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MORFOLOGICAL PROPERTIES OF ISOTATIC POLYPROPYLENE, i-PP, SUBMITTED TO A PLANAR-STRAIN COMPRESSION.



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The morphological properties of the isotactic polypropylene (i-PP) submitted to plane deformation were investigated through x-ray diffraction and transmission electron microscopy. Two crystalline phase were identified in the undeformed polymer, namely α and β phase, although some amorphous halo coexist with these phases. After deformation with 10 MPa, a transition from the β to α phase occurs together with an increase of the amorphous contribution. The relaxation of internal energy during the uniaxial deformation can generate a high temperature pulse, which can be responsible by the phase transition as well as the decrease of crystallinity.

1. Introduction

There are many groups involved in the research to a better understanding of the morphological properties of isotactic polypropylene (i-PP). Although in the last 30 years many studies have been done in this field, many questions concerning to the morphological properties of plastic deformation of semi-crystalline polymer are still open from the point of view of basic science. Flory and Peterlin studied the morphological changes in semi-crystalline polymer after stress application. Flory [1] claim that the plastic deformation occurs by fusion and recrystallization of the crystalline phase, while Peterlin [2] added three stages of plastic deformation during the stress increase on the sample. In the first stage, a pre-necking occurs at the micro structure, that is, the plastic deformation of the original spherulitic structure. In the second one, there is a discontinuous transformation of the spherulitic structure into fibre structure by micro necking, and in the third stage a plastic deformation of the fibre structure takes place. Peterlin added to the Flory's proposal the micro-necking mechanism.

Garcia and Samios [3] observed that the deformation process affects the thermodynamic properties of polymers, and that during plastic deformation of semi-crystalline polymers, an irregular thermal expansion behavior can be verified in the deformed direction (Y and Z). Machado and Samios [4] studied morphology evaluation of semicrystalline polymeric materials deformed through axial forces using Scanning Electronic Microscopy evidencing the spherulitic deformation.

Lin and Argon [5] studied nylon 6 textures by plane strain compression at 170°C. Galeski [6] analyzed the evolution of deformed textured of a high density polyethylene (HDPE) by plane strain compression, where it was possible to solve the changing of spherulitic morphology due to the plastic deformation in channel die compression. Bartzak [7] studied the plastic resistance and crystallographic deformation mechanisms, submitting the high-density polyethylene (HDPE) to the room temperature uniaxial deformation. Recently Cohen et al [8] studied ultra-high-molecular-weight-polyethylene (UHMWPE) using compression in a channel die, comparing their results with previous studies realized in the HDPE under the same compression conditions. It was verified that crystallographic texture in UHMWPE shows a molecular orientation along the flow direction, being able to control it by channel die compression, Machado, et al [9] studied the orientation of micro structural elements in isotactic polypropylene through computer analysis of SEM images before and after deformation verifying the orientation of the spherulitic structure.

The plastic deformation in polymers is a complex process. For instance, in the case of semi-crystalline polymers, the application of high pressures, can transform completely the initial micro-spherulitic structure in a fibrillar orientation. There are many mechanisms that control these deformations. Among them, the lamellar separation, crystalline plastic sliding, and eventually, ruptures in various degrees of plastic deformation of a semi-crystalline polymer, can be mentioned [5,7]. There are also crystalline

modifications regarding the α , β , and γ phases involved in these process [10,11,12]. The α and β phases have a monoclinic hexagonal unitary cells, respectively and can coexist in a same specimen.

Between the two crystalline phases, the monoclinic α is the most stable, and it's well documented in the literature [12,13]. The β phase was firstly mentioned by Padden and Keith [14]. This phase can be only obtained with peculiar conditions, being thermodynamically less stable than the α phase. It was verified that in the i-PP, the mechanical, physical and stability properties of the β is very different from the α phase. Considering the complexity of these structures, it is conceivable that the mechanical behavior of a given polypropylene sample should be highly dependent on its previous processing.

In the last years, several authors showed that the semi-crystalline polymeric materials submitted to uniaxial deformation presented morphological changes reflecting mainly in the variation of their crystallinity.

