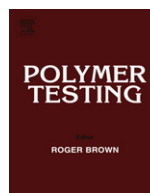


Contents lists available at [SciVerse ScienceDirect](http://SciVerse.ScienceDirect.com)

Polymer Testing

journal homepage: www.elsevier.com/locate/polytest

Material properties

Plasticiser effect of oleic acid polyester on polyethylene and polypropylene

Marcela Mantese Sander, Aline Nicolau, Rafael Guzzatto, Dimitrios Samios*

Laboratory of Instrumentation and Molecular Dynamics, Institute of Chemistry, Federal University of Rio Grande do Sul, Bento Gonçalves Avenue 9500, Postal Box 15003, Postal Code 91501-970 Porto Alegre, RS, Brazil

ARTICLE INFO

Article history:

Received 27 June 2012

Accepted 14 August 2012

Keywords:

Polyolefin plasticiser

Oleic acid polyester

Crystallinity

Plane strain compression

Thermal stability

ABSTRACT

The potential application of a polymeric fatty acid derivative as a plasticiser for polyethylene and polypropylene was evaluated through the study of torque during melt processing, apparent crystallinity, crystalline plane orientation, plane strain compression and thermogravimetric analysis of polymer blends. The polymeric derivative is a polyester produced from epoxidised oleic acid, cis-1,2-cyclohexanedicarboxylic anhydride and triethylamine as initiator. The results suggested that the oleic acid polymer had a plasticising effect in blends with polyethylene (PE) and polypropylene (PP). Reduction of processing torque, no loss of crystallinity, maintenance of mechanical properties and an improvement in thermal stability were observed for PP. For PE, a slight reduction of processing torque, crystallinity and mechanical resistance were observed.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

The replacement of phthalates as plasticiser additives in the manufacture of plastics is of great importance for applications such as food packaging, products for children, insect repellents, automotive products, blood storage bags and medical devices because these compounds present potential risks to human health and the environment [1,2]. Some authors have investigated the suitability of alternative plasticisers to replace phthalates [3–7]. Different epoxidised vegetable oils were tested as plasticisers for polyvinyl chloride (PVC) [6–11]. Sun et al. [9] compared epoxidised safflower oil with DEHP (Bis(2-ethylhexyl) phthalate) as plasticisers for PVC films, studying their resilience, elastic modulus, toughness and glass transition temperature. Bueno-Ferrer et al. [10] evaluated the performance of epoxidised soybean oil (ESBO) as a plasticiser and stabiliser for PVC by means of structural and thermal studies. Fenollar and co-authors [11] applied epoxidised linseed oil (ELO) as a PVC plasticiser. According

to their results, ELO improves migration transfer in PVC relative to the problems observed in PVC plasticised with traditional phthalates.

In the literature, there are few studies about the use derivatives of renewable resources as co-processing materials for polyolefins. Sastry and co-workers [12] studied the application of sunflower oil as a compatibiliser in polyethylene-starch blends; they concluded that it acted as a plasticiser (improved the film quality) and as a pro-oxidant (accelerated the film degradation). Other studies regarding the processability and final properties of polyethylene (PE)/vegetable oil derivative blends described their interaction, structure formation and thermal properties [13,14]. Reports about blends of polypropylene (PP) with vegetable oil derivatives showed that there were interactions between both phases [15], and enhancement of the PP mechanical properties such as tensile strength, elongation at break, impact strength and tear strength [16]. However, no evaluations of polymerised epoxy fatty acid esters as co-processing materials for PE and PP have been published.

A series of recent publications reported the synthesis and possible applications of materials derived from

* Corresponding author. Tel.: +55 5133086290; fax: +55 5133087304.
E-mail address: dsamios@iq.ufrgs.br (D. Samios).

epoxidised oils and biodiesel. Martini et al. [17] investigated polymers obtained from epoxidised linseed oil biodiesel with different cyclic anhydrides. Reiznautt et al. [18] studied polyesters derived from sunflower oil biodiesel. Nicolau and co-authors reported the properties of linear polyesters produced from oleic acid and methyl oleate in bulk [19] and in solution [20]. Roza and co-workers prepared different types of polyesters from epoxidised soybean oil biodiesel, including biodiesel, as a green solvent. The polymerisation process [21] and the physico-chemical properties of the products were evaluated [22]. These materials possess important physicochemical properties. The olefinic chains of the fatty acids in these polymers suggest that it may be possible to apply them in blends with PE and PP. It is necessary to evaluate their plasticiser effects in this and other important applications. The properties of polyesters produced from epoxidised biodiesel depend on the type of vegetable oil used as a starting material. Vegetable oils are fatty acid triglycerides that have different degrees of unsaturation. Fatty acids differ in the length of their carbonic chains and the number and orientation of their double bonds. For example, linseed and sunflower oils contain predominately polyunsaturated fatty acids; they form crosslinked materials when polymerised under optimum cure conditions. However, the polymerisation of oleic acid, a monounsaturated fatty acid, yields linear polyesters.

