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EFFECTS OF ELECTRON-BEAM RADIATION ON THERMO-MECHANICAL PROPERTIES OF HDPE/BRAZIL NUT SHELL FIBER/CLAY NANOCOMPOSITE

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ABSTRACT

This work studied the effects of electron-beam radiation on thermo-mechanical properties of HDPE/Brazil nut shell fiber/clay nanocomposite (67:30:3 wt %) obtained by extrusion and injection molding processes. HDPE/Brazil nut shell fiber/Clay (***Nanocomposite***) samples were irradiated at 100 kGy using a 1.5 MeV electron beam accelerator, at room temperature in presence of air. The irradiated and non-irradiated specimen tests samples were submitted to thermo-mechanical and melt flow index (MFI) tests and the correlation between these properties was discussed. The results showed significant changes in HDPE thermo-mechanical properties due to the addition of Brazil nut shell fibers and nanoclay. Significant increases around 200 % in tensile strength at break and 40 % in flexural strength of HDPE were observed because of Brazil nut shell fiber and nanoclay addition. However, elongation at break, flexural modules, Izod impact and MFI presented reduction. Concerning electron-beam irradiation, the thermo-mechanical properties of both, HDPE and ***Nanocomposite***, presented a significant increase except in relation to the elongation at break properties. MFI test conditions for irradiated samples of both the HDPE and the ***Nanocomposite*** could not be determined because irradiated samples did not show any flow.

1. INTRODUCTION

Polymer nanocomposites are materials in which inorganic particles in a nanometric scale, typically 10-100 Å in at least one dimension, are dispersed in an organic polymer matrix in order to improve the performance properties of the polymer. Systems in which the inorganic particles are the individual layers of a lamellar compound, most typically a smectite clay or nanocomposites of a polymer embedded among layers of silicates exhibit highly altered physical properties relative to the pristine polymer. These include increased modulus and strength, outstanding barrier properties, improved solvent and heat resistance and decreased flammability [1].

Polyolefin/clay nanocomposites have generated significant interest due to their potential to offer enhanced performance at very low loadings when compared with conventional composites in many engineering applications, such as packaging, automobile and others. [2]

Polyolefins are some of the most widely used types of commercial polymers. The most important polyolefins include polyethylene (PE) and polypropylene (PP). PE is produced by polymerizing the olefin ethylene, whilst PP is made from the olefin propylene. PE is widely used in industries such as packaging, consumer goods, pipes and cable insulation. PE is characterized as a semi-crystalline polymer, made up of both, crystalline and amorphous regions, and it is classified into several different categories based principally on its density and branching once the extent and type of branching, the crystal structure and the molecular weight all strongly affect the mechanical properties of PE. Of these, high-density polyethylene (HDPE), a linear polymer defined by a density of 0.94 g/cm^3 or higher has a greater proportion of crystalline regions than low-density polyethylene. The size and distribution of crystalline regions are determinant to the tensile strength and environmental stress crack resistance of the final product. HDPE, with fewer branches than MDPE or LDPE, has a greater proportion of crystals, which results in greater density and greater strength. HDPE consumption continues to grow annually, with product substitution and potential new applications increasing volume sales growth [3, 4].

HDPE is hydrophobic and has poor miscibility with hydrophilic clay silicates, so homogenous dispersion of the silicate layers in HDPE is difficult to accomplish. In general, clay is modified with alkylammonium groups to increase its interaction with nonpolar polymers and increase gallery space of clay, and HDPE is modified with a polar monomer such as maleic anhydride (MA) to enhance its compatibility with inorganic clay [5, 6].

The melt flow index (MFI) is a measure of the plastic's ability to flow and it is inversely related to melt viscosity. MFI provides an indication of the polymer flow qualities. It has been widely used in industry to characterize the flow properties of polymers due to simplicity and agility of the technique used in its determination. Melt flow index of a plastic decreases with increasing molecular weight and increases with decreasing molecular weight. MFI is an indirect measurement of the molecular weight and structure of thermoplastic polymers. It is an indicator of average molecular weight and it is inversely related to it. [7]

Electron beam radiation has been efficiently applied for controllable modification in polymers. In general, irradiation of polymers causes two simultaneous and concurrent processes: cross-linking and degradation. Under irradiation with high energy beams, HDPE predominantly undergoes cross-linking in the amorphous regions; cross-linking effectively increases intermolecular bonds in this region of HDPE, resulting in an improvement in material properties, such as better mechanical, thermal and chemical properties [8, 9].

