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EVALUATION OF THERMAL AND MECHANICAL BEHAVIOR OF HDPE/MOLLUSK SHELL COMPOSITES PREPARED IN SINGLE SCREW EXTRUDER

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Abstract

Economical activities of molluscs (Anomalocardia brasiliana and Tivela mactroides) produce mollusc shell as main waste, impacting environment. A possible mitigation scenario for this problem is to develop potential applications for waste of calcareous mollusc shell, for example, as polymer filler reinforcement. In this work the influence of mollusc shell filler in thermal and mechanical properties of High Density Polyethylene (HDPE) composite is discussed. For sake of comparison, a pure polymer and composites made with different compositions (5 and 8%wt of milled mollusc shell) were processed in a single-screw extruder under temperature range 180°C (zone 1) to 210°C (zone 5) and rotational speed of 50rpm. Composite specimens were submitted to Thermal analyses (DSC and DTA) and tensile test as well. Results suggest an encouraging scenario for application of calcareous mollusc shell as a filler reinforcement of HDPE, so that both degree of cristalinity and stiffeness of HDPE were increased, even under low concentrations of filler. Maximum values of tensile stress and strain of HDPE did not sensitively increased by filler addition.

Key-words: Mollusc Shell, Properties mechanical and thermal, HDPE.

Introduction

Sustainable development is "development that meets the needs of the present without compromising the ability of future generations to meet their own needs". Irrespective of meeting the basic needs of all, sustainable development implies in maintaining the systems supports of natural life on Earth and in extending to all the opportunity to satisfy their aspirations for a better life [1, 2]. Every day this concern increases, as well as the interest for the utilization and recycling of different types of waste. With increased tourism on the coast of Paraiba, the activity of pickering shellfish has grown in recent years. Obtaining these bivalve molluscs represents the livelihood of communities of shellfish pickers. But collecting these molluscs has caused environmental impact related to the inappropriate disposal of shells. Faced with this situation, the IBAMA (Brazilian Institute of Environment and Renewable Natural Resources) has suggested studies that contemplate an adjustment in the disposal of these shells [3]. In Korea, for example, about 300 thousand tons of oyster shells are generated annually, which may be a great source of unpleasant odor [4].

Based on previous studies, it was proven that there is a high content of calcium carbonate in the shells of oysters and mussels [4], as well as in the mollusc shells. It was performed a chemical analysis of molluscs shell powder and a content of about 97 % of calcium carbonate ($CaCO_3$) was found. It has been observed that the carbonates contribute with more than half of the consumption of fillers in polymers. The reasons for this demand of calcium carbonate are low cost, non abrasiveness, non-toxicity and easy pigmentation due to be white filler. There are two basic types of $CaCO_3$, natural and synthetic (precipitated) [4, 5].

The addition of mineral fillers in thermoplastic polymers such as polypropylene (PP) and polyethylene (PE) has been associated for a long time only with attempts to reduce the cost of the final polymeric products. In recent years, however, these inorganic fillers, especially talc and calcium carbonate ($CaCO_3$), have been gaining ground in the study of composite materials once they enable optimizing some specific properties of polymer matrices such as, hardness and dimensional stability [6, 7]. Fillers and fibers have been routinely used in polymer matrices in order to reduce their cost and improve their mechanical, optical and thermal properties. Fibers are notoriously able to reinforce polymer matrices, while fillers cannot contribute substantially as reinforcement. However, fillers are more abundant and less expensive than fibers, which have motivated the search for plastics reinforcement systems based on particulate materials [8].

The $CaCO_3$ is among the most widely filler used in polymeric composites. Among the thermoplastic polymers stand out polyolefins, which represent about 65% of plastics produced in Brazil. The polyethylenes correspond to 43% of polyolefins production, being high density polyethylene (HDPE) one of the most used [6]. Specifically for HDPE, its use has excelled in different segments of the plastics processing industry, covering the blow molding, extrusion and injection molding processes. Examples of HDPE injection molding parts are: bowls, buckets, trays, infant bathtubs, toys, tupperware, toilet seats, lids, jars, crates, water boxes, among others [6].