The aim of this work is to investigate the plasticiser action of oleic acid polyesters (OAP) in blends with PE and PP. The polyester was obtained from the polymerisation of oleic acid, the main fatty acid component of olive and canola oils, with *cis*-1,2-cyclohexanedicarboxylic anhydride and triethylamine as initiator.

2. Experimental

2.1. Materials

Oleic acid P.A., toluene (99.5%) and hydrogen peroxide (30% w/w) in water were purchased from Synth (São Paulo, Brazil). Triethylamine (99%), *cis*-1,2-cyclohexanedicarboxylic anhydride (99%), formic acid (85%) and sulphuric acid (98%) were purchased from Aldrich Chemical Co. The blends were prepared with polyethylene HC 7260 and polypropylene H 301, both from Braskem S.A (São Paulo, Brazil).

2.2. Epoxidation and polymerisation of oleic acid

The epoxidation of oleic acid was performed with formic acid generated *in situ*. The molar ratio of hydrogen peroxide/formic acid/unsaturation (double bonds) was 20/2/1. The oleic acid, toluene and concentrated formic acid were placed together in a well-stirred, round-bottom glass reactor kept at room temperature. Then, 30% (w/w) hydrogen peroxide was added dropwise. The reactor temperature was raised slowly to 80 °C to complete the reaction. This entire procedure took approximately 2 h. Afterwards, the organic layer (containing the epoxide) was separated and washed with water to remove residual H₂O₂. Anhydrous sodium sulphate was used to dry traces of water and the epoxide was concentrated in a rotary evaporator.

The ¹H and ¹³C NMR characterisation, which proves the epoxidation of oleic acid, was presented elsewhere [19,20].

The OAP was prepared by reacting epoxidised oleic acid (EOA) with *cis*-1,2-cyclohexanedicarboxylic anhydride (CH) and triethylamine (TEA) as the initiator. The molar composition of the reaction mixture was 0.5/0.5/0.0085 (EOA/CH/TEA). The mixture was placed in a glass beaker and heated in an oven at 165 °C for 3 h. The products were stored in desiccators at room temperature [19,20].

2.3. Blend mixtures and torque evaluation

The blends were prepared in a Haake Reomix 600p with two co-rotors. The composition of the PE and PP blends is given in Table 1. The polyester was added in the mixing chamber as an ethyl acetate solution (30% w/v, polyester/ethyl acetate). The processing time was 10 min at 40 rpm, the applied torque being monitored during this period. The mixture temperature was 160 °C for PE blends and 190 °C for PP blends. This procedure guaranteed the evaporation of ethyl acetate at the beginning of the process.

The blends were moulded as sheets with a Carver Monarch model 3710 press, cut into small pieces and injected with a Thermo Scientific Haake Minijet II to produce the test specimens. The injection temperature was 160 °C for PE blends and 210 °C for PP. The conditions were as follows: injection at 280 bar for 4 s, followed by application of pressure of 500 bar for 8 s and subsequent cooling. The test specimens were 57 mm long, 12 mm wide and 3.2 mm thick. The PE and PP blend specimens were annealed at 120 °C and 150 °C, respectively, for 30 min and cooled to room temperature.

2.4. Differential scanning calorimetry experiments

Differential scanning calorimetry (DSC) was used to determine the melting temperature (*T_m*), heat of fusion (*H_f*) and crystallinity (*X_c*) of neat PP and PE and their blends with OAP. Approximately 5 mg of sample was weighed in an aluminium capsule and analysed in a DSC 2920 apparatus from TA Instruments. The temperature range was from 30 to 180 °C for PE blends and from 30 to 200 °C for PP blends. For both types of blends, the samples were heated at a rate of 10 °C/min until the maximum temperature was reached, kept at an isothermal condition for 2 min and then cooled to 30 °C at a rate of −40 °C/min. Then, samples were heated again at a rate of 10 °C/min to their respective maximum temperature. This procedure erased the thermal history of the blends. The data from both heating cycles and the respective results are shown in Section 3.2, Table 2.

