

Influence of ECAPressing temperature on crystallinity and mechanical behaviour of polypropylene and high-density polyethylene

Influência da temperatura de ECAPressing na cristalinidade e comportamento mecânico do polipropileno e do polietileno de alta densidade

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ABSTRACT

In this paper, the influence of single equal channel angular pressing, ECAPressing, pass and processing temperature on crystallinity evolution and mechanical behaviour of the polymers polypropylene, PP, and high-density polyethylene, HDPE was investigated. ECAPressing tests were performed at the temperatures of 25, 50, 75 and 100°C for HDPE and 25, 90 and 120°C for PP. The materials mechanical behaviour before and after

ECAPressing tests was evaluated from room temperature compression tests while their crystallinity changings were analyzed through differential scanning calorimetry, DSC, experiments. In terms of strengthening and by comparison with as-received materials, it was observed an interesting efficiency of ECAPressing performed at 100°C for HDPE and 120°C for PP. In relation to crystallinity evolution, the results obtained from DSC tests showed its considerable increasing for higher pressing temperatures also by comparing either to as-received conditions or after single pass of equal channel angular pressing at room temperature.

Keywords: equal channel angular pressing, polypropylene, high-density polyethylene.

RESUMO

Neste trabalho, foi investigada a influência da prensagem angular de canal único igual, ECAPressing, pass e temperatura de processamento na evolução da cristalinidade e comportamento mecânico dos polímeros polipropileno, PP e polietileno de alta densidade, HDPE. Os testes de ECAPressing foram realizados às temperaturas de 25, 50, 75 e 100°C para HPDE e 25, 90 e 120°C para PP. O comportamento mecânico dos materiais antes e depois dos testes de ECAPressing foi avaliado a partir de testes de compressão de temperatura ambiente enquanto suas alterações de cristalinidade foram analisadas através de calorimetria diferencial de varredura, DSC, experimentos. Em termos de reforço e em comparação com os materiais recebidos, foi observada uma eficiência interessante do ECAPressing realizado a 100°C para o PEAD e 120°C para o PP. Em relação à evolução da cristalinidade, os resultados obtidos nos testes de DSC mostraram seu considerável aumento para temperaturas de prensagem mais altas também por comparação com as condições no estado de recepção ou após uma única passagem de prensagem angular de canal igual à temperatura ambiente.

Palavras-chave: prensagem angular de canal igual, polipropileno, polietileno de alta densidade.

1 INTRODUCTION

Equal channel angular pressing technique, ECAPressing, is a very interesting severe plastic deformation, SPD, process in order to provide bulk ultra-fine grained materials with improved mechanical properties [1,2]. Following ECAPressing technique, a well lubricated billet with a constant squared or round cross-sections is forced to pass through a die designed with identical channels by the action of a plunger. Also, this SPD method can be repetitively performed by processing routes that attribute higher accumulative plastic strain levels to the deformed materials [3-5].

Actually, effect of die geometry, tribology and processing conditions are widely investigated during ECAPressing on crystalline materials (especially metals) through either physical simulations or mathematical modelling [5-10]. However, the mechanical behaviour of other materials, like polymers for example, when deformed by the equal

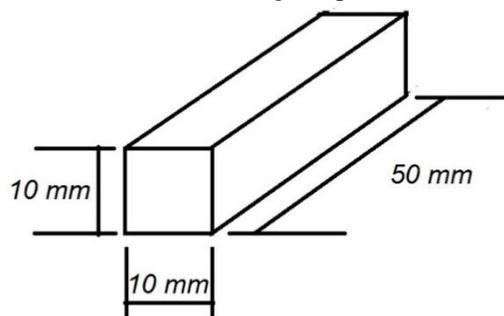
channel angular pressing technique started to play a significant role in the last two decades [11-15]. In this way, semicrystalline polymers as polypropylene, PP, and high-density polyethylene, HDPE, represent an interesting choice to analyze the relationship between ECAPressing and improve of mechanical properties once they are characterized by a considerable crystallinity. For these two materials deformed by ECAPressing, the literature reports works that evolves the analysis of tooling and processing conditions and even multiple pressing passes on their work hardening [16-20]. After this review, we see that ECAPressing has an important role on the crystallinity evolution of these materials and it is directly correlate to their strengthening capability. Thus, the present work aims to investigate crystallinity and mechanical behaviour changings of both PP and HDPE polymers after single pass of ECAPressing at distinct temperatures, in comparison to as-received materials, from differential scanning calorimetry and compression tests.

