Mechanical Properties and Microstructural Evolution of Semi-Crystalline Polymer treated by the Multipasses ECAE process

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Abstract:

Our study is the analysis and interpretation of the results of characterization tests of a semi-crystalline polymer (polypropylene) having undergone plastic deformation by the process of Equal Channel Angular Extrusion (ECAE). Two completely different methods and processes do this characterization; microstructural characterization by means of X-ray diffraction using the Fit2d software, and mechanical characterization using the measurement technique by the method of Digital Images Correlation (DIC) using Davis software. The ECAE multi-pass realized in the route A shows that increasing the number of passes significantly reduces the effort required to achieve the extrusion operation. More than the number of passes increases more than the extrusion force decreases. The extrusion according the route C has revealed a very special phenomenon of that the extrusion forces has completely different looks depending on whether the number of passes is odd or even. For odd number of passes, the extrusion force exhibits an increase progressively as the sample passes through the channel. This has the same behavior as the route A. For number of even's passes, the extrusion force has decreased gradually as the sample passes through the channel. The analyse by DIC shows that the extrusion according the route C gives a more homogenous structure compared to theses given by the route A.

Keywords: DIC, ECAE, Polypropylene, WAXS.

1 Introduction

The polymer materials know, during the last decades, an exceptional development which is due to their interesting properties, the improvement of industrial production processes, and the possibility of its properties vary widely by various processes and methods [1]. Among these methods which are used to improve or to vary the properties of those polymers, especially thermo-mechanical, is the equal channel angular extrusion (ECAE). This method was applied for the first time by Segal et al in the early 1980s on metals [2]. This process was the subject of intense study because of its ability to produce fully dense metallic materials with ultrafine grain sizes. The advantage of this technique is that it allows you to repeat the process several times while maintaining the original cross- section of the sample [3]. The application of this process was extended to polymer materials in the 1990s, and H J Sue et al [4] are the first to apply this technique to a polymer which is the low density polyethylene (LDPE).

This work involves the analysis and interpretation of the characterization test results of a polypropylene having undergone plastic deformation by the multi-pass ECAE process, according to route A and route C. The technique of Wide-angle X-ray scattering diffraction (WAXS) is used for the microstructural characterization of the samples taken from the materials that have undergone extrusion tests under different conditions. These results were obtained using the Fit2d software, which processes X-rays photography, obtained by WAXS installation, with digital recording software.
The Fit2d allowed us to trace the different diffraction patterns, in the radial and azimuthal direction, as it allowed us to see the different turns per representation in three dimensions (3D); so that lists the various properties of the structure at the molecular scale of the materials studied, and the influence of ECAE on this structure. The method of non-contact measuring digital image correlation (DIC) is used for the displacement-measuring fields and surface deformation during mechanical characterization tests using tensile tests. Characterization tests are performed on samples cut from the bars has undergone various extrusion methods, and behavior are studied for comparison, to see the influence of some extrusion parameters on the behavior of these materials. Calculations are made using Davis software of digital image correlation, with the ability to trace the strain fields and also the stress-strain curves.

2 Concept of ECAE

As shown in figure 1, the basic principle of the ECAE process is to press a sample through a die having two intersecting channels, where the two channels have identical cross-sections so that the cross-section of the sample experiences no change during pressing.
As shown in figure 1, a specially-designed die is used in ECAE and two internal angles φ and ψ are defined as the curvature associated with the two channels [2,5]

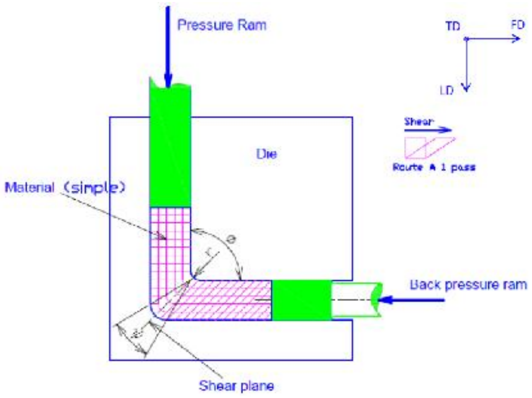


Figure 1. Schematic illustration of a 90° ECAE die

3 Working principles of ECAE

A detailed description of the different processing routes in ECAE has been given by Furukawa et al [6] and Zhu et al [7]. They distinguished four different processing routes, which they designated routes A, B_A, B_c and C. Figure 2 and figure 3 schematically illustrates for the route A and the route C how the billet is rotated in between consecutive passes.