Table 1
Blend compositions in percentage (% w/w).

Polymer	PE0	PE1	PE3	PE5	PP0	PP1	PP3	PP5
PE	100	99	97	95	–	–	–	–
PP	–	–	–	–	100	99	97	95
OAP	0	1	3	5	0	1	3	5

Table 2

Thermal analysis and crystallinity results.

Sample	ΔH_f (J/g)	T_{m1} (°C)	X_1 (%)	ΔH_{f2} (J/g)	T_{m2} (°C)	X_2 (%)	ΔH_c (J/g)	X_{XRD} (%)
PE0	157.7	132.5	56.9	152.6	131.1	55.1	166.1	59.0
PE1	146.3	132.0	52.8	146.3	131.8	52.8	159.3	57.1
PE3	142.4	133.9	51.4	140.7	132.3	50.8	160.4	55.2
PE5	140.5	130.7	50.7	141.3	130.7	51.0	156.5	54.0
PP0	61.7	166.6	29.5	61.7	164.4	29.5	89.3	43.9
PP1	60.1	164.6	28.7	59.2	162.3	28.3	88.5	42.9
PP3	63.2	163.6	30.2	64.1	162.2	30.6	101.4	42.2
PP5	60.9	165.5	29.1	59.8	164.5	28.6	95.1	42.9

The subscripts (1 and 2) refer to the first and second heating, as described on Section 2.4.

2.5. X-ray diffraction measurements

The crystallinity data were obtained via X-ray diffraction (XRD) with a Siemens Diffraktometer D5000. The XRD data were compared to the DSC data. In addition, the XRD patterns were used to determine the relative orientation of the crystalline planes [23–27]. The data were analysed with peak integration using Microcal Origin 6.0 software; the amorphous halo was separated from the crystalline peaks using the baseline correction method [26,27].

2.6. Plane strain compression tests

The mechanical properties were evaluated using a channel plane strain compression device in an EMIC dynamometer, model DL10000, equipped with a 100 kN compression-tension cell, as previously described [28,29]. The tests were performed at 25 and 75 °C; the strain rate was 2.7 mm/min. The injected specimens were adjusted to the dimensions of 30.0 mm long, 6.35 mm wide and 3.2 mm thick, which were the dimensions required for the plane strain compression tests. The strain percentage of the stress-strain curves was normalised with respect to the initial sample thickness.

2.7. Thermogravimetric analysis

The thermal stability of the blends was evaluated using thermogravimetric analysis in an SDT Q600 instrument from TA Instruments. Approximately 5 mg of neat PE, PP and their respective blends were heated from 50 to 800 °C at a rate of 20 °C/min.

3. Results and discussion

3.1. Melt blends torque evaluation

To verify the melting behaviour, processing data were collected during mixing in the Haake chamber. The three variables in this process are chamber temperature, rotating speed and rotor torque. The first two variables were fixed, and torque data were collected and related directly to the melt viscosity, i.e., the material resistance to flow. During processing, the melt temperature remained approximately constant. Fig. 1 presents the torque values relative to the proportion of polyester in the blend for the processing time of 10 min. Torque reduction was observed when the level of polyester increased.

The torque of neat PE (PE0) decreased from 4.5 N·m to 3.2 N·m for a blend with a 5% of polyester (PE5), which corresponds to 29% reduction. In the case of PP, the addition of the same amount of polyester decreased the torque from 3.8 N·m to 2.4 N·m, corresponding to a 37% reduction. This torque reduction is the first criterion that indicates that the polyester acts as a plasticiser, reducing the viscosity of the melt and improving the processing.

3.2. Crystallinity evaluation

Table 1 presents the values of the melting temperature (T_m), heat of fusion (ΔH_f) and crystallinity (X_c) for PE, PP and their blends with OAP obtained by DSC. The crystallinity was evaluated from the relation, $X_{DSC} = (100 \Delta H_f) / (\Delta H_0)$, where ΔH_0 is the heat of fusion for a perfect crystal of PE or PP taken from the literature. In this work, the values used were $\Delta H_{0(PE)} = 277$ J/g [30] and $\Delta H_{0(PP)} = 209$ J/g [31]. According to these results, the melting temperatures of the blends did not change significantly with polyester addition and were very similar to those of the neat polyolefins. The blend crystallinity, evaluated through the heat of fusion, showed a slight decrease from PE0 to PE5 and no significant modification for PP blends.

The blends were also analysed by XRD. Figs. 2 and 3 show diffractograms for PE and PP blends, respectively.