In the present study, a hybrid nanocomposite has been prepared with HDPE, Brazil nut shell fiber and bentonite chocolate clay, a Brazilian smectite clay, and the effects of electron-beam irradiation on their thermo-mechanical properties have been investigated.

2. MATERIAL AND METHODS

2.1. Materials

HDPE resin (HDPE JV060U – commercial grade by Braskem S/A), with MFI = 6.4 g/10 min at 190 ^{0}C/2.16 Kg, specific density = 0. 957 g/cm³, maleic anhydride grafted HDPE (PEgMA) as compatibilizer (1 wt %). Brazil nut shell fiber residues disposed by Brazil nut's industries, and bentonite chocolate clay (Pegmatech Especialidades Tecnologicas Ltda.) as a powder with toluene swelling of 8 mL/g.

2.2. Bentonite Chocolate Clay Modification

Bentonite chocolate clay was modified by the addition of a quaternary salt and sodium carbonate to obtain hydrophobic surfaces, diminishing surface energy and making the silicate layers compatible with polymer and easing dispersion in HDPE matrix.

2.3. Brazil Nut Shell Fibers Preparation

Brazil nut shell fiber residues were scraped, washed and kept in distilled water for 24 hours. Then the fiber was dried at 80 ± 2 ºC for 24 hours in an air-circulating oven. The dry fiber was reduced to fine powder, with particle sizes equal to, or smaller than, 250 µm by using a ball mills and then it was dried again at 80 ± 2 ºC for 24 hours to reduce its moisture content to less than 2 %.

2.4. Nanocomposites Preparation

The HDPE resin reinforced with 30 % Brazil nut shell fiber and 3 % bentonite chocolate organophilic nanoclay and HDPE grafted with 1 % (w/w) maleic anhydride was obtained using a twin-screw extruder machine "ZSK 18 MEGAlab extruder" made by Coperion Werner & Pfleiderer GmbH & Co. KG. The samples for thermo-mechanical tests were prepared using the injection molding machine supplied by Indústrias Romi S.A.

2.5. Electron-beam Irradiation

Part of the material obtained was irradiated with 100 kGy using a 1.5 MeV electrostatic accelerator (Dynamitron II, Radiation Dynamics Inc., 1.5 MeV energy, 25 mA current and 37.5 kW power), at room temperature, in air, dose rate 28.02 kGy/s. Irradiation doses were measured using cellulose triacetate film dosimeters "CTA-FTR-125" from Fuji Photo Film Co. Ltd.

2.6. Characterization

2.6.1. Statistical analysis

The difference between the results for irradiated and non-irradiated samples were then statistically assessed by ANOVA using BioEstat software (version 5.0, 2007, Windows 95, Manaus, AM, Brazil). Significance was defined at $p < 0.05$.

2.6.2. Thermo-mechanical tests

Tensile tests (ASTM D 638), flexural tests (ASTM D 790), heat distortion temperature (HDT) (ASTM D 648) and Vicat softening temperature (ASTM D 1525) were performed in this work in order to evaluate the thermo-mechanical behavior of the materials studied. [10 - 13]

2.6.3. MFI measurements

MFI measurements were determined with a Microtest extruder plastometer (ASTM D 1238-04) in the conditions specified for HDPE. [14]

3. RESULTS AND DISCUSSION

3.1 Thermo-mechanical Tests

The results of the average values obtained in the tensile strength at break tests for HDPE and the HDPE/Brazil nut shell fiber/Clay (***Nanocomposite***) are shown in the Fig. 1. As it can be seen, there was a significant increase about 180 % in tensile strength at break of HDPE due to fiber and nanoclay addition ($p < 0.05$). Concerning electron-beam irradiation, the results showed a gain of ca. 200 % for irradiated HDPE, when compared with non-irradiated HDPE and a slight increase of ca. 10 %, for the irradiated ***Nanocomposite***, in comparison with the non-irradiated ***Nanocomposite***,