3.1 Route A

The billet orientation is the same at each pass: the distortion of material elements is continuously increased with each successive passes (Figure 2).

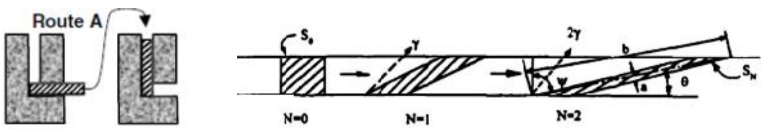


Figure 2. Billet orientation and element transformation for route A

3.2 Route C

The billet is rotated 180° around its axis at each pass. Heavily deformed but uniform and equiaxed grain structures (Figure 3).

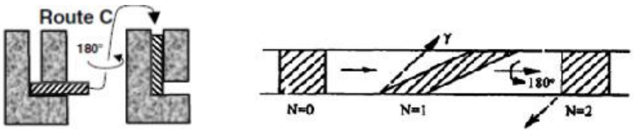


Figure 3. Billet orientation and element transformation for route C

4 Experimental procedures and material
4.1 ECAE experiments

The ECAE tests were conducted at room temperature (about 23°C) with a constant velocity of the piston in the range of 0.45 to 45 mm/min. The extruded samples were cut from the as-received PP along the same direction. Samples have a square section 10x10 mm^2 and a length of 75 mm. The ECAE die was made of stainless steel. It is shown schematically in figure 1. An internal angle φ of 90° between the two channels an outer corner angle ψ of 10° and an inner radius r of 2 mm were adopted.

4.2 Material

The material used in this investigation is a polypropylene (PP) of weight–average molar weight of 180 kg/mol purchased from Goodfellow©. The material was supplied in the form of 10 mm thick compression-molded plates.

4.3 Multi-pass ECAE
4.3.1 According to the Route A.

The figure below (figure. 4.) shows that increasing the number of passes significantly reduces the effort required to achieve the extrusion operation. More than the number of passes increases more than the extrusion force decreases. Following this, we can conclude that the number of passes only further break the macromolecular chains of polypropylene, which becomes softer and less durable.

4.3.2 According to the Route C

The extrusion die according to route C has revealed a very special phenomenon which consists in that the extrusion force has completely different gaits depending on whether the number of passes is odd or even (figure. 5). For odd number of passes, after the passage of the sample through the bend in the matrix, the shape of the curve of the extrusion load exhibits an increase progressively as the sample passes through the channel. This exhibits the same behavior as extrusion according to road A. For number passes pairs, unlike the odd number of passes, the shape of the extrusion force curve presents a decrease as and as the sample passes through the channel

The studies that have been devoted to the study of the influence of the choice of route and the number of extrusion passes over the behavior of a semi-crystalline polymer material, found so far are limited to numerical simulations. One can note the study Aour B et al [8]. According to these authors the route C taken in number of passes (04-08 passes) increases the homogeneity of the distribution of equivalent plastic deformation along the extrusion direction, and it becomes more isotropic in this direction. The results of this study clearly show that the material also becomes more ductile in the case of the route C after number of passes.

5 Result and discussion

5.1 Wide-angle X-ray scattering (WAXS) experiments

Wide-angle X-ray scattering (WAXS) experiments were carried out in order to characterize the macromolecular structure after ECAE processing.