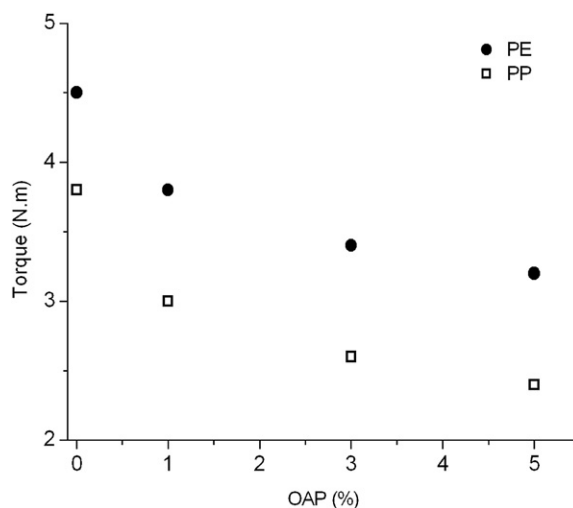


Fig. 1. Torque variation during blends mixing in relation to the polyester (OAP) content.

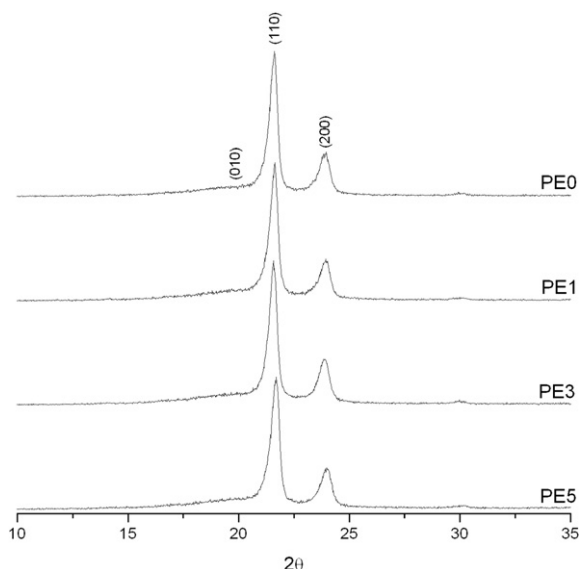


Fig. 2. X-ray diffractograms of the PE blends and the crystallographic planes.

Table 2 also shows the crystallinity values obtained after the XRD data treatment. The apparent crystallinity values were calculated from diffractograms (X_{XRD}) using the relation, $X_c = [I_c / (I_c + I_a)] \cdot 100$, where I_c is the integration of the diffraction peaks and I_a , the integration of the amorphous halo.

The PE blend diffractograms corroborate the DSC analysis and show a small decrease of crystallinity values. For PP blends, the values were practically constant and agreed with the conclusion from the DSC analysis. The difference between the analyses for the two types of blends is related to the absolute crystallinity values, as predicted by Lima et al. [26].

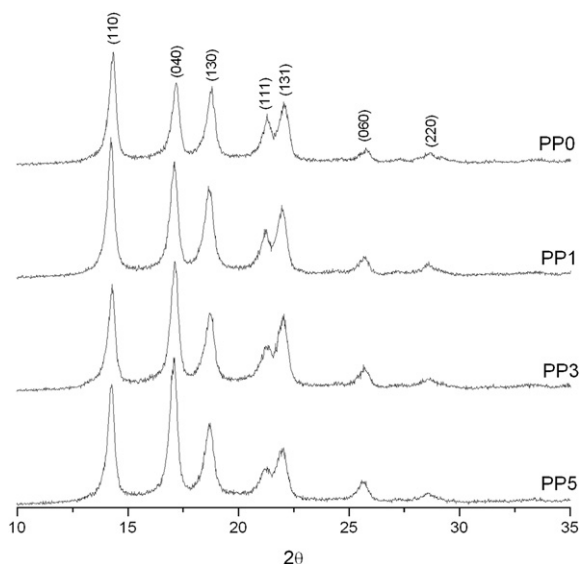


Fig. 3. X-ray diffractograms of the PP blends and the crystallographic planes.