Considering HDPE one of the most versatile, easy processing and low cost thermoplastic in the market, it is proposed in this paper to evaluate the influence of incorporation of mollusk shell powder in the mechanical, morphological and thermal properties of HDPE. Mixtures of HDPE and shell powder at two concentrations (5 and 8 wt%) was processed into a single screw extruder and injection molded. The morphological, thermal and mechanical characterizations were performed by scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermogravimetry (TG) and tensile test.

Materials and Methods

Materials

The materials used in this study were high density polyethylene (HDPE) supplied by Polyutil S.A. and the mollusks shell powder provided by the Department of Civil Engineering, used as filler.

Preparation of mollusc shell

The shells were washed and dried at room temperature for 24 hours, then ground in a disk mill Marconi, model MA 700, and passed through a 200 mesh sieve.

Composite Processing

Extrusion: The composite mixtures were processed in a single screw semi-industrial extruder of Lessa Máquinas Ltda. The screw rotation speed was 50 rpm and the temperature profile was 180°C/200°C/200°C/210°C/210°C.
Injection: The tests specimens were molded in a BATTENFELD HM45/210 injection molding machine. The molding conditions were: injection speed, 75cm/s; holding pressure, 600bar; hold time, 15 s; and cooling time, 30 s. The temperature profile used was 170°C/180°C/190°C/190°C and the mold temperature was maintained at 30 °C. Before injection, the materials were dried in an air circulating oven for two hours at 60°C.

Characterization

Scanning Electron Microscopy(MEV)

It was used a scanning electron microscope, ZEISS LEO 1430, to analyze the dispersion and interfacial adhesion of mollusks shell powder in the HDPE matrix. The injected test specimens were fractured with liquid nitrogen and coated with a thin layer of gold for analysis of the fracture surface. The images were obtained with different magnifications, using an accelerating voltage of 15 kV electron beam.

Differential Scanning Calorimetry (DSC)

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Thermograms were obtained from a Shimadzu DSC 60 calorimeter. Calibration was done with indium and saphire in the temperature range of 0 to 350 ^{o}C. The sample weight was approximately 6.0 to 6.4 mg. All samples were first heated at 10 ^{o}C.min^{-1} to 200 ^{o}C for 5 min to get rid of thermal history. Then, samples were cooled to 30 ^{o}C at 10 ^{o}C.min^{-1} and heated again to 200 ^{o}C at the same rate, under nitrogen flow rate of 50 mL.min^{-1}. The crystallization temperature (Tc) was determined in the cooling and melting temperature (Tm) was determined on the second heating scan. Melting enthalpies were determined using constant integration limits. The degree of crystallinity (Xc) was determined using the following equation:

$$X_c(\%) = \frac{\Delta H_m}{(1-W_f).\Delta H_{100\%}} \quad (1)$$

Where: ΔHm is the melting enthalpy per unit weight of HDPE in the formulation, W_f is the weight fraction of mollusk shell powder in the formulation, and $\Delta H_{100\%}$ denotes the enthalpy per unit weight of the 100% crystalline HDPE, which is assumed to be 293 J.g^{-1} [9, 10].

Thermogravimetric analysis (TGA)

The TGA weight loss curves were obtained in a Shimadzu DTG-60H Simultaneous DTA-TG apparatus. The samples weighed from 10 to 11 mg and were heated from 30^{o}C to 900^{o}C at 10 ^{o}C.min^{-1} under 50 mL.min^{-1} of argon flow.

Mechanical Properties

Tensile tests: The tensile tests were carried out using a Shimadzu universal mechanical testing machine, model AG-X 10KN, according to ASTM D 638. The test speed was 50 mm.min^{-1} and it has been tested at least five specimens for each formulation.

Results and Discussion

Table 1 presents the results of DSC analysis of neat HDPE and its composites with mollusks shell powder. These results showed an increase relative to the neat polymer of 14% and 16% in the degree of crystallinity of compositions with 5 and 8 wt% of mollusks shell, respectively. This behavior indicates a possible nucleating effect of the mollusks shell powder. The melting and crystallization temperatures were scarcely changed with the addition of the mollusks shell powder in HDPE.