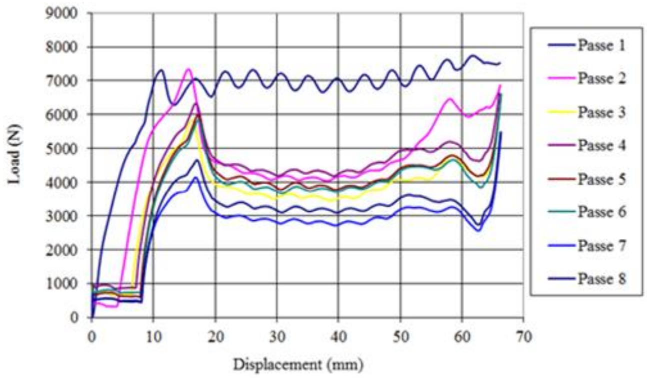


Figure 4. Ram load of multi-pass ECAE. According to the Route A

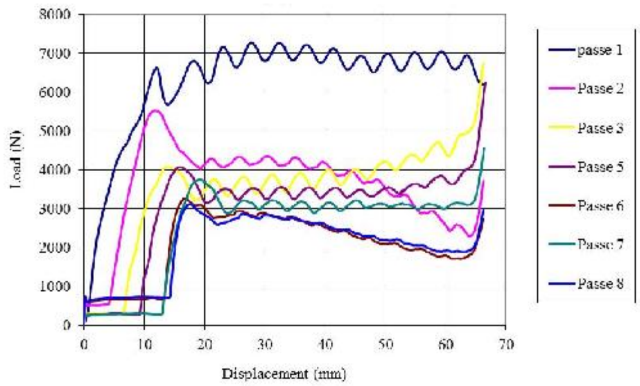


Figure 5. Ram load of multi-pass ECAE. According to the Route C

5.1.1 2D-WAXS patterns of an as-received PP.

Similarly, as for the extruded material, we prepared lamellae of an as-received PP to be analysed by X-ray. We observed the structure in the middle of the sample (figure 6.). The X-ray (WAXS) of this lamella gave the image of (figure 7.). The WAXS patterns recorded with the X-ray beam along the FD show that the material is isotropic, since the lines observed at different points are identical.

Figure 6. Samples after ECAE of PP for WAXS measurements.

The two-dimensional representations through the Fit2d software of the registered rays are given in figure 8. We notice although the intensity is the same for each spire that shows the distribution in the azimuthal direction is the same. It is obvious that the crystal planes don't undergo any microscopic deformation. The different spire with different intensities tells us about the texturing material. The direction favoured in this case corresponds to the first spire, where the intensity is highest.

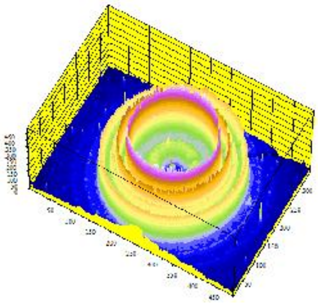


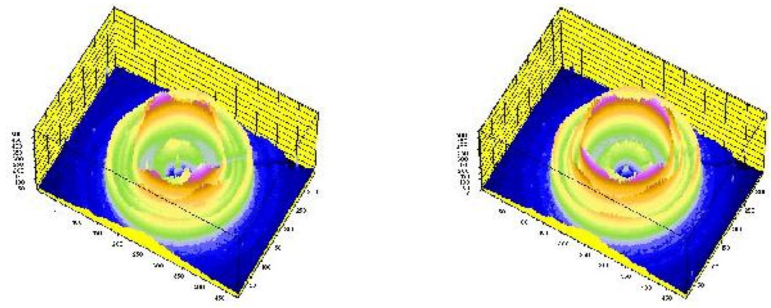
Figure 7. 2D-WAXS patterns, viewing along the TD axe of an as-received PP

5.1.2 2D-WAXS patterns of PP after a single passe of ECAE at a ram speed of 45 mm/min.

Without backpressure (figure 8), the sample does not fill up the outer corner of the die and exhibits a wavy shape on the top surface in the exit channel: the summit of the waves is in contact with the surface of the die whereas the bottom of the waves is not. This suggests a heterogeneous strain field in the bulk, which is confirmed by the occurrence of dark grey and light grey alternated stripes inclined at about 45° from FD along the sample length. This was explained in detail in our previous work [9-13].

