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COMPARATIVE STUDY OF THE PROPERTIES OF POST-CONSUMPTION HIGH DENSITY POLYETHYLENE USED IN THE INJECTION PROCESS

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Abstract

The high-density polyethylene, thermoplastic widely-used in the production of industrial domestic utilities, was collected in two situations: virgin high-density polyethylene (JV 060) and post-consumption high-density polyethylene (with features of low-density polyethylene). After collecting the samples, they were submitted to natural aging with the quantification of the incident solar radiation for 180 days. The samples were characterized by melt flow index, differential scanning calorimetry, tensile strength, rupture load, elongation at break and infrared. The results showed that after 180 days of exposure the virgin high-density polyethylene presented physical properties similar to the post-consumption polyethylene.

Keywords: DSC, injection process, polyethylene

Introduction

Environmental Protection Agency defines recycling as: collection, processing, commercialization and use of materials considered as waste. The classical definition affirms that the same material is used various times for making the same or equivalent product [1]. The recycling of solid waste consists in its conversion in useful products. It is constituted diverse processes such as thermal conversion (pyrolysis or gasification), chemical conversion (hydrolysis or oxidation) and biological conversion (fermentation or composting).

The recycling of materials is necessary from ecological as well as commercial aspect. The attention to environment takes back to the Industrial Revolution and ever since, the human concern with the nature has increased by virtue of organic dependence of life on earth in relation to intensely altered environmental conditions. In a commercial way,

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environmental management is becoming a relevant aspect in competition. Until recently, the environmental responsibility compromised the industrialized products. However, in the market there is not necessarily a conflict between ecology and economy [2].

The increasing use of plastic materials, stimulated by diversity of characteristics and properties, has resulted in multiple utilization these materials and contributed in a very rapid form for aggravation of ecological problem caused by the accumulated solid waste. Statistical data indicate the annual production and discard 52 million tons of a group of plastics, the commodities, which can take more than 50 years in their degradation. This situation suggests the following measures: control, biodegradation and recycling [3].

The control occurs by reduction of the kinds and/or by segmentation of the market. The biodegradation is a process in which the degradation of the plastic is done by the action of live organisms, such as bacteria, fungi, insects and others, which attack cellulose, starch and other polysaccharides added to the polymers. In terms of recycling of plastics, the developments of the process by which the synthetic polymers are obtained have been responsible for the extraordinary growth of chemical industry of this century. As a result there are several types of plastics: polyethylene, polystyrene, vinyl polychloride, ABS, among others, which present specific characteristics [4, 5]. These materials, in spite of the increasing progress in the development of biodegradable plastics, do not have this property, which indicates recycling to become a promising alternative for deviation of plastic rejects from the route of waste dumping and sanitary fillings [6–9].

Low-density polyethylene (LDPE) and high-density polyethylene (HDPE) are more used materials in manufacturing diverse artifacts, e.g., domestic utilities, automobile parts, toys, etc. [10–14].

The demand for plastics has grown in Brazil. During the period 1992–1996, the consumption of polyethylene increased by about 14.7% per year. In Paraíba, primary recycling predominates, which means, the factories recycle the internally generated waste. However, Petromix S/A, company of the group Polyutil S/A Indústria e Comércio de Materiais Plásticos, processes approximately 500 ton/month polyethylene, acquired directly from the waste dumping sites, reincorporating it to the productive process.

The objective of this study is to evaluate the conditions of the materials proceeding from the cities Campina Grande, João Pessoa, Recife, Natal and Salvador and of a virgin polyethylene, submitted to the known degradation conditions and to evaluate them for their mechanical, thermomechanical and chemical properties.

Experimental

Materials

In this work two types of materials were used, donated by Polyutil S/A: the polyethylene JV 060 virgin and the post-consumption polyethylene originated from waste dumping sites.

The polyethylene JV 060 virgin was collected after receiving additives and in conditions to be processed by the injection method. The post-consumption polyethylene was collected after being selected according to the city of origin (Salvador, Campina Grande, Natal, Recife and João Pessoa). Later on, these materials were washed, dried and milled. After obtaining the samples and repeating the typical conditions of a recycling unit, the materials were molded in appropriate form for tensile strength test according to the norm ASTM D638-87b. The equipment used was a thermoplastic injector with the following characteristics: thread diameter 40–45 mm, L/D ratio 14–18, theoretical volume of injection 125–159 cm^3, pressure on the material 1200–1300 kg cm^{-2} and closing force 80 ton.

Mechanical tests

Tensile alterations in the materials were quantified monthly, during the six-month period. Elongation, tensile and tear strengths were evaluated. The tests were executed in a Testometric Micro 350 universal test instrument. The standard test samples presented nominal dimensions of length 75.0, breadth 12.5 and thickness 3.0 mm. The work velocity was 30 mm min^{-1}.