The X-ray diffraction data were used to determine the orientation of the crystallographic planes before and after OAP addition. No significant changes were observed in the main orientation planes (110) and (200) for PE blends. For PP, there was a reorientation with a continuous increase of the (040) plane contribution from 19% (PP0) of the crystalline phase up to 33% (PP5). A systematic decrease of the (110) plane was observed from 27% for neat PP to 21% for the PP5 blend. Other orientation planes such as (130), (111) and (131) showed small variations with OAP addition that can be related to the amount of amorphous phase present in each polymer (PE: 40–50%, PP: 60–70%) and the type of polyolefin crystalline lamellae. The plasticisers and, in this case, the OAP, normally act on the amorphous phase. The polyolefin with a higher amount of the amorphous phase can better accommodate the plasticiser without crystallinity loss. For that reason, PE showed a crystallinity decrease, whereas PP had no significant crystallinity loss. This result was corroborated by the reorientation of the PP crystalline planes with OAP addition, while this was not the case for PE. The DSC and XRD results suggested that the polyester was compatible with the amorphous phase of both polyolefins.

3.3. Plane strain compression and mechanical resistance

Compression is a method employed to study the flow behaviour and workability of materials. The data generated by compression tests can be used to identify the optimum parameters for thermo-mechanical processing [32]. Figs. 4 and 5 represent the stress-strain curves for the neat PE and PP and their blends with 5% OAP. The compression behaviour of the other blends (1 and 3%) was intermediate with respect to the results for the neat and 5% OAP samples. These experiments were performed by plane strain compression of polymer bars at 25 and 75 °C. The stress-strain compression graphs show three characteristic regions. The first region is related to elastic deformation, i.e., a linear increase of the strain as a function of the stress.

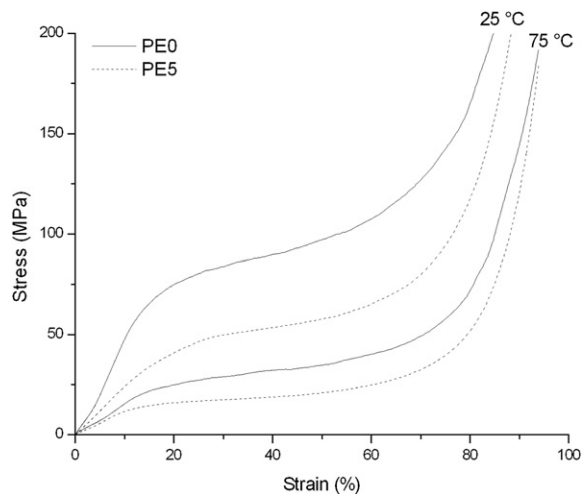


Fig. 4. Stress-strain curves of PE blends deformed at 25 and 75 °C.

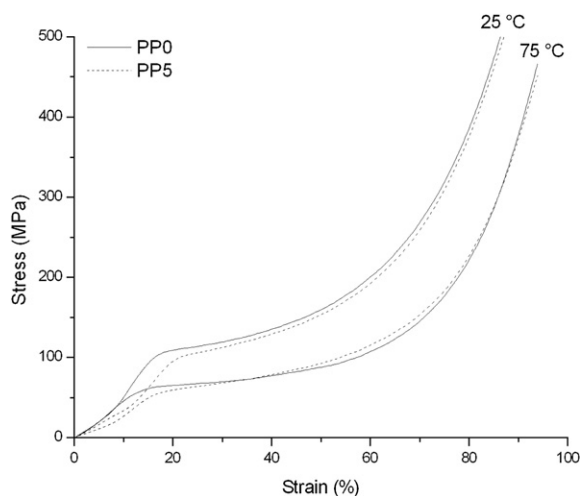


Fig. 5. Stress-strain curves of PP blends deformed at 25 and 75 °C.

The second region is plastic deformation, which corresponds to an increase of the strain with a small increase of the stress. The third region is characterised by a strong increase in the stress-strain curve, which is known as strain hardening [28,29,33,34].

According to the stress-strain graphs, the behaviour of the PE/OAP and PP/OAP blends differed when the blends were submitted to plane compression deformation. In the case of PE and its blends with OAP, the difference in the mechanical resistance was remarkable. For 40% strain at 25 °C, the stress value changed from 89.4 to 52.9 MPa; at 75 °C, the change was from 31.7 to 18.6 MPa. For stress at 50 MPa, the strain difference was pronounced, from 10% up to 80%. On the other hand, in the case of PP, the addition of up to 5% (w/w) OAP did not cause any significant changes in the mechanical resistance. These results indicated that OAP acted as plasticiser for both polyolefins. However, the PE blends underwent a slight crystallinity decrease (confirmed by DSC and XRD) and mechanical resistance loss (confirmed by plane strain compression), while the PP blends maintained their crystallinity and mechanical resistance properties (with reorientation confirmed by XRD).