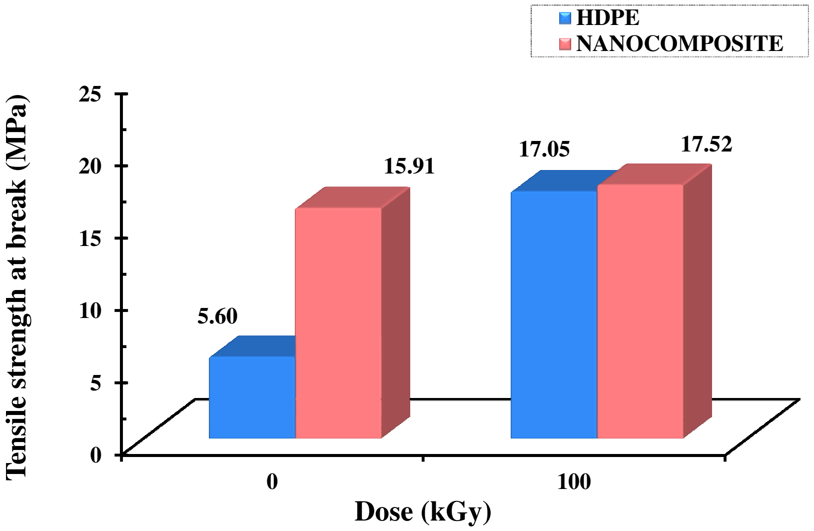

Figure 1. Tensile strength at break (%) as a function of electron-beam radiation dose for HDPE and HDPE/Brazil nut shell fiber/clay nanocomposite.

The results of elongation at break tests are shown in Fig. 2. There was a significant decrease of about 89 % in elongation at break of HDPE due to fiber and nanoclay addition ($p < 0.05$). Concerning electron-beam irradiation, the results showed a decrease of ca. 18 % for the irradiated ***Nanocomposite***, in comparison with non-irradiated samples. On the other hand, the neat HDPE showed a gain of about 63 % in elongation at break after electron-beam radiation treatment.

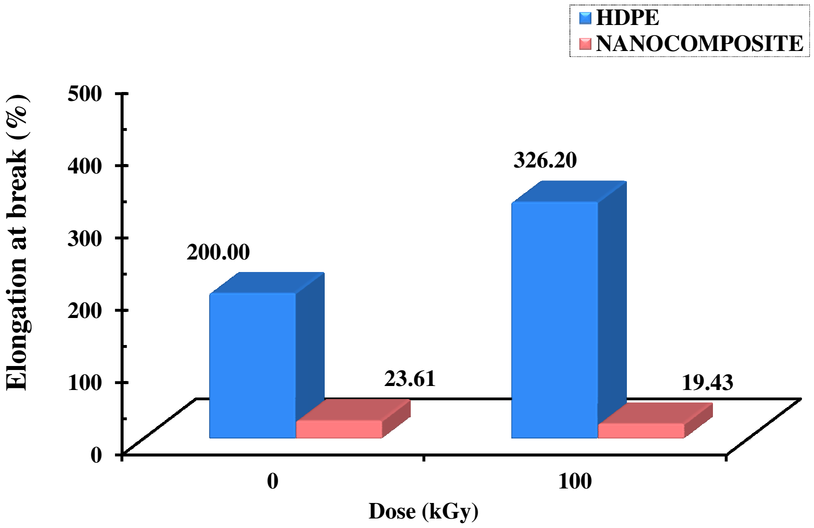

Figure 2. Elongation at break (%) as a function of electron-beam radiation dose for HDPE and HDPE/Brazil nut shell fiber/clay nanocomposite.

The flexural strength average values for both, HDPE and HDPE/Brazil nut shell fiber/Clay nanocomposite are represented in Fig. 3. As it can be seen, the ***Nanocomposite*** flexural strength was, significantly, ca. 26 % higher than for neat HDPE ($p < 0.05$). Concerning the electron-beam radiation treatment, the Fig.3 shows that irradiated ***Nanocomposite*** presented a gain of ca. 13 % in flexural strength when compared with non-irradiated ***Nanocomposite*** while a increase of ca. 18 % was presented by irradiated HDPE, in comparison with neat HDPE.

