Copolymer got from PET-BC as a technological alternative in the reuse of solid waste

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Abstract: Oil has been a non-renewable source of plastic material production and it is demanded a lot for its physical, chemical and mechanical characteristics. One of the most used plastics is Polyethylene Terephthalate (PET). This generates environmental problems due to the inadequate final use; the aim was to obtain a PET-BC copolymer as a technological alternative in the reuse of solid waste, it was obtained by extrusion. Physicochemical properties of PET and BC were determined the results for PET were melting point 247.67C, humidity 0.93% and ash 0.50%, adjusted humidity BC 5.308%. The PET-BC copolymer was prepared in three proportions A, B and C, it was characterized by infrared spectroscopy (FT-IR-ATR) and Thermogravimetry (TGA), the thermal stability of the material up to 290C, mechanically the Rockwell Hardness (DR) 46.5 ± 4.0; 59.0 ± 4.0; 96.75 ± 1.75; 170 ± 0.03 and Impact Charpy (ICh) 0.25 ± 0.005; 0.45 ± 0.005; 0.40 ± 0.005; 2 ± 0.007 for A, B, C and Control respectively. It is concluded that the physicochemical characteristics of the PET and BC were in line with the initial conditioning, the TGA analyzes with degradation temperatures of 350 to 600C and FT-IR-ATR the vibrational bands that proved the formation of the new material, while the mechanical behavior DR and ICh differences were observed with the control.
Palabras claves: Bagazo de caña, desechos sólidos, PET, tecnológica.
Keywords: Sugacanebagasse, solid waste, PET, technologial

I. Introduction

PolyethyleneTerephthalate (PET) is one of the materials commonly used in the beverage and packaging bottling industry due to its characteristics of crystallinity and transparency, high resistance to wear, chemical resistance, humidity, generation of barrier to CO_2 and O_2 and mechanical resistance that favor the distribution, storage and presentation of some products[1–3]. Therefore, the main detrimental characteristic of this material is its chemical, mechanical and biological resistance, since degradation in the environment by microorganisms or chemical processes such as oxidation is very difficult. In this order of ideas, the high levels of consumption of this product, also has large amounts of waste [1,2].

According to the ANEP-PET [4], establishes that throughout the 40 years it has been in the market, PET has diversified into multiple sectors, replacing traditionally implanted materials or proposing new packaging alternatives unthinkable until now, where the largest quantity of this material is destined to the carbonated beverage industry, in 52.8% and the remaining percentage is divided into containers of: edible oil, detergents, medicines, cosmetics, food and others. Over time the production of PET has increased significantly; Due to the increase in population worldwide, it has contributed to the increase in the consumption of carbonated beverages and easy-to-prepare foods where PET containers are present in these containers. Commonly these plastic containers made of PET, are thrown into garbage deposits which are dragged to different places by agents of nature generating pollution in several areas mainly the soil and the sea [5]. Thus, of the 12 million tons produced of PET in the world, only 20% of this material is allocated for recycling, while the other large part of plastic residue of PET is thrown into the environment, creating an alteration in the ecosystem preventing fertility in the soil, death of marine and terrestrial animals due to its agglomeration in a large proportion in the rural, urban and coastal areas[5].

According to Verdejo[3], in Spain for 2008, only 19.32% of PET consumed was recycled for that year; while in all of Latin America 15% of all consumer material was not reached [6]. Therefore, in Venezuela the pollution problem by PET has been increasing every day, since the production of this material for the bottling industry is increasing; Due to its great demand, due to the culture in the Latin American towns, there is no mechanism for the collection of this material by the citizens, in the same way recycling is currently in a critical stage because the lack of collectors and selectors of the different plastic materials just reuse 5% of all the plastic PET material that is thrown to the different sanitary warehouses[6].

On the other hand, sugar cane bagasse is a waste in large quantity that is generated in most of the sugar mills of the country, which part is sent to be used as fertilizer in the agricultural area, and another is incinerated,

generating amounts of carbon dioxide and other agents that affect the environment [7]. Likewise, this is rich in cellulose which is a natural polymer that is constituted mainly by glucose. Accordingly, it will also provide thermal and acoustic insulation to the mixture and is estimated to increase the action to the mechanical stress of the synthetic polymer[7]. Similarly, the study on transformation of the molecular structure of PET is very scarce because in it the main factor that affects is the melting temperature for that polymer, although there are several studies done on this material, no one has produced a convincing result so far nor give exact figures of the modification of this polymer for the conservation of the planet although a very scarce structural change is established with a low projection [8].

PET is increasingly becoming the material of choice for packaging and bottling product designers. An indication of this trend can be observed in the increase of the use of this material in products such as non-perishable foods, soft drinks and refrigerators over the past 20 years[5]. Therefore, the objective of this research is to obtain a PET-CEL copolymer as a technological alternative in the reuse of solid waste.

II. Materials and Methods

2.1 Sampling: Discarded PET containers were collected in the city of Santa Ana de Coro and sugar cane bagasse was obtained in the town of Curimagua in the Sierra de Falcón located in Latitude: 11.1699, Longitude: -69.6768 of the Petit municipality of the state of Falcón Venezuela.

2.2 Treatment of the samples: The samples of recycled PET were treated following the Norm COVENIN 64-96 [9], the cellulose obtained from the sugarcane bagasse was treated for the creation of the copolymer following the Norm COVENIN 2519-88[10], samples of sugarcane bagasse were processed in Vencedora® Maqtron mill, washed with abundant water and a solar drying was applied for a period of 3 days to guarantee the removal of all the water absorbed, subsequently it was conditioned as a function of the relative humidity for the polymerization.