3.4. Thermogravimetric analysis results

The thermal stability of the PE and PP blends with OAP was evaluated by means of thermogravimetric analysis. The thermograms for PE and PP are shown in Figs. 6 and 7, respectively.

As shown in previous work [19], the OAP underwent a two-step degradation process at 283 and 391 °C, which is typical of polymers obtained from vegetable oils [35]. When PE and PP blends were evaluated, the first evidence of degradation was observed at approximately 280 °C in the thermograms, which was compatible with the first step of plasticiser degradation. The thermograms of the PE and PP blends indicated that the polyolefin degradation process shifted towards the second degradation step of OAP. This effect was stronger and more pronounced in the PP blends compared to the PE blends.

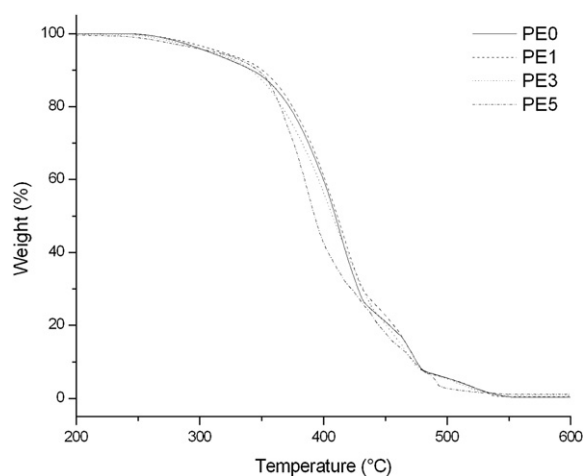


Fig. 6. TGA curves of PE blends.

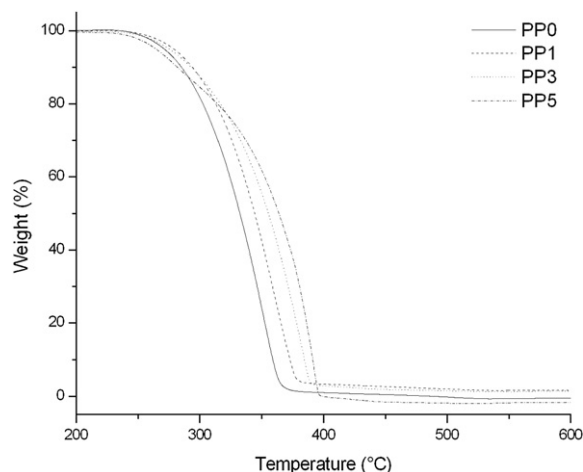


Fig. 7. TGA curves of PP blends.

4. Conclusions

This study demonstrated the potential of a polymer obtained from fatty acid derivatives as a co-processing additive for polyolefins. Observations of torque during melt processing, crystallinity through DSC and XRD, crystalline plane orientation, mechanical resistance and thermal stability characterised the plasticising action. Torque reduction was observed (29% for PE, 37% for PP), indicating the reduction of viscosity and the improvement of processing. The melting temperature of the blends did not change significantly with OAP addition relative to the neat polyolefins. The crystallinity of the blends, evaluated through the heat of fusion (DSC), showed a slight decrease from PE0 to PE5 and no significant modification for PP blends. Crystallinity evaluation through XRD corroborated the DSC analysis. The orientation of the crystallographic planes did not show significant changes for PE blends, but a reorientation was observed for PP blends. These results can be related to the amount of amorphous phase present

in each polymer and the type of the polyolefin crystalline lamellae. The DSC and XRD results suggest that the polyester is compatible with the amorphous phase of both polyolefins. The stress-strain graphs demonstrated quite different behaviour when PE/OAP and PP/OAP were submitted to plane strain compression. For PE and its blends, the mechanical resistance reduction was remarkable, while for PP blends the addition of OAP up to 5% (w/w) did not cause significant changes in the polymer mechanical resistance. These results indicate that OAP acts as a plasticiser for both polyolefins. However, the PE blends underwent decreases in crystallinity and mechanical resistance, while the PP blends maintained their crystallinity and mechanical resistance and underwent only a reorientation of the crystalline planes. The thermograms of the blends indicated that the polyolefin degradation process shifted towards the second degradation step of the OAP. This shift was stronger and more pronounced in the PP blends compared to the PE blends.

Acknowledgements

The authors are grateful to CAPES, FINEP and CNPq for the financial support and to Braskem S.A. for the PE and PP pellets.