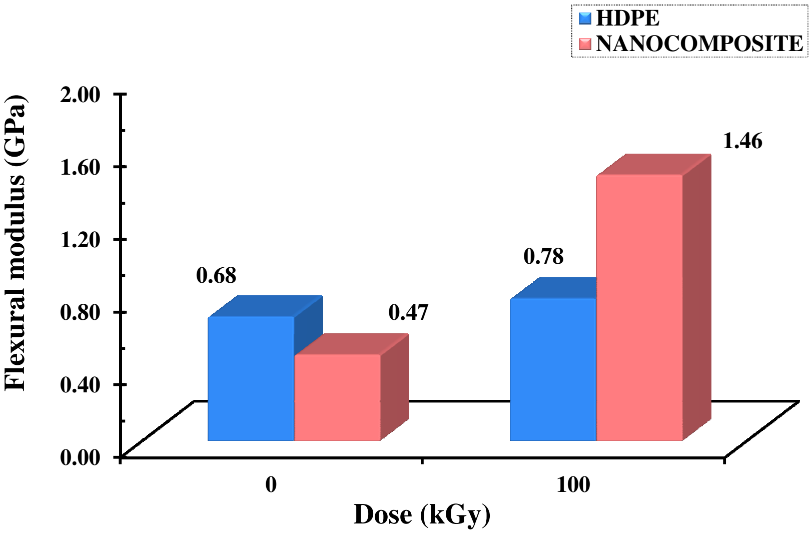

Figure 3. The flexural strength as a function of electron-beam radiation dose for HDPE and HDPE/Brazil nut shell fiber/clay nanocomposite.

Figure 4 shows the results of the flexural module average data for both the HDPE and the HDPE/Brazil nut shell fiber/Clay nanocomposite. As it can be observed the flexural module of HDPE decreased of ca. 30 % due to the incorporation of fibers and bentonite nanoclay. However, after electron-beam irradiation, both, irradiated HDPE and ***Nanocomposite*** samples presented a significant increase about 16 % and 200 %, respectively, when compared with non-irradiated samples.

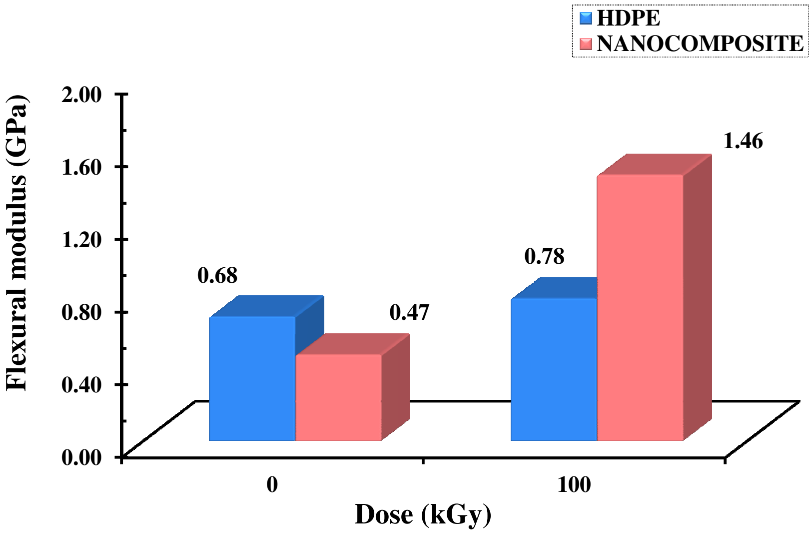

Figure 4. The flexural modulus as a function of electron-beam radiation dose for HDPE and HDPE/Brazil nut shell fiber/clay nanocomposite.

In Figure 5, the heat distortion temperature (HDT) testing results are presented, respectively, for both the HDPE and the HDPE/Brazil nut shell fiber/Clay nanocomposite. Figure 5 shows a slight gain of around 6 % concerning HDT of the ***Nanocomposite*** in comparison with neat HDPE. On the other hand, no significant changes, in HDT for both the HDPE and the ***Nanocomposite*** were observed after electron-beam irradiation.