Figure 8. Macrographs of PP samples after a first pass ECAE at a ram speed of 45 mm/min.

In the case of the higher ram velocity 45 mm/min and no back-pressure, figure 9. displays two 2D-patterns recorded from consecutive dark–light stripes. The light stripe looks roughly isotropic whereas the dark ones exhibit a strong diagonal reinforcement of the 3 first reflections. This is relevant to a preferred orientation of the (110), (040) and (130) planes containing the chain axis parallel to the shear direction.



(a) dark stripe. **(b)** light stripe.

Figure 9. 3D-WAXS patterns, viewing along TD axe, of PP after ECAE at a ram speed of 45 mm/min and without back-pressure.

5.2 2D-WAXS patterns of PP after a ECAE multipasse at a ram speed of 45 mm/min

In previous cases where a single pass is applied, the diffraction patterns do not show a large difference from the reference state which is the as-received PP. Against by, in the case of multi-pass and with respect to the same reference state (virgin PP), the diffractograms have larger differences in the intensity values of the peaks. RX observations are performed on the extruded PP multi-pass and in two types of routes; Route A and Route C

5.2.1 2D-WAXS patterns of PP after ECAE According to the Route A.

RX images in two dimensions are shown below for two, four and eight passes of ECAE according to route A (figure 10). By analyzing these diffraction patterns, it can be concluded that the microstructural characteristics of the extruded PP according to the A strain rate of $10^{-2}s^{-1}$ against and no-pressure are better for the case of extrusion in two passes. By increasing the number of passes these characteristics are degraded, while remaining better than those of a virgin PP and the extruded at a single pass.

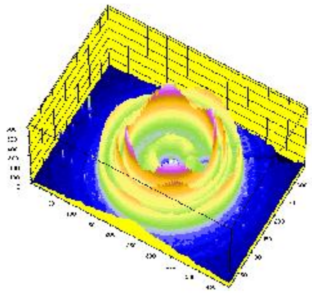
5.2.2 2D-WAXS patterns of PP after ECAE According to the Route C.

The figure 11 below show the X-rays of an extruded PP at the speed of 45 mm/min without a back-pressure. These figures reveal that the extrusion according to C homogenizes the distribution of deformation. Comparing the 2D figures of this case with those of as-received PP in figure 7., we note that there is a similarity of their structures. It is noted that for this case, increasing the number of passes is even improving the characteristics of the material without application of the back-pressure, unlike the case of the route A.

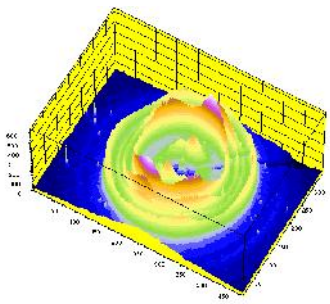
5.3 Tensile Tests

The tensile tests were conducted on the Instron© testing machine at room temperature under a constant cross-head speed 0,75 mm/min, i.e. a nominal strain rate of $10^{-3}s^{-1}$, using sample of gauge length

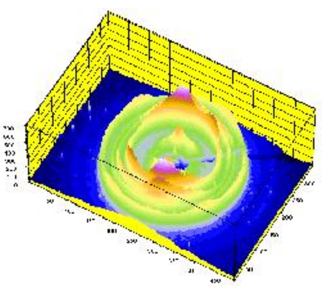
12,5 mm. Full-field strain measurements were achieved during tensile tests using digital image correlation (DIC) technique.