2 MATERIALS AND METHODS

2.1 MATERIAL

In this work, rectangular plates of polypropylene, PP, and high-density polyethylene, HDPE, polymers were purchased from Grupo Macedo Plásticos Comércio de Acrílicos e Plásticos de Engenharia LTDA - EPP with 291 mm (height), 210 mm (width) and 10 mm (thickness) to obtain samples for equal channel angular pressing tests. From these as-received materials, workpieces with squared cross-sections were machined into dimensions of 10 mm x 10 mm x 50 mm, see Fig.1. Also, all samples were cut along the height (or length) of the original plates to prevent any possible effect of planar anisotropy [13].

Figure 1: Dimensions of ECAPressing samples used in the present work.



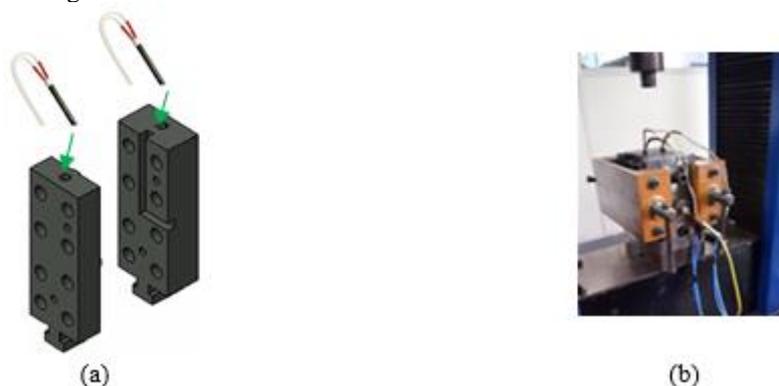
2.2 METHODS

Equal channel angular pressing, ECAPressing, experiments were performed by

using the H13 tool steel sharp die with two square cross-section channels detailed in Fig. 2a. As one can observe, there is no fillet radii at channels intersection and it denotes one of the most severe geometrical condition to deform materials by ECAPressing technique. Also, two cylindrical holes were machined close to die inlet channel in order to insert cartridge-type electrical resistances to perform tests at elevated temperatures. In addition, a H13 tool steel plunger with square cross section of 10 mm x 10mm and 110 mm in long was used to deform the workpieces inside the die channels.

ECAPressing experiments were performed, either at cold or warm, in an EMIC universal test machine with a load cell of 600 kN, at a constant ram speed of 1 mm/min that corresponds to nominal strain rate of $3.33 \cdot 10^{-4} \text{ s}^{-1}$. Samples and die channels were lubricated with silicone grease before each pressing. Test temperatures of 25, 50, 75 and 100°C were considered to high-density polyethylene while for polypropylene were assumed the values of 25, 90 and 120°C. Thus, for both polymers, temperature range permitted to evaluate their crystallinity evolution from room to maximum values that correspond up to 90% of their melting points. Heating control was realized through thermal controller Omega CN740, operating at on-off mode, in which two Ibrel cartridge-type electrical resistances with diameter of 12 mm, 150 mm of length and power of 650W that leads to upper temperature $\sim 900^\circ\text{C}$ were installed. By mean of this thermal apparatus, ECAPressing tests, except in the case of room temperature, were performed at a rate of 2°C/min once polymers crystallinity is highly sensible to heating velocity. Details of tooling assemblage are presented in Fig 2b.

Figure 2: Mechanical apparatus for ECAPressing tests: (a) dies with detail to electrical resistances and (b) close view of tooling.