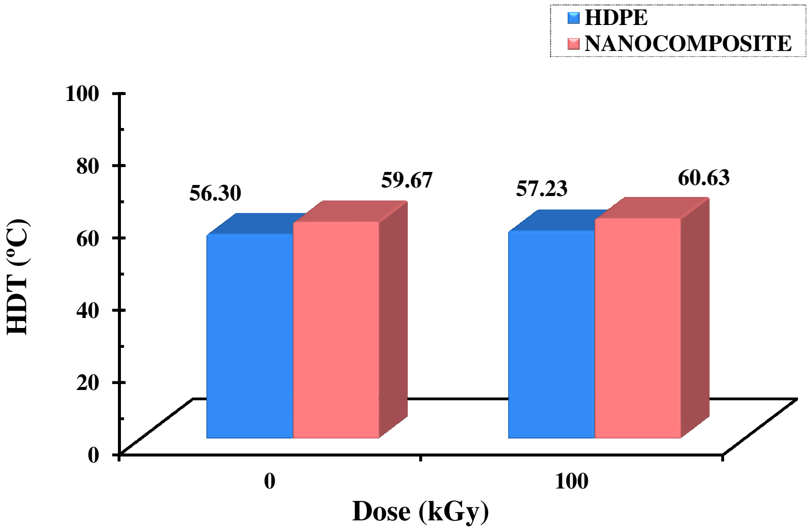

Figure 5. HDT as a function of electron-beam radiation dose for HDPE and HDPE/Brazil nut shell fiber/clay nanocomposite.

The results for the Vicat tests for both the HDPE and the HDPE/Brazil nut shell fiber/Clay nanocomposite are showed in Fig. 6. As it can be seen, no significant changes in Vicat HDPE were observed due to fiber and nanoclay addition, as well as due to the electron-beam radiation treatment.

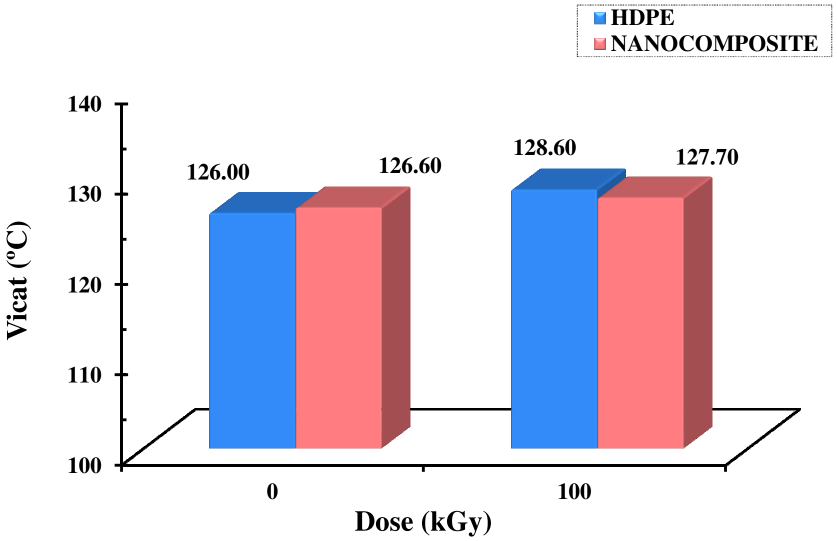

Figure 6. Vicat as a function of electron-beam radiation dose for HDPE and HDPE/Brazil nut shell fiber/clay nanocomposite.

These results suggest that electron-beam irradiation introduced cross-linking between polymer molecules leading to the improvement of the thermo-mechanical properties of the HDPE resin and HDPE/Brazil nut shell fiber/Clay nanocomposite. Moreover, the addition of polyethylene grafted with maleic anhydride to the polyethylene matrix may have favored the intercalation and exfoliation process of clay in the HDPE matrix and also improved interfacial adhesion between the nonpolar fibers and the polar matrix, thereby contributing to the increase of thermo-mechanical properties of the manufactured ***Nanocomposite***. However, to investigate the effectiveness of the clay intercalation/exfoliation and the interfacial adhesion between the fiber and HDPE matrix in the future, additional tests, such as XRD, TEM and SEM should be performed [15,16].

3.2 Melt Flow Index (MFI) Measurements

The results for MFI measurements carried out at 190 ^{0}C/2.16 kg conditions for the non-irradiated HDPE and the HDPE/Brazil nut shell fiber/Clay nanocomposite were 6.41 g/10 min for the HDPE and 4.59 g/10 min for the nanocomposite. These results showed a significant reduction in the nanocomposite MFI values when compared with those of the neat HDPE. It seems that the fibers and nanoclay affect the dynamic viscoelastic melt of polymer, since they could reduce molecular mobility and, consequently, the flow. Under MFI test conditions, neither the irradiated samples of HDPE nor the irradiated samples of nanocomposites showed any flow and, therefore, MFI could not be determined. In fact, the samples showed a rubber-like behavior with no flow. This indicates that the level of radiation doses used for cross-linking was quite sufficient to cross-link HDPE chains and to convert their plastic nature to a more rubber - like material.