Table 1 - Thermal properties of HDPE/mollusks shell powder composites at concentrations of 5 wt% (95/5) and 8 wt% (92/8) and neat HDPE.

Composition	Melting Enthalpy (J.g^{-1})	Xc (%)	Tc (°C)	Tm (°C)
neat PEAD	129.72	44.3	102.8	130.9
95/5	162.63	58.4	101.2	131.1
92/8	162.47	60.3	101.2	131.4

From TGA weight loss curves shown in Figure 1, it is observed that there was no significant difference in thermal stability between neat HDPE and HDPE composite with 5 wt% of mollusks shell powder, as the first stage of mass loss, associated with HDPE matrix decomposition, starts and end at about 365 °C and 498 °C, respectively. Although the HDPE composite with 8 wt% of mollusks shell powder presented a similar weight loss profile, this composition showed a slight increase in thermal stability because the onset temperature of HDPE decomposition was changed to 405 °C. For composite formulations containing mollusks shell powder, it was also observed a second stage of mass loss that begins at approximately 630 °C. This thermal event is probably associated with decarbonation reaction of $CaCO_3$ content in the mollusks shell powder [11].

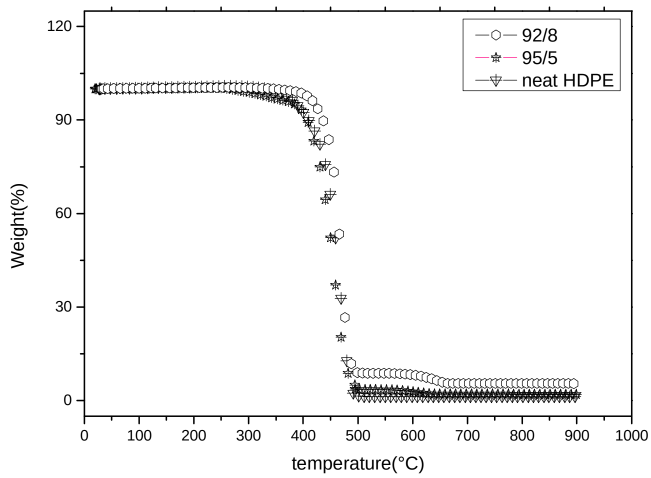

Figure 1. TGA weight loss curve of the HDPE/mollusks shell powder composites at concentrations of 5 wt% (95/5) and 8 wt% (92/8) and neat HDPE.

Figure 2 shows the results of tensile strength of neat HDPE and its composites with mollusks shell powder. It is observed that the tensile strength of the composites showed an optimal point with increasing the mollusks shell powder content in the HDPE matrix. The maximum increment achieved in tensile strength was around 5.3% for the HDPE composite with 5 wt% of mollusks shell powder. The increment of tensile strength for the HDPE composite with 8 wt% of mollusks shell powder was less than 2%. On the other hand, the elongation at break of HDPE decreased with addition of the mollusks shell powder, leaving the material less ductile [6].

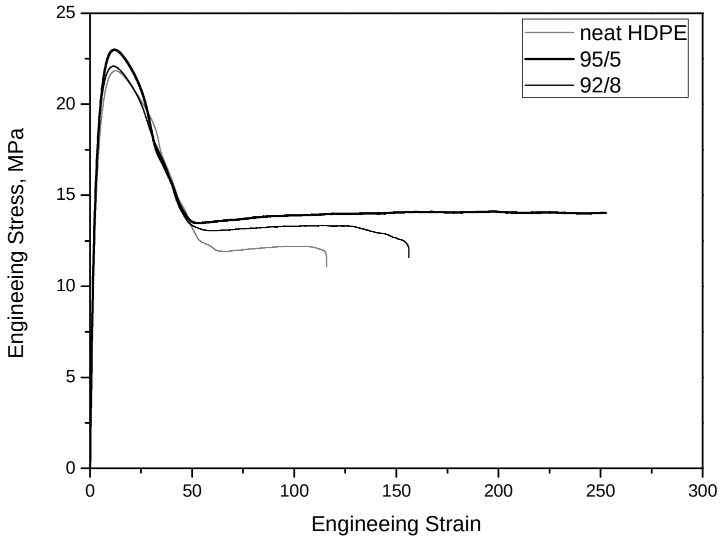

Figure 2. Representative stress-strain curve of the HDPE/mollusks shell powder composites at concentrations of 5 wt% (95/5) and 8 wt% (92/8) and neat HDPE.