Crystallinity increasing, here termed as crystallinity degree, for both HDPE and PP polymers, in the as-received condition and after single pass of ECAPressing, was

estimated from Differential Scanning Calorimetry tests based on standards ASTM D3417 [21] and ASTM D3418 [22] to calculate melting and crystallization enthalpies. Also, glass transition, TG, melting, TM, temperatures and DSC curves were obtained. For that, a Netzsch DSC 204 F1 Phoenix calorimeter, with temperature range between -180°C and 700°C was used together with liquid nitrogen to assure higher precision for the results. Samples of HDPE and PP with 5.81 mg and 5.45 mg, respectively, were undergone to two heating stages. The first one, was performed from 20°C to 280°C with heating rate equal to $20^{\circ}\text{C}/\text{min}$ in order to eliminate the previous materials thermomechanical behavior, especially after ECAPressing. During this experiment, fusion enthalpies, ΔH_{F} , were calculated in J/g to polypropylene and high-density polyethylene before and after pressing. Second heating level was realized in order to determine melting and crystallization enthalpies without any influence of either thermal or deformation effects imposed on the materials.

Crystallinity degree, X, for both HDPE and PP polymers was calculated by comparing the respective melting enthalpies, obtained from DSC tests, those by hypothetically assumed fully crystalline materials, that is,

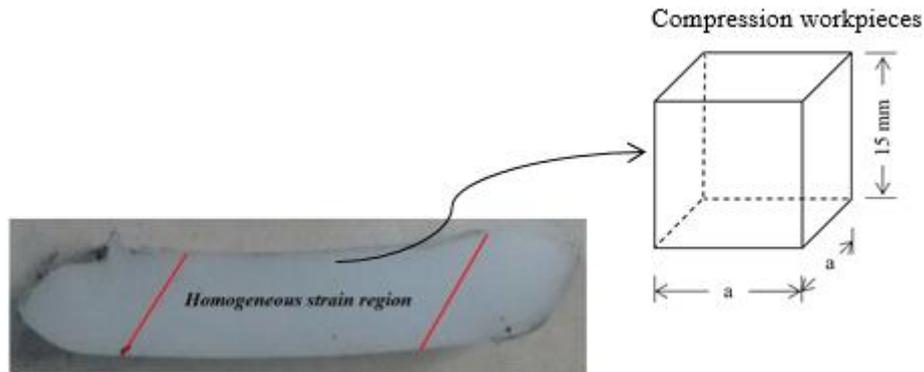
$$X = \frac{\Delta H_{\text{F}}}{\Delta H_{\text{F}}^0} 100\% \quad (1)$$

where ΔH_{F}^0 denotes melting enthalpy for fully crystalline polymers, in J/g. It was assumed the values of 293 J/g and 195 J/g to HDPE and PP, respectively. [23]

Compression tests, following ASTM D695 standard, were performed in order to evaluate the effect of single ECAPressing pass on the mechanical behavior of both HDPE and PP polymers in comparison to starting conditions. For that, compression bar-type samples with square cross sections of 100 mm^2 and 15 mm in-long were used. For the as-received condition, these samples were machined from material original plates following an analogous procedure that those previously discussed in Section 2.1 Material. On the other hand, after ECAPressing, compression samples were machined from materials deformed surface that experienced simple shear, which is called homogeneous plastic strain region, as presented in Fig. 3. All compression tests were performed at room temperature by using an EMIC universal test machine with a load cell of 20 kN, at a constant ram speed of 1 mm/min, that is, at a nominal strain rate of $1.11 \cdot 10^{-3} \text{ s}^{-1}$. Thus, true stress-strain curves were obtained and compared before and after ECAPressing for

HDPE and PP polymers. Also, the effect of processing temperature on the materials mechanical behaviour yield stress could be investigated in terms of their yield stresses.

Figure 3: Scheme to machining of compression test samples.



3 RESULTS AND DISCUSSION

Figure 4 shows true stress-strain curves obtained during compression tests on HDPE and PP polymers in the as-received condition. In general words, these polymers revealed considerable deformation capability. However, due to its higher molar mass and mechanical strength, polypropylene provided a superior yield stress (close to 22 MPa) value in comparison to high-density polyethylene that was ~ 14 MPa.

Figure 4: Compression true stress and strain curves to PP and HDPE in the as-received condition.