2 passes route A

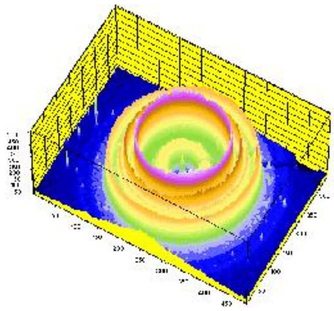


4 passes route A

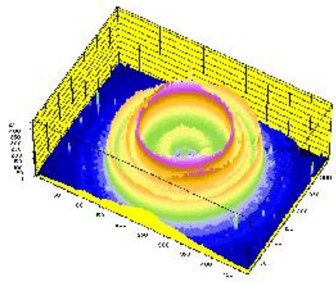


8 passes route A

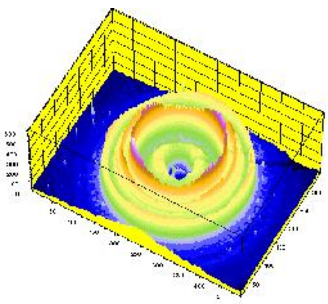
Figure 10. 2D-WAXS patterns viewing along TD axe of PP after ECAE according to the Route A.



2 passes route C



4 passes route C



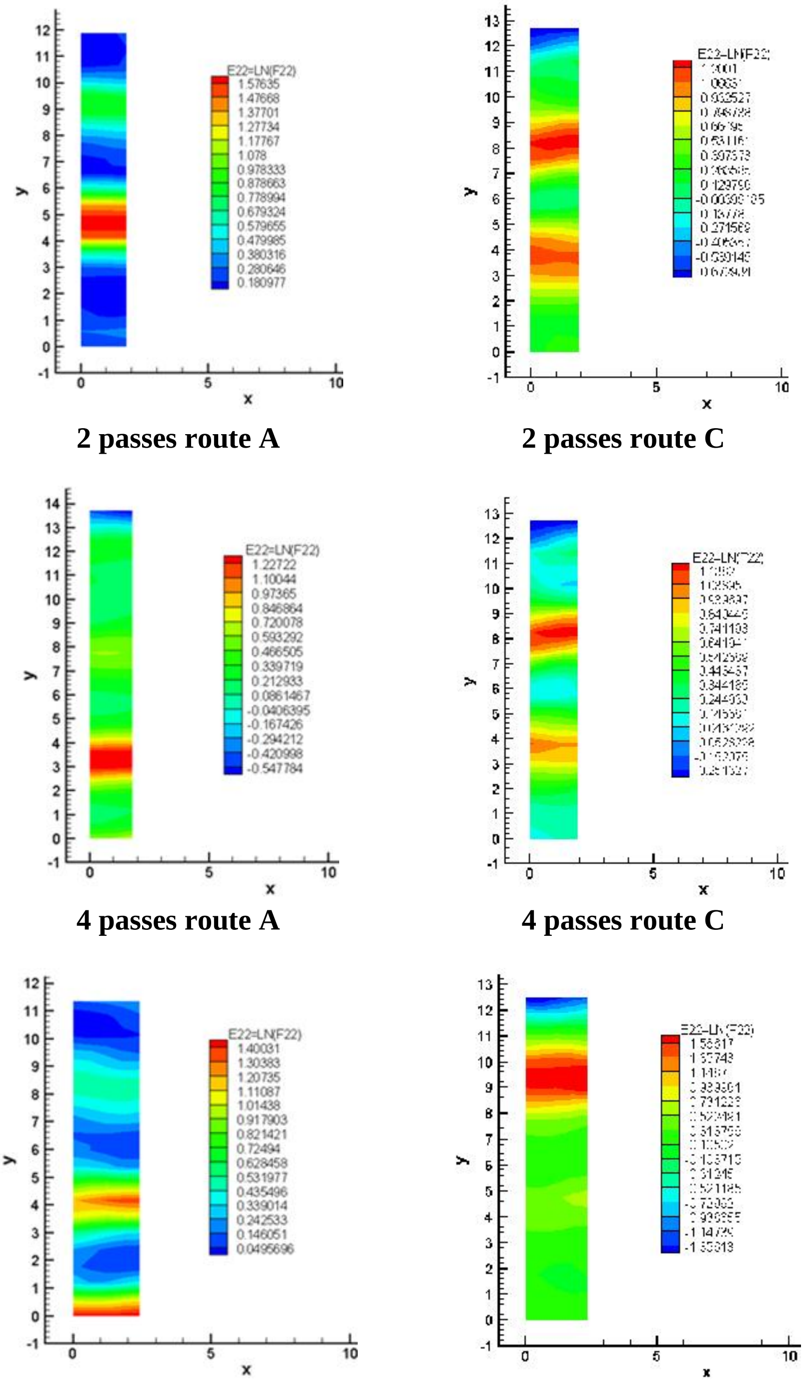
8 passes route C

Figure 11. 2D-WAXS patterns viewing along TD axe of PP after ECAE according to the Route C

We note that the extruded material according to the route A provides improvements to these mechanical properties such as Yong modulus and elastic limit. This is explained by the accumulation of plastic shear deformations after each pass. Contrary to the road A, the extruded material according to route C has a degradation of mechanical properties as and as the number of passes increases. This can be explained by the fact that the extrusion according to the route A, the deformation is not accumulating. HS Kim [3] and Aour B. et al [8] confirm the peculiarity of the C compared to the road A. The extruded material according to the Route C is more isotropic in the direction of extrusion.

5.4 DIC Procedure

DIC measurements require an artificial random speckle pattern which was generated by green dots sprayed on the surface of each sample. The random speckle pattern was applied so that speckles do not overlap. The illuminated random speckle pattern was captured during the deformation by a digital CCD camera placed in front of the sample [11,12].



2 passes route A **2 passes route C**

4 passes route A **4 passes route C**

8 passes route A **8 passes route C**

Figure 12. Contour plots of axial strain at 100% of cross-head displacement of a PP tensile sample after ECAE multi-passes without back-pressure**.**

The displacement vector was calculated using the corresponding sub-image pairs extracted from the reference and deformed states of the sample. By achieving the analysis on numerous subimages, the full-field contours of displacement were obtained.
The analysis was performed with Davis© software developed by Lavision©.
Figure 12. presents full-field contours of axial strain for different number of ECAE-passes according to the Route A and C at the cross-head displacement uy=12.5 mm (100% of displacement). The strain field is shown in colour level scale.