Figure 3 shows the values of modulus of elasticity, which increases with the increment in the filler content in HDPE. This behavior corroborates with the increment in the crystallinity and decrease in the elongation at break of the composites with the increased filler content in the polymer matrix, leaving the material stiffer and less ductile than neat HDPE.

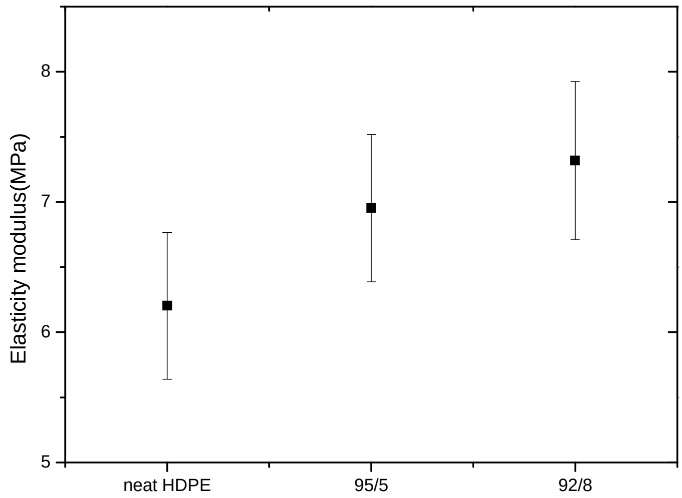

Figure 3. Results of modulus of elasticity of the HDPE/mollusks shell powder composites at concentrations of 5 wt% (95/5) and 8 wt% (92/8) and neat HDPE.

In the micrographs for the composition with 5 wt% of mollusks shell powder (Figure 4), it can be observed a good dispersion of these particles in the HDPE matrix. However, the micrographs for the composition with 8 wt% of mollusks shell powder (Figure 5) showed the presence of agglomerates, which agrees with the smallest increase in tensile strength observed for this composition.

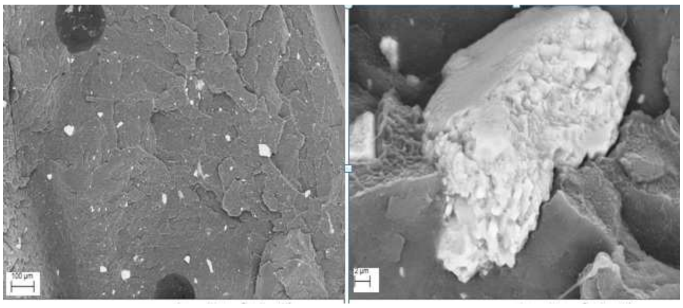

Figure 4. SEM micrographs of HDPE composite with 5 wt% of mollusks shell powder, with different magnifications.

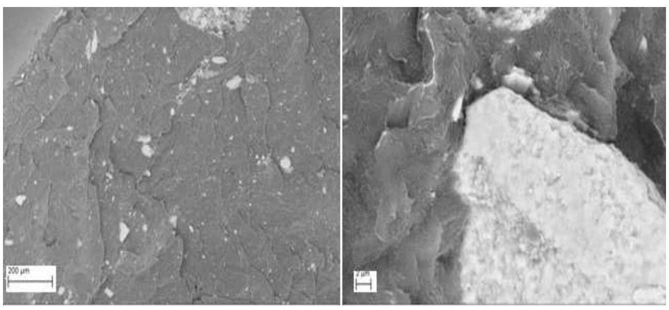

Figure 5. SEM micrographs of HDPE composite with 8 wt% of mollusks shell powder, with different magnifications.

In both compositions, it can be observed some mechanical anchoring between phases and also, voids at filler/matrix interface, indicating a poor interfacial adhesion between the present phases. Thus, it suggests that the observed improvement in the resistance of the composites is more associated to possible mechanical anchoring and increased degree of crystallinity of the polymer matrix, than to the transfer of stresses between phases.