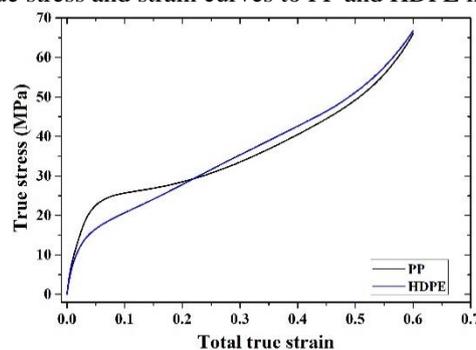


Figure 5 presents DSC curves for HDPE and PP polymers and their respective melting temperatures, T_M , and fusion enthalpies, DH_F . Specifically in terms of DH_F , higher prediction was observed to high-density polyethylene (180.9 J/g) while a value of 71.3 J/g was obtained to polypropylene. Increasing in DH_F means higher crystallinity and, according to Eq. (1), it was calculated the values of 61.7% to high-density polyethylene and 36.6% to polypropylene. These results confirmed the direct influence of DH_F on the crystallinity.

Figure 5: DSC curves in the as-received condition to: (a) HDPE and (b) PP.

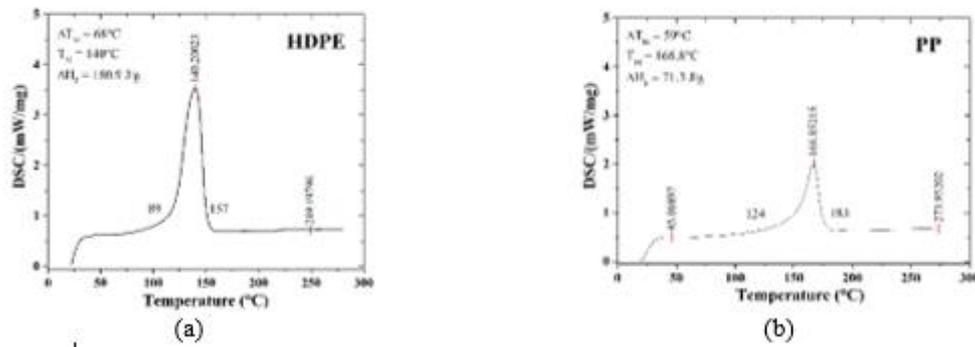


Figure 6 shows force vs displacements curves obtained during ECAPressing tests on HDPE and PP polymers at the temperatures considered in the present work. In fact and as expected, increasing in the temperature continuously led to decreasing of the processing force need to deform the materials. It is due to the continuous softening of thermoplastic polymers at elevated temperatures, as in the case of both HDPE and PP ones. Also, at room temperature, maximum force to deform polypropylene was higher than high-density polyethylene. However, in the case of polymers, the strain-hardening peaks observed at the first 10 mm of displacement (for both HDPE and PP deformed samples), specially to temperatures higher than 25°C, are strongly associated to increasing of crystallinity. The relationship between pressing temperature and crystallinity will be discussed later in Fig. 10. In addition, although at room temperature pressing force achieved maximum values for both investigated polymers, it was unfavourable to crystallinity evolution once the materials fusion enthalpies obtained from DSC tests, at this condition, provided the lower results in comparison those provided to most elevated temperatures (see discussions about Figs. 8-9).

Figure 6: Force-displacement curves obtained during ECAPressing at distinct temperatures to: (a) HDPE and (b) PP.

