro.bortolotti@ing.unitn.it, luca.lutterotti@ing.unitn.it, luca.fambri@ing.unitn.it

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 crystallinity 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 specimens. Diffraction data from two different polymers, Isotactic polypropylene and Nylon-6, has been collected using a laboratory imaging plate system. The images were acquired using a Synchrotron facility as well as a conventional x-ray equipment used for collecting the fiber diffraction images (1) and an example of a typical ring pattern (2). The crystal structures were refined in the monoclinic space group P21 containing 4 molecules in the unit cell. The analysis of these data allowed to determine accurate orientations of the polymer crystals and to deduce the orientation distribution of the fibers within the matrix. This was achieved by a combination of Rietveld Textuanalysis and Directional Analysis (3).

Experimental setup
Measurement were carried out using an x-ray diffractometer in both transmission and reflection geometry. A non-monochromated copper radiation of 1.5406 Å wavelength was used. Samples consisting of a single fiber were placed in orthogonal position with respect to the beam, using an appropriate attachment (4); diffraction data were collected using a phosphor coated imaging plate placed 60 mm behind the sample holder. The exposure time were approximately 60 minutes for each sample.

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 parameters.

Isotactic polypropylene
The α3 IPP structure (C2/c), as indexed by Natla and Cordini 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 description of the fiber, a set of rigid-body structural fragments was used. A rigid-body structural fragment, whose coordinates (center of mass and orientation angle) 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.

Conclusions
The high-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 anistropic 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.

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 fragment 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.

Sample images are shown below.