References

- [1] T. Chen, W. Yang, Y. Li, X. Chen, S. Xu, Mono-(2-ethylhexyl) phthalate impairs neurodevelopment: inhibition of proliferation and promotion of differentiation in PC12 cells, *Toxicol. Lett.* 201 (1) (2011) 34.
- [2] D. Zhou, H. Wang, J. Zhang, X. Gao, W. Zhao, Y. Zheng, Di-n-Butyl Phthalate (DBP) exposure induces oxidative damage in testes of adult rats, *Syst. Biol. Reprod. Med.* 56 (6) (2010) 413.
- [3] N. Firlotte, D.G. Cooper, M. Maric, J.A. Nicell, Characterization of 1,5-pentanediol dibenzoate as a potential "green" plasticizer for poly(vinyl chloride), *J. Vinyl Addit. Technol.* 15 (2) (2009) 99.
- [4] F. Chabert, F. Tournilhac, N. Sajot, S. Tencé-Girault, L. Leibler, Supramolecular polymer for enhancement of adhesion and processability of hot melt polyamides, *Int. J. Adhes. Adhes.* 30 (8) (2010) 696.
- [5] J. Wehlmann, Use of esterified rapeseed oil as plasticizer in plastics processing, *Fett/Lipid* 101 (7) (1999) 249.
- [6] O. Fenollar, D. García, L. Sánchez, J. López, R. Balart, Optimization of the curing conditions of PVC plastisols based on the use of an epoxidized fatty acid ester plasticizer, *Eur. Polym. J.* 45 (9) (2009) 2674.
- [7] P. Karmalm, T. Hjertberg, A. Jansson, R. Dahl, K. Ankner, Network formation by epoxidised soybean oil in plastisol poly(vinyl chloride), *Polym. Degrad. Stab.* 94 (11) (2009) 1986.
- [8] P. Karmalm, T. Hjertberg, A. Jansson, R. Dahl, Thermal stability of poly(vinyl chloride) with epoxidised soybean oil as primary plasticizer, *Polym. Degrad. Stab.* 94 (12) (2009) 2275.
- [9] T. Sun, R. Thom, The effect of epoxidized safflower oil on the properties of polyvinyl chloride films, *J. Elastom. Plast.* 42 (2) (2010) 129.
- [10] C. Bueno-Ferrer, M.C. Garrigós, A. Jiménez, Characterization and thermal stability of poly(vinyl chloride) plasticized with epoxidized soybean oil for food packaging, *Polym. Degrad. Stab.* 95 (11) (2010) 2207.
- [11] O. Fenollar, D. García-Sanoguera, L. Sanchez-Nacher, J. Lopez, R. Balart, Effect of the epoxidized linseed oil concentration as natural plasticizer in vinyl plastisols, *J. Mater. Sci.* 45 (16) (2010) 4406.
- [12] P.K. Sastry, D. Satyanarayana, D.V.M. Rao, Accelerated and environmental weathering studies on polyethylene–starch blend films, *J. Appl. Polym. Sci.* 70 (11) (1998) 2251.
- [13] E. Mlecnik, F.P. La Mantia, Influence of calcium-based fillers and vegetable oil on the processability and yield behavior of polyolefins, *J. Appl. Polym. Sci.* 65 (13) (1997) 2761.
- [14] S. Thiebaud, J. Aburto, I. Alric, E. Borredon, D. Bikiaris, J. Prinos, C. Panayiotou, Properties of fatty-acid esters of starch and their blends with LDPE, *J. Appl. Polym. Sci.* 65 (4) (1997) 705.
- [15] G.J.L. Griffin, Advances in chemistry series, 134, in: *Fillers and Reinforcements for Plastics*, American Chemical Society, Washington, D.C., 1974, pp. 159–170.
- [16] E.R. Jusoh, M.H.S. Ismail, L.C. Abdullah, R. Yunus, W.A.W.A. Rahman, Crude palm oil as a bioadditive in polypropylene blown film, *Bio-resources* 7 (1) (2012) 859.
- [17] D.S. Martini, B.A. Braga, D. Samios, On the curing of linseed oil epoxidised methyl esters with different cyclic dicarboxylic anhydrides, *Polymer* 50 (13) (2009) 2919.
- [18] Q.B. Reiznaut, I.T.S. Garcia, D. Samios, Oligoesters and polyesters produced by the curing of sunflower oil epoxidized biodiesel with cis-cyclohexane dicarboxylic anhydride: synthesis and characterization, *Mater. Sci. Eng. C* 29 (7) (2009) 2302.