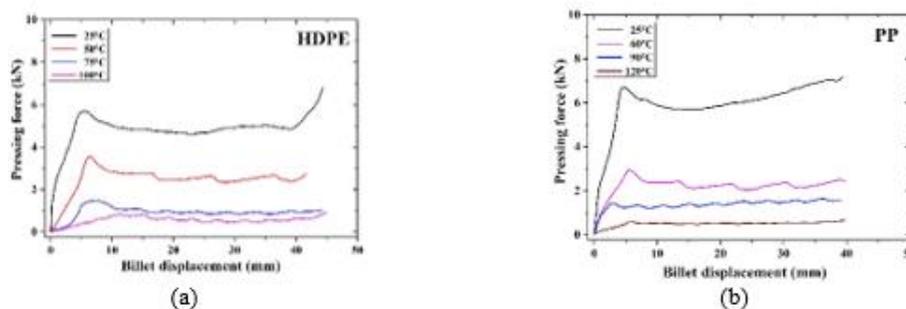
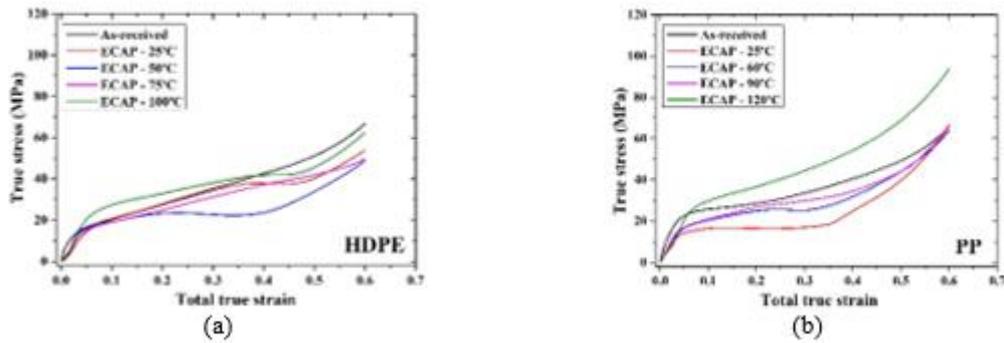


Figure 7 presents true stress vs total strain curves from cold compression tests on HDPE and PP polymers before and after single pass of ECAPressing at the interesting

temperatures considered in this work. It was evident the great influence of the pressing temperature on the mechanical strength of both polymers, that is, higher temperatures provided an increasing of the stress levels, for a given strain value. Also, as expected, most elevated stress predictions were observed to polypropylene in comparison to HDPE and it is coherent with the aspects previously discussed in relation to Fig. 4. Also, for both polymers ECAPressing at the maximum temperatures prevailed on as-received materials.

Figure 7: Compression true stress and strain curves at distinct temperatures to: (a) HDPE and (b) PP.



Figures 8 and 9 show DSC curves obtained, respectively, to HDPE and PP polymers at the considered temperatures. In fact, and as expected, at 25°C both polymers provided lowest values for fusion enthalpy and melting points once this condition only evolved the heat generation during ECAPressing as energy source. Increasing of processing temperature was responsible to higher predictions of fusion enthalpy and melting points.

Figure 8: DSC curves after ECAPressing to HDPE: (a) 25°C; (b) 50°C; (c) 75°C and (d) 100°C.