The aim of the present work is the investigation of the morphological modifications, through X-ray diffractometry (XRD) and transmission electron microscopy (TEM), of semi-crystalline i-PP polymers submitted to deformation by an uniaxial compression process.

2. Experimental Details

The samples of isotactic polypropylene ($M_w = 271,000$ g/mol; $M_n=43,700$, $M_w/M_n=6.2$), 17 mm long, 4.7-mm large and 3.0 mm thick, were molded by injection and underwent plastic deformation at ambient temperature using compression pressures of 10 MPa. The pressure of 10 MPa was associate with 40.0 %.

For the present study the plane strain compression in channel die was chosen as deformation mode. The samples were placed in a deep channel die, and then deformed. By convention, the coordinate reference system adopted here were: Z-axis, defined as the loading direction, Y, as the flow direction and X, as the unaffected direction, that limited by the chamber edges.

The samples were stain prepared [15] and after were embedded in an epoxy resin and cured at 40°C for 72 h. The embedded specimens were first trimmed with a razor blade and then were cut with an Ultra cut microtome LEICA model UCT 2.0 using a room temperature Diatome knife with 35°. The ultra-thin sections were mounted on 200 mesh copper grids and dried in a desiccator. Finally, they were examined using a Jeol JEM - 1200 EXII TEM operating at an accelerating voltage of 80 kV.

X-ray analyses were performed in a Philips X'PERT MRD diffractometer using Cu K α radiation. The diffraction data were collected in a 2θ range between 3 and 48°. Phase identification and indexation were carried out using the Rietvelt refinement [16, 17].

Results and Discussion

X-ray diffraction is very often used to determine the crystallinity of polymers [16]. Semi-crystalline polymers have two phases, an amorphous and another crystalline. Although there is no a well defined interface between the two phases, this model is very well accepted to describe the structure of semi-crystalline polymers. Fig.1 shows the x-ray spectra of undeformed and 10MPa deformed i-PP, respectively. The spectra were taken in the z direction, that is, the XY plane normal to the applied deformation. As indicate in the Fig.1, the presence of the crystalline α and β phases are very clearly identified. There is also an amorphous halo that appears as a very broad peak at the bottom part of each spectra. The Rietvelt refinement was performed without considering atomic positions, but leading into account the lattice parameters [10,12,13], and after subtract the amorphous contribution from the spectra, as detailed in [16]. This is a standard procedure that gives very good results. After deformation there is a decrease of the β phase with an enhancement of the amorphous contribution, see Fig.1b, indicating the beginning of the transformation of the less stable β into a more stable α phase. The decrease of crystallinity is also evidenced by the increase of the full width of a half maximum of the crystalline reflections.

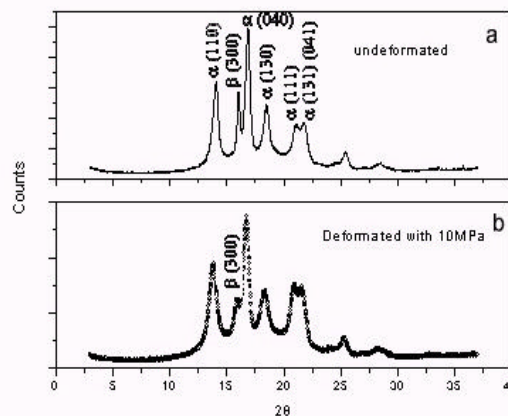


Figure 1. a) X-ray spectra of i-PP for the undeformed sample and b) for deformed sample with 10MPa.

Fig.2 shows the TEM images of the undeformed i-PP, where the spherulitic structure can be easily identified. Enhanced the resolution, Fig.2b, a crosshatched lamellae structure corresponding to the α phase is evidenced. It is important to point out that both, α and β phases are present in the whole image, in accord to the x-ray measurements, but to emphasize the presence of the α phase only a small part of the image was chosen. These observations are in agreement with the x-ray spectrum of Fig.1a.