4. CONCLUSIONS

In the present study, the contribution of electron-beam irradiation on thermo-mechanical properties of HDPE and Brazil nut shell fiber/Clay nanocomposite was investigated. In general, the results showed that the incorporation of Brazil nut shell fiber and nanoclay combined with electron-beam radiation treatment, at radiation dose 100 kGy, led to obtaining a material with a better thermo-mechanical performance than neat HDPE. The addition of polyethylene grafted with maleic anhydride to the polyethylene matrix may have favored the intercalation and exfoliation process of clay in the HDPE matrix and also improved interfacial adhesion between the nonpolar fibers and the polar matrix, thereby contributing to the increase of thermo-mechanical properties of manufactured nanocomposite. In conclusion, based on these results, it may be claimed that incorporation of Brazil nut shell fiber and bentonite chocolate organophilic nanoclay and electron-beam irradiation effectively improved the thermo-mechanical properties of the HDPE and provided valuable information for adequate hybrid HDPE/Fiber/Clay nanocomposites preparation with good thermo-mechanical properties for several industrial applications.

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REFERENCES

1. A. Lagashetty, A. Venkataraman, “Polymer Nanocomposites”, *Resonance,* **July**, pp. 49-60 (2005).
2. R.Rezanavaz, M. K. R. Aghjeh, A. A. Babaluo, “Rheology, Morphology, and Thermal Behavior of HDPE/Clay Nanocomposites.” *Polymer Composites*, **Volume 31-6**, pp.1028-1036 (2010).
3. S. Kittinaovarat, W. Suthamnoi, “Physical Properties of Polyolefin / Bamboo Charcoal Composites,” *Journal of Metals, Materials and Minerals*, **Volume 19-1**, pp.9-15 (2009).
4. “Chapter 1 History and Physical Chemistry of HDPE.” http://www.plasticpipe.org/pdf/chapter-1 history_physical_chemistry_hdpe.pdf (2010)
5. K. H. Wang, M. H. Choi, C. M. Koo, Y. S. Choi, I. Chung, “Synthesis and Characterization of Maleated Polyethylene/Clay Nanocomposites,” *Journal of Polymer* **Volume 42**, pp.9819 (2001).
6. Y. Lei, Q. Wu, C.M. Clemons, F. Yao, Y. Xu, “Influence of Nanoclay on Properties of HDPE/Wood Composites.” *Journal of Applied Polymer Science*, **Volume 106**, pp.3958–3966 (2007).

7. J. Z. Lu, Q. Wu, I. I. Negulescu, Y. Chen, “The Influences of Fiber Feature and Polymer Melt Index on Mechanical Properties of Sugarcane Fiber / Polymer Composites.” *Journal of Applied Polymer Science*, **Volume 102**, pp.5607–5619 (2006).
8. D. W. Clegg, A. A. Collyer, “*Irradiation Effects on Polymers,*” Elsevier Science Publishers Ltd., Sheffield & United Kingdom, pp.68-69 (1991).
9. D. Gheysari, A. Behjat, M. Haji-Saeid, “The Effect of High-energy Electron Beam on Mechanical and Thermal Properties of LDPE and HDPE,” *European Polymer Journal*, **Volume 37-2**, pp.295–302 (2001).
10. American Society for Testing and Materials - ASTM, D 638-01, Standard Test Method for Tensile Properties of Plastics, (2001).
11. American Society for Testing and Materials - ASTM, D 790 – 00, Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials, (2000).
12. American Society for Testing and Materials - ASTM, D 648 – 01, Standard Test Method for Deflection Temperature of Plastics Under Flexural Load in the Edgewise Position, (2001).
13. American Society for Testing and Materials - ASTM, D 1525 – 00, Standard Test Method Vicat Softening Temperature of Plastics, (2000).
14. American Society for Testing and Materials - ASTM D1238 – 10, Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer, (2004).
15. M. Biswal, S. Mohanty, S. K. Nayak. “Influence of Organically Modified Nanoclay on the Performance of Pineapple Leaf Fiber-Reinforced Polypropylene Nanocomposites.” *Journal of Applied Polymer Science,* **Volume 114**, pp. 4091–4103, (2009).
16. S. Filippi, C. Marazzato, P. Magagnini, A. Famulari, P. Arosio, S. V. Meille, “Structure and morphology of HDPE-g-MA/organoclay nanocomposites: Effects of the preparation procedures.” *European Polymer Journal - Macromolecular Nanotechnology,* **Volume 44**, pp. 987–1002 (2008).