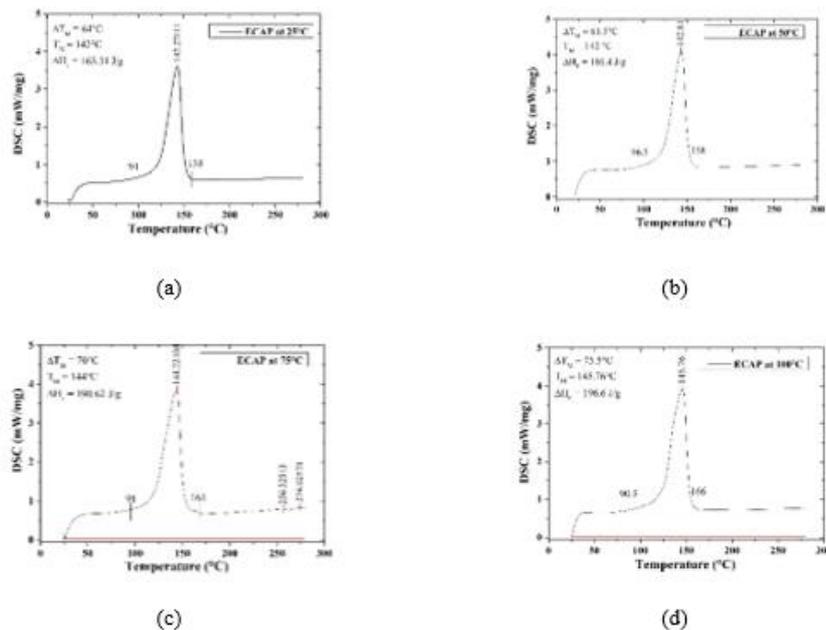
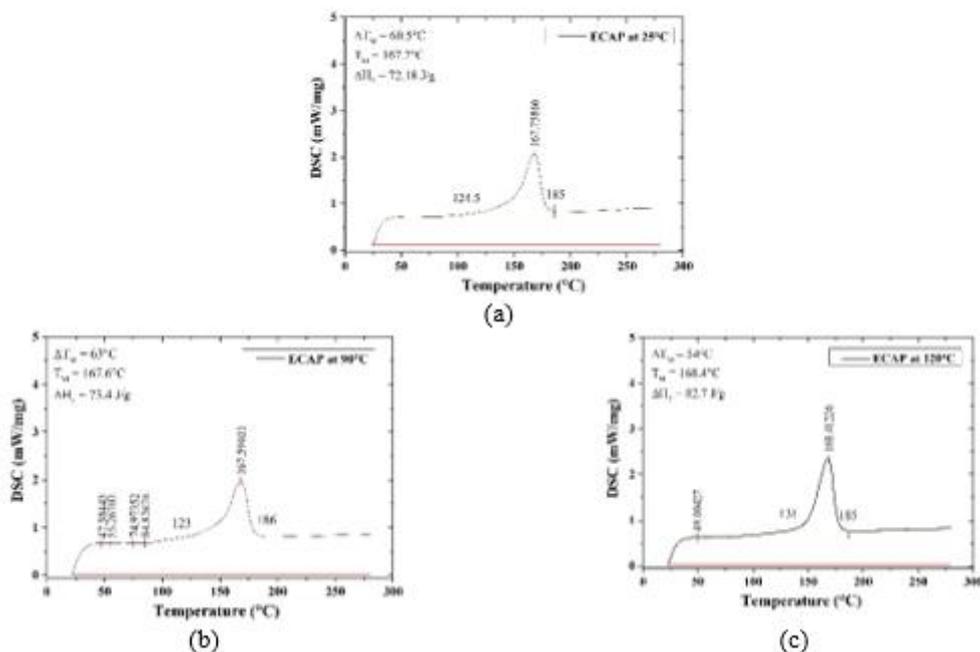
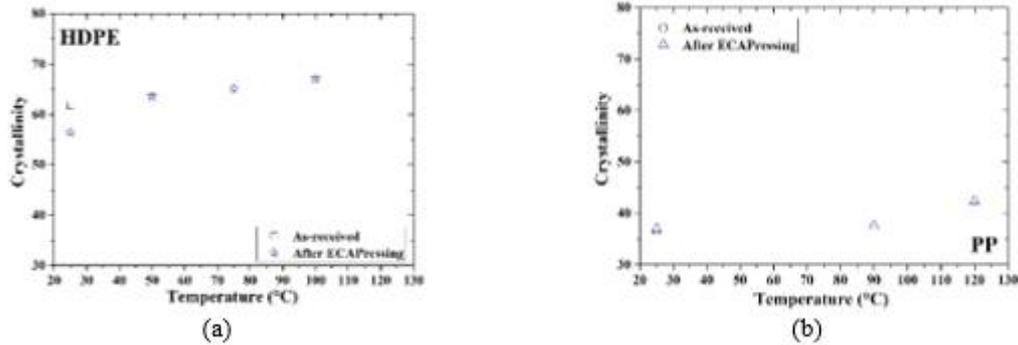