The TEM image of the deformed i-PP is depicted in Fig.3a, where a deformed spherulitic structure can be seen. Increasing the resolution, Fig3b, a different

lamellae structure is evidenced. As can be observed, this lamellae structure corresponding to the α phase is much less crystalline than that presented in Fig.1b. The crosshatched is less visible indicating the decrease of crystallinity with an increase of the amorphous phase, according to the x-ray measurements displayed in Fig.1b.

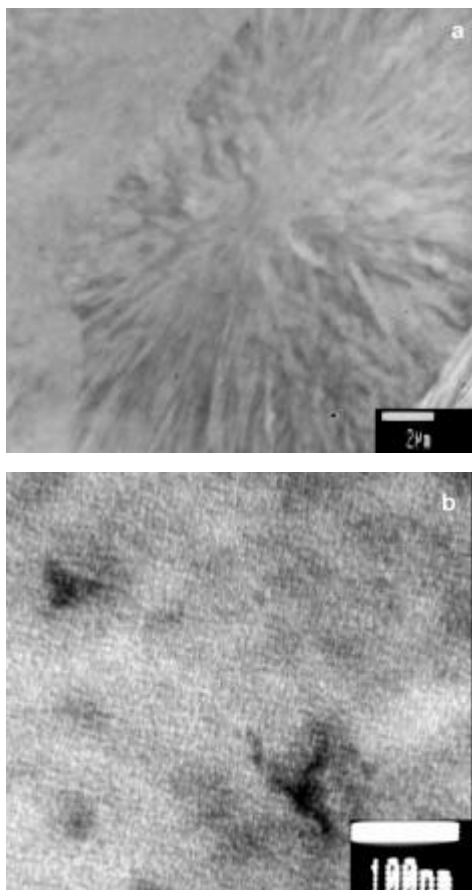


Figure 2-Undeformed I-PP. a) spherulitic structure and b) lamellae structure

Conclusions

The morphological properties of i-PP submitted to plane strain compression were accessed by XRD and TEM. It was evidenced the presence of two crystalline phases, namely α and β and an amorphous phase, an halo at the bottom side of the x-ray spectra. The room temperature deformation induces a transformation from a less stable β to more stable α phase, besides an increase of the amorphous phase. The transition of the β to α phase is evidenced by both XRD and TEM, however the origin of this transformation is not still clear. There is a possible temperature increase during deformation that would be the driving force to promote the β to α transformation and an increase of the amorphous phase. For that transition, a high enough temperature is necessary, and it would be possible if

we consider that a pulse of high temperature could be created during a fast deformation process, even at low pressure as 10 MPa. The relaxation of internal energy during the uniaxial deformation can generate a high temperature pulse which can be responsible by the phase transition as well as the decrease of crystallinity. It is only a possibility and is still subject of investigation.

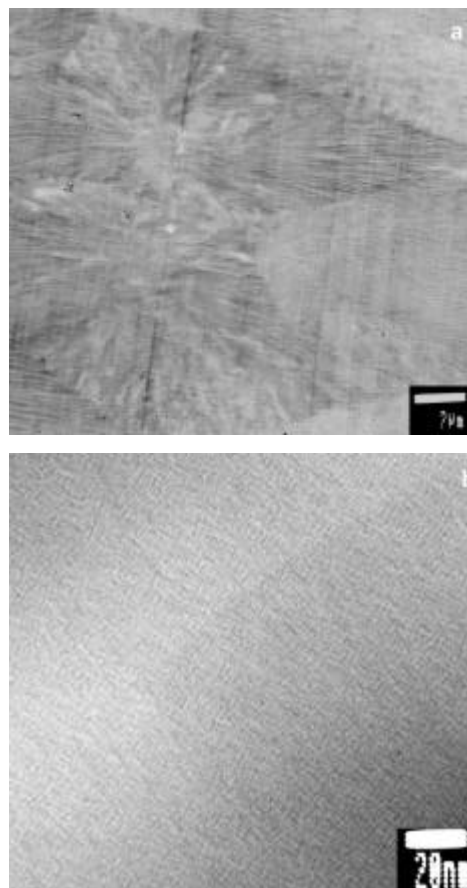


Figure 3-10 MPa uniaxial deformed I-PP. a) Spherulitic structure and b) lamellae structure

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