We note that for the PP sample extruded at two passes according to the route A presents a strain localization. It corresponds to the necking observed in the area of instability due to the stick-slip phenomena [9]. The second extrusion pass according to the route C homogenized the deformation over the entire length of the sample. For the fourth and eighth passes, the same phenomenon is observed.
We can conclude that the extrusion multi-passes according to the route C gives a more homogenous structure because the strains are better distributed over the surface of the sample. Unlike the route C, the extrusion according to the route A only accentuates the stick-slip phenomena. The increase of the number of passes only concentrates the deformation.

6 Conclusion

The X-ray analysis using the software Fit2d shown us several observations that can lead us to advance the following conclusions:

- Our material has been treated by the ECAE has a certain homogeneity and isotropy according to the viewing direction. In the case where the extrusion strain rate at $10^{-2}s^{-1}$ and without Back pressure the extruded material after the stick-slip phenomenon two bands alternating different appearance, clear and dark, where each structure which differs from one band to another has a certain homogeneity.

- To achieve better results extrusion, it is preferable to precede by route C with a reasonable number of passes, or by the route A but by applying a suitable back-pressure. The comparison of the behavior of these materials with that of as-received PP allows us to observe some reduction and degradation of the mechanical properties of these materials compared to as-received PP and mainly the significant decrease of the elastic limit.

That is to say, the extrusion operation has unfortunately contributed to further deterioration especially spherulitic structure of PP, despite the tendency to increase the orientation of the macromolecular chains to the extrusion direction [9,10,13]
Of all the foregoing, and to benefit from the operation of the extrusion that provides oriented materials; care must be taken to keep these materials their spherolitic structure even if they have a preferred orientation of the macromolecular chains. This objective will be achieved by the introduction of other parameters and factors affecting both the behavior of these polymeric materials, and also on the operation of extrusion. The factor that immediately comes to mind is the temperature.

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