Conclusions

According to the results, it was observed that increasing the mollusks shell content in the polymer matrix the degree of crystallinity increases, as well as the elastic modulus of the polymer, making it more rigid and less ductile. For concentrations up to 5 wt%, the mollusks shell powder behaved as a reinforcing filler, improving the mechanical strength of the polymer matrix and giving good characteristics to the final product. The influence of the filler in the degree of crystallinity of polymer matrix is very expressive, revealing a probable nucleating effect. Despite its morphology did not show a good interfacial adhesion between the matrix and the filler, the addition of up to 8 wt% of mollusks shell powder did not compromise the mechanical performance of the polymer.

Since the use of this kind of filler at concentration up to 8 wt% improves the rigidity and crystallinity degree of neat HDPE, the use of mollusks shell powder in HDPE matrix may be a promising opportunity for recycling these this seafood waste, and also for income generation to the pickering community of these shells. In addition to also decrease the environmental impact generated by this residue in the coastal of Paraiba and others states.

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References

1. Steudner S. H. , H.W., M. D. R. Clemesha, *Aproveitamento de Resíduos da Rizicultura (casca do arroz) em Compósito a base de Polipropileno.* ICTR – Instituto de Ciência e Tecnologia em Resíduos e Desenvolvimento Sustentável NISAM - USP – Núcleo de Informações em Saúde Ambiental da USP, 2004.
2. Boicko, A.L., *UTILIZAÇÃO DE CONCHAS DA OSTRA CRASSOSTREA GIGAS COMO CARGA PARA PRODUTOS DE POLICLORETO DE VINILA (PVC)* Universidade Federal de Santa Catarina - UFSC 2011.
3. Ulisses Targino Bezerra, F.L.P.A., Lucineide Balbino Silva, Normando Perazzo Barbosa, Tiberio A. Passos e Daniella G. L. Cavalcante, *Production of Filler Aggregate from Waste of Bivalves Molluscs Shells.* Jornal of Civil Engineering and Architecture, Issn 1934-7359, USA, 2011. Volume 5: p. pp 363-367.
4. Hamester, M.R.R.B., P. S. Becker, D., *Characterization of Calcium Carbonate Obtained from Oyster and Mussel Shells and Incorporation in Polypropylene.* Mater. Res.-Ibero-am. J. Mater., 2012. 15(2): p. 204-208.
5. RABELLO, M.S., *Aditivos de Polímeros*, ed. A. Editora. Vol. I. 2000, São Paulo.
6. MIGUEL, J.J.P., *Estudo Comparativo das Propriedades Térmicas e Mecânicas do Polipropileno Reforçado com Oxido de zinco, Carbonato de cálcio e Talco.* Dissertação de Mestrado em Engenharia, 2010.
7. Samayamutthirian Palaniandy, Nurdina Abd Kadir, Mariatti Jaafar, *Value adding limestone to filler grade through an ultra-fine grinding process in jet mill for use in plastic industries* Elsevier - Minerais Engineerir, 2009. Vol. 22(7-8): p. 695-703.
8. Giovanna M. X. de Carvalho, H.S.M., Wander L. Vasconcelos, Rodrigo L. Oréfice, *Obtenção de Compósitos de Resíduos de Ardósia e Polipropileno.* Scielo - Polímeros: Ciência e Tecnologia, 2007. Vol. 17 nº 2: p. p. 98-103.
9. R. Quijada, A.N., M. D. Pizzol, S. Liberman, A. A. Filho and G. B. Galland, *Structural Evaluation of Copolymers of ethylene and 1-octadecene by using the temperature rising elution fractionation technique. Journal of Applied Polymer Science*, 2001. vol. 79: p. pp 221-227.
10. CANEVAROLO, S.V.J., *Técnicas de Caracterização de Polímeros*, ed. A.E. Ltda. 2007, São Carlos- SP.
11. Kingery W. D., H.K.B., D. R. Uhlmann, *Introduction to Ceramics*. 1976, New York.