- [19] A. Nicolau, R.M. Mariath, E.A. Martini, D.S. Martini, D. Samios, The polymerization products of epoxidized oleic acid and epoxidized methyl oleate with cis-1,2-cyclohexanedicarboxylic anhydride and triethylamine as the initiator: chemical structures, thermal and electrical properties, *Mater. Sci. Eng. C* 30 (7) (2010) 951.
- [20] A. Nicolau, R.M. Mariath, D. Samios, Study of the properties of polymers obtained from vegetable oil derivatives by light scattering techniques, *Mater. Sci. Eng. C* 29 (2) (2009) 452.
- [21] M.B. da Roza, A. Nicolau, L.M. Angeloni, P.N. Sidou, D. Samios, Thermodynamic and kinetic evaluation of the polymerization process of epoxidized biodiesel with dicarboxylic anhydride, *Mol. Phys.* (2012). <http://dx.doi.org/10.1080/00268976.2011.647717>.
- [22] M.B. da Roza, A. Nicolau, R. Guzzatto, D. Samios, Polyesters produced by the reaction of epoxidized biodiesel with phthalic anhydride using biodiesel as a green solvent, *Mater. Sci. Eng. C* (2012). Forthcoming.
- [23] C.P. Lafrance, P. Chabot, M. Pigeon, R.E. Prud'homme, M. Pérolet, Study of the distribution of the molecular orientation in thick polyethylene samples by X-ray diffraction, infra-red dichroism and Raman spectroscopy, *Polymer* 34 (24) (1993) 5029.
- [24] L. Zheng, A.J. Waddon, R.J. Farris, E.B. Coughlin, X-ray characterizations of polyethylene polyhedral oligomeric silsesquioxane copolymers, *Macromolecules* 35 (6) (2002) 2375.
- [25] C.P. Lafrance, M. Pérolet, R.E. Prud'homme, Study of the distribution of molecular orientation in highly oriented polyethylene by X-ray diffraction, *Macromolecules* 24 (17) (1991) 4948.
- [26] M.F.S. Lima, M.A.Z. Vasconcellos, D. Samios, Crystallinity changes in plastically deformed isotactic polypropylene evaluated by X-ray diffraction and differential scanning calorimetry methods, *J. Polym. Sci. Part B: Polym. Phys.* 40 (9) (2002) 896.
- [27] G. Machado, E.L.G. Denardin, E.J. Kinast, M.C. Gonçalves, M.A. de Luca, S.R. Teixeira, D. Samios, Crystalline properties and morphological changes in plastically deformed isotactic polypropylene evaluated by X-ray diffraction and transmission electron microscopy, *Eur. Polym. J.* 41 (1) (2005) 129.
- [28] D. Samios, S. Tokumoto, E.L.G. Denardin, Investigation of the large plastic deformation of iPP induced by plane strain compression: stress-strain behavior and thermo-mechanical properties, *Int. J. Plasticity* 22 (10) (2006) 1924.
- [29] R. Guzzatto, M.B. da Roza, E.L.G. Denardin, D. Samios, Dynamical, morphological and mechanical properties of poly(ethylene terephthalate) deformed by plane strain compression, *Polym. Test.* 28 (1) (2009) 24.
- [30] V. Khunová, J. Hurst, C. Liauw, Reactive processing of particulate filled polymers: m-phenylene bismaleimide modified polyethylene/magnesium hydroxide composites, *Polym. Bull.* 42 (4) (1999) 457.
- [31] A.L.N. Da Silva, M.I.B. Tavares, D.P. Politano, F.M.B. Coutinho, M.C.G. Rocha, Polymer blends based on polyolefin elastomer and polypropylene, *J. Appl. Polym. Sci.* 66 (10) (1997) 2005.
- [32] D. Samantaray, S. Mandal, A.K. Bhaduri, A critical comparison of various data processing methods in simple uni-axial compression testing, *Mater. Des.* 32 (5) (2011) 2797.
- [33] S.R. Bodner, Y. Partom, Constitutive equations for elastic-viscoplastic strain-hardening materials, *J. Appl. Mech.* 42 (2) (1975) 385.
- [34] J.L. Chaboche, A review of some plasticity and viscoplasticity constitutive theories, *Int. J. Plasticity* 24 (10) (October 2008) 1642–1693.
- [35] I. Javni, Z.S. Petrović, A. Guo, R. Fuller, Thermal stability of polyurethanes based on vegetable oils, *J. Appl. Polym. Sci.* 77 (8) (2000) 1723.