Figure 9: DSC curves after ECAPressing to PP: (a) 25°C; (b) 90°C and (c) 120°



In terms of the HDPE and PP crystallinity evolution presented in Fig. 10, when ECAPressing driving force was elevated, that is, deformation temperature, it was observed that the materials became more crystalline when deformed at temperatures close to their melting points. In this way, HDPE exhibited a crystallinity value $\sim 55\%$ during its processing at 25°C and close to 65% after ECAPressing at 100°C, that is, a crystallinity increasing of 18% associated to high deformation temperatures. In relation to polypropylene, ECAPressing at room temperature provided a crystallinity lever near to 37% while at 120°C this value was $\sim 42\%$ that means an increasing of 14%. Also, it is interesting to evaluate ECAPressing effectiveness at 25°C, in terms of crystallinity, by comparing the obtained results to as-received materials. In the case of HDPE, its crystallinity dropped from $\sim 62\%$ (as-received condition) to 56% after single pass of ECAPressing, i.e., a decreasing of almost 10%. For polypropylene, it was observed that ECAPressing was slightly benefit to crystallinity, that is, DSC tests revealed an increasing from 36.6% (as-received condition) to 37.02% after ECAPressing or an elevation of 1.15%. Higher molar mass and molecular chains of propylene, when it was compared to high-density polyethylene, can explain the apparent stabilization of its crystallinity at room temperature, especially after processing by equal channel angular pressing technique.

Figure 10: Crystallinity versus ECAPressing temperature: (a) HDPE and (b) PP.



4 CONCLUSIONS

Influence of single pass of equal channel angular pressing on polypropylene, PP, and high-density polyethylene, HDPE, polymers was investigated, at distinct test temperatures, in terms of their mechanical behaviour and crystallinity evolution in comparison to as-received conditions. From the obtained results, the following conclusions can be outlined:

1) Although force vs sample displacement curves obtained during ECAPressing confirmed the expected characteristic behaviour of load decreasing for higher temperatures due to materials softening, subsequent compression tests performed on PP and HDPE deformed workpieces showed their strengthening associated to warm processing. Also, by comparing with as-received materials it was verified that ECAPressing was interesting for maximum considered temperatures, that is, at the values of 100°C for HDPE and 120°C for PP.

2) Crystallinity evolution obtained before and after ECAPressing by DSC tests showed a considerable increasing for both polymers when they were deformed at elevated temperatures in comparison to as-received conditions. It was clearly evidenced by fusion enthalpies also provided by DSC tests.

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REFERENCES

- [1] SEGAL, V.M., “Materials processing by simple shear”, *Materials Science and Engineering A*, v. 197, pp. 157-164, Jul. 1995.
- [2] SEGAL, V.M., “Severe plastic deformation: simple shear versus pure shear”, *Materials Science and Engineering A*, v. 338, pp. 331-344, Dec. 2002.
- [3] VINOGRADOV, A., ESTRIN, Y., “Analytical and numerical approaches to modelling severe plastic deformation”, *Progress in Materials Science*, v. 95, pp. 172-242, Jun. 2018.
- [4] SILVA, D.C., REZENDE, M.C., MEDEIROS, N., “Microstructural characterization and evaluation of the thermomechanical behavior of an Al 7075-T651 alloy deformed by two passes of ECAP”, *Materials Research*, v. 20, pp. 657-661, Nov. 2017.
- [5] VALIEV, R.Z., LANGDON, T.G., “Principles of equal-channel angular pressing as a processing tool for grain refinement”, *Progress in Materials Science*, v. 51, pp. 881-981, Sep. 2006.
- [6] IWAHASHI, Y., WANG, W., HORITA, Z., NEMOTO, M., LANGDON, T.G., “Principle of equal-channel angular pressing for the processing of ultra-fine grained materials”, *Scripta Materialia*, v. 35, pp. 143-146, Jul. 1996.
- [7] MEDEIROS, N., MOREIRA, L.P., “Upper-bound analysis of die corner gap formation for strain-hardening materials in ECAP process”, *Computational Materials Science*, v. 91, pp. 350-358, Aug. 2014.
- [8] EIVANI, A.R., KARIMI TAHERI, A., “An upper bound solution of ECAE process with outer curved corner”, *Journal of Materials Processing Technology*, v. 182, pp. 555-563, Feb. 2007.
- [9] ALKORTA, J., SEVILLANO, J.G., “A comparison of FEM and upper-bound type analysis of equal-channel angular pressing (ECAP)”, *Journal of Materials Processing Technology*, v. 141, pp. 313-318, Nov. 2003.
- [10] PÉREZ, C.J.L., LURI, R., “Study of the ECAE process by the upper bound method considering the correct die design”, *Mechanics of Materials*, v. 40, pp. 617-628, Aug. 2008.
- [11] ZAÏRI, F., AOUR, B., GLOAGUEN, J.M., NAÏT-ABDELAZIZ, M., LEFEBVRE, J.M., “Numerical modelling of elastic–viscoplastic equal channel angular extrusion process of a polymer”, *Computational Materials Science*, v. 38, pp. 202-216, Nov. 2006.
- [12] AOUR, B., ZAÏRI, F., NAÏT-ABDELAZIZ, M., GLOAGUEN, J.M., RAHMANID, O., LEFEBVRE, J.M., “A computational study of die geometry and processing conditions effects on equal channel angular extrusion of a polymer”, *International Journal of Mechanical Sciences*, v. 50, pp. 589-602, Mar. 2008.
- [13] BOUAKSA, F., OVALLE RODAS, C., ZAÏRI, F., STOCLET, G., NAÏT-ABDELAZIZ, M., GLOAGUEN, J.M., TAMINE, T., LEFEBVRE, J.M., “Molecular chain orientation in polycarbonate during equal channel angular extrusion: Experiments