Differential scanning calorimetry (DSC)

Alterations occurred in degradation process of the polymers can have repercussion in thermal properties [15, 16]. During the exposition period were determined the crystal fusion and crystallization temperatures. The samples, obtained directly from the test bodies injected, were cut in a form to accommodate in sample-port of equipment. The calorimetric curves were obtained in the Shimadzu DSC-50 Differential Scanning Calorimeter, under nitrogen atmosphere, flow 50 mL min^{-1}, heated 50 to 210ºC, heating rate of 10ºC min^{-1} and cooling in the same heating rate.

Melt flow index measurements

The melt flow index, as comparative measurement, can indicate alterations in molecular mass of the polymer. The samples placed after each exposure period was milled in mill of small size blades in a form to adequate them to the test observing the norm ASTM D1238-86 and the temperature of the cylinder was 190ºC. The equipment used was a plastomer DSM MI3.

Spectroscopic characterization

The presence of functional groups was confirmed by infrared absorption spectroscopy. The infrared region absorption spectra were obtained in a Bomem MB102 spectrophotometer of 4000 to 400 cm^{-1}.

Exposure of samples to natural aging

The exposure was realized on an exposure stand made according to the standard ASTMD 1435–85, mounted at a place free from shadow and with minimum risk of undesired actions. The reading of level of incident global radiation, besides the environmental factors: pluviometric precipitation, insolation, evaporation and daily maximum and mean temperatures, was recorded and provided by Embrapa.

Results and discussion

Thermomechanical characterization

The influence of natural exposure on melt flow index was determined and three groups were evidenced. The first consists in the virgin material, which presented an increase in the melt flow index during the period of zero to 180 days of exposure. The post-consumption material originated from Salvador presented a decrease in the melt flow index during the period of zero to 180 days of exposure. The third group, post-consumption material originated from Campina Grande, Natal, Recife and João Pessoa, presented no significant changes (Fig. 1).

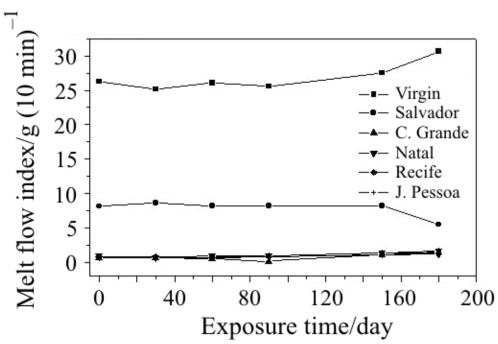

Fig. 1 Effect of exposure time on melt flow index of the polyethylene

Spectroscopic characterization

Infrared radiation absorption frequency is characteristic of functional groups, which makes possible the recognition of the presence of different structural groups. From this information it is possible to define the presence of characteristic groups. However, the identification of polymers is done by means of comparison of the material of interest with reference spectrum. It was possible to identify the alterations occurred in chemical structure of the material, from the comparative analysis of reference spectrum of LDPE (722, 1375.2, 1467.9, 2844.4 cm^{-1}). The presence of bands attributed to the formation of carbonyls was evidenced in the post-consumption materials (Campina Grande, Recife, Natal and João Pessoa) from the spectra in the initial period indicating that these materials were already in a stage of degradation. Spectrum reading in a later period (30, 60, 90, 150 and 180 days) did not show a significant variation indicating that the radiation to which they were submitted was not capable of interfering in the degradation significantly or they were already in the stage of degradation limit. The results obtained indicate, in the period, the degradation stabilization of the materials originated from the cities of Campina Grande, Recife, Natal and João Pessoa and other level for the virgin and city Salvador materials.

Thermal characterization by DSC

Based on the results obtained by analysis of DSC curves (Table 1), it was verified that a significant change in the fusion and crystallization points of the samples of the cities analyzed did not occur, during the exposure time, when each city sample was studied individually.

Table 1 Effect of exposure time on polyethylene by DSC

Polyethylene	Crystal fusion temperature/°C		Crystallization temperature/°C	
	30 days exposure	180 days exposure	30 days exposure	180 days exposure
Virgin	126.22	124.03	117.20	126.00
Salvador	127.31		118.54	
Campina Grande	125.85		117.39	
Natal	124.03		117.97	
Recife	125.46		117.75	
João Pessoa	123.49		117.86	

Regarding the crystal fusion temperature of virgin HDPE there was a variation of only 0.27% during the period indicating the absence of any effective chemical alteration. In relation to the recycled materials the highest variation was of 2.31% indicating that the radiation of the period did not cause significant alteration in these materials.