- and simulations”, Computational Materials Science, v. 85, pp. 244-252, Apr. 2014.
- [14] BELOSHENKO, V.A., VOZNYAK, A.V., VOZNYAK, Y.V., “Control of the mechanical and thermal properties of semicrystalline polymers via a new processing route of the equal channel multiple angular extrusion”, Polymer Engineering and Science, v. 54, pp. 531-539, Feb. 2014.
- [15] QIU, J., MURATA, T., KITAGAWA, M., KUDO, M., “Plastic deformation mechanism of crystalline polymer materials in the equal channel angular extrusion process”, Journal of Materials Processing Technology, v. 212, pp. 1528-1536, Jul. 2012.
- [16] BOULAHIA, R., GLOAGUEN, J.M., ZAÏRI, F., NAÏT-ABDELAZIZ, M., SEGUELA, R., BOUKHAROUBA, T., LEFEBVRE, J.M., “Deformation behaviour and mechanical properties of polypropylene processed by equal channel angular extrusion: Effects of back-pressure and extrusion velocity”, Polymer, v. 50, pp. 5508-5517, Nov. 2009.
- [17] BARTCZAK, Z., ARGON, A.S., COHEN, R.E., “Texture evolution in large strain simple shear deformation of high density polyethylene”, Polymer, v. 35, pp. 3427-3441, Aug. 1994.
- [18] BELOSHENKO, V.A., VOZNYAK, A.V., VOZNYAK, Y.V., DUDARENKO, G.V., “Equal-channel multiple angular extrusion of polyethylene”, Journal of Applied Polymer Science, v. 127, pp. 1377-1386, May 2012.
- [19] REINITZ, S.D., ENGLER, A.J., CARLSON, E.M., VAN CITTERS, D.W., “Equal channel angular extrusion of ultra-high molecular weight polyethylene”, Materials Science and Engineering C, v. 67, pp. 623-628, Oct. 2016.
- [20] WILHELM, H., PARIS, A., SCHAFLE, E., BERNSTORFF, S., BONARSKI, J., UNGAR, T., ZEHETBAUER, M.J., “Evidence of dislocations in melt-crystallised and plastically deformed polypropylene”, Materials Science and Engineering A, v. 387-389, pp. 1018-1022, Dec. 2004.
- [21] ASTM D3417-99, Standard Test Method for Enthalpies of Fusion and Crystallization of Polymers by Differential Scanning Calorimetry (DSC), (Withdrawn 2004), ASTM International, West Conshohocken, PA, 1999.
- [22] ASTM D3418-15, Standard Test Method for Transition Temperatures and Enthalpies of Fusion and Crystallization of Polymers by Differential Scanning Calorimetry, ASTM International, West Conshohocken, PA, 2015.
- [23] WYPYCH, G., *Handbook of Polymers*, 2 ed., ChemTec, Canada, 2016.