Regarding the crystallization temperature, there was a significant difference of 3.43% (Campina Grande) and 8.67% (Salvador) indicating effective alterations in the amorphous phase provided by increase of gels and confirmed by reduction in melt flow index. Besides these conditions, it is worth showing the possibility of presence of other materials as polypropylene (PP), other additives as peroxide and hydroxy-peroxide agents and different contaminants, when one treats the post-consumption material originated from waste dumping sites of these cities which can provoke behavior change and provide different mechanisms of degradation.

Mechanical characterization

The analysis of influence of natural aging by quantification of solar radiation, was evaluated during the period of 180 days with a measurement in periods of 30 days of the following properties: elongation, tensile and tear strengths. Figures 2–4 illustrate the behavior of the mechanical properties during the exposure period.

The tensile strength presented no significant difference in 90 days. Up to this period the materials presented a clear fall in the values. The elongation at break showed to be the property where the post-consumption recycled material, originated from the waste dumping sites, presented more accented loss. From 90 days the virgin material suffered an accentuated fall in this property. As for the rupture load, the difference of 20% continued up to the period of 90 days, with a clear fall after this period. The dispersion of the data in tensile tests, relatively common, accentuate when one treats the post-consumption recycled materials.

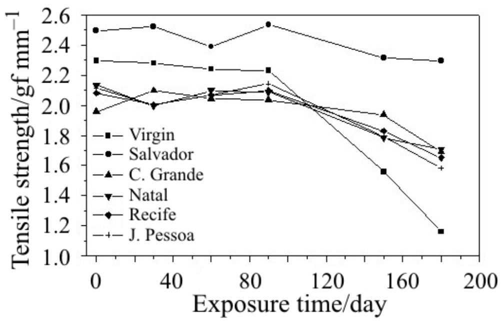

Fig. 2 Effect of exposure time on tensile strength of the polyethylene

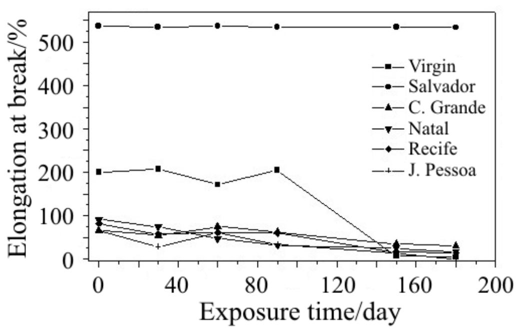

Fig. 3 Effect of exposure time on elongation at break of the polyethylene

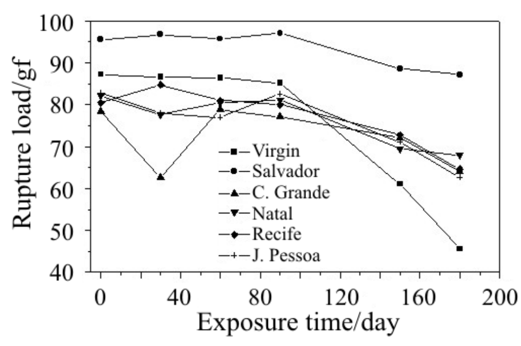

Fig. 4 Effect of exposure time on rupture load of the polyethylene

Conclusions

According to the objective of this work, to calculate/correlate the level of degradation of polyethylene of distinct origins and unknown conditions of storage and disposition, it can be observed that as for the post-consumption materials two groups were detected: Salvador (Group I) and Campina Grande, Natal, Recife and João Pessoa (Group II), because significant variations among the evaluated properties in the post-consumption materials of the cities Campina Grande, Natal, Recife and João Pessoa occurred.

Tensile strength, elongation at break and rupture load of the virgin material after submission to natural aging for 180 days presented lower values than the material from all the cities when measured at zero day of exposure. This fact demonstrates that the degradation conditions applied during the 180-day period were more severe than all the previous degradation conditions to which the materials from the cities were submitted previously.

Regarding the melt flow index, the virgin material presented a significant elevation starting to 150 days of exposure evidencing degradation by chain scission, the post-consumption materials from Campina Grande, Natal, Recife and João Pessoa presented no meaningful changes, while the post-consumption material from Salvador presented a reduction in the melt flow index in this same period.

Related to the data obtained from the thermal tests, the crystal fusion temperature varied between 0.27% (virgin) and 2.31% (Campina Grande) indicating that no significant alterations in the crystalline phase occurred. Regarding the crystallization temperature, the variations occurred from 3.43% (Campina Grande) to 8.67% (Salvador) indicating effective alterations in the amorphous phase, which were confirmed in the melt flow index measurements.

The characterization of the polyethylene evaluated, for density, additives, molecular mass distribution and application for the processing technique, should be considered, in virtue of the fact such factors can lead to different behavior of the properties of degradation.

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