2.3 Physicochemical properties: the humidity of PET was determined following the methodology of the Standard COVENIN 1156-79[11], likewise the Ashes according to that established in the Standard COVENIN 1646-80[12], and the melting point according to the methodology of Reyes and Márquez[13].

2.4 Polymerization: It was carried out by the extrusion method and the mass technique at atmospheric pressure 0.94 atm and at the fusion temperature of the materials $247 \pm 2C$, in prototype laboratory scale extruder, three mixtures were prepared for the copolymerization in PET-BC proportions where A: 95: 5, B: 90:10 and C: 85:15.

2.5 Analysis Gravimetric thermostat (TGA): According to the methodology of Márquez[14] for the realization of a thermal decomposition curve, this was modified for the most accurate interpretation of the results and adjusted to the partially degradable polymer. The virgin matter obtained in the present investigation and the samples were exposed inside crucibles (pyrex) previously tared at a temperature of 30C in an oven (Memmert) for a period of 20 min, were placed in the desiccator for 40 min and finally weigh them. In the same way the procedure was followed by increasing the temperature 30C above that registered until reaching a maximum temperature of 810C using a muffle. A thermal degradation curve was constructed. The percentage determination in weight was through Equation 1[15].

$$\% \text{ Weight} = \frac{\text{Final Mass} * 100}{\text{Initial Mass}} \qquad \text{Eq. 1}$$

2.6 Infrared Spectroscopy with Fourier Transform with Attenuated Total Reflectance (FT-IR-ATR): For the infrared analysis in ATR (Attenuated Total Reflectance) the Nicolet Is10 model was used, Thermo Fisher Scientific model. The data was taken with an absorbance scale from 4000 to 600 cm^{-1} with 4 cm^{-1}, with a resolution of 64 scans, and a gain of 8 and an optical speed of 0.4747. Using the Thermo ITR ZnSe accessory. Before the readings of the samples, the equipment was conditioned by taking the air as reference before the collection of each spectrum of the sample (background). The samples were placed directly on the ZnSe crystal. Each sample of the copolymer mixtures and their control were measured in duplicate and placed in the ATR cell without any preparation or dilution, the OMNIC program was used to process the spectra. The different concentrations of the copolymer were analyzed.

2.7 Mechanical properties: Charpy Impact (ICh) was determined according to the standard method of ASTM E23-72[16], and Rockwell Hardness (DR) according to ASTM E18-03a Rockwell durometer equipment. Brand: MITUTOYO, Model: AR-20, Total Capacity: 150 Kg, Scale: F, Load: 60 kg and a Penetrator of Ball 1/16 were used.

2.8 Statistical analysis of data was performed using the Minitab 17® statistical package for Window®, performing an analysis of variance with linear adjustment by ANOVA and a post hoc multiple comparison of Tukey being the significance of P-value ($p \leq 0,05$), expressed in letters in the images and tables

III. Results and Discussion

Table 1 presents the results of the characterization of the PET where the humidity was $0.93\% \pm 0.534$ it determined that this type of material can adsorb moisture according to the place where it is stored by being taken as recycled sample from the manufacture of gaseous drinks this should be washed, dried and conditioned to the space where the tests were carried out it had this characteristic humidity [17]. The ash content in the recycled polymer material was $0.502\% \pm 0.032$ Schrowang[18] states that all plastic material to be calcined after this process appear all the inorganic compounds used in its preparation as glass, clay, talcum, flame retardants, pigments and others. The melting point of $257.66C \pm 0.577$ showing a similarity in relation to Pérez and Ruíz[19] since the PET has a melting temperature between 252-260C and that will depend on the conditions of storage, transportation, and treatment, it decreases its melting point because the process to which it is submitted for the manufacture of the containers of PET to be marketed considerably lowers the melting point thereof.

Properties	Gottenvalue
Humidity (%)	0,9302 ±0,534
Ashes (%)	0,5019 ±0,032
Melting Point (°C)	257,666 ±0,577

Tabla 1.Physicochemical properties ofPolietilenTereftalato(PET). It shows mean values of n=3 and standard desviation.

Figure 1 shows the FT-IR-ATR spectrum of PET in the mid-infrared area of 4000 to $600 cm^{-1}$, where is observed in the area from 3700 to $3400 cm^{-1}$ a low intensity peak at $3683 cm^{-1}$ referring to the C = O bond by stretching the carbonyl ester[20], followed by three peaks (2969, 2925, $2851 cm^{-1}$) corresponding to the symmetric, asymmetric vibration of the methylenic bond CH_2[20,21]. At $1713 cm^{-1}$ is the peak corresponding to the carbonyl ester bond C=O by stretching[20–23]. Then peaks are observed that go 1614, 1578 and $1504 cm^{-1}$ referring to the vibrations of the C-C Aromatic ring, C=C Aromatic[20,21]. While at 1455 and $1408 cm^{-1}$ two peaks are observed that refer to the vibration of the symmetrical $-CH_2$ bond in the plane[20,21,23].Then we can see three peaks 1371, 1338 and $1239 cm^{-1}$ corresponding to the flexural vibrations of the C=C bond and the vibrations of the C-O-C, C-C(O)-O bond and symmetric deformation of the $-CH_2$[20,21,23,24]. Below are peaks at 1169, $1091 cm^{-1}$ which refer to the flexural bond of $-CH_3$ and voltage of the C-O- bond[21,24], likewise in 1016, 969, $903 cm^{-1}$ are observed the peaks referring to the vibration of C-H-Ar[21]. In the area of 800 - $700 cm^{-1}$ are the vibrations outside the plane and pitch of the C-H link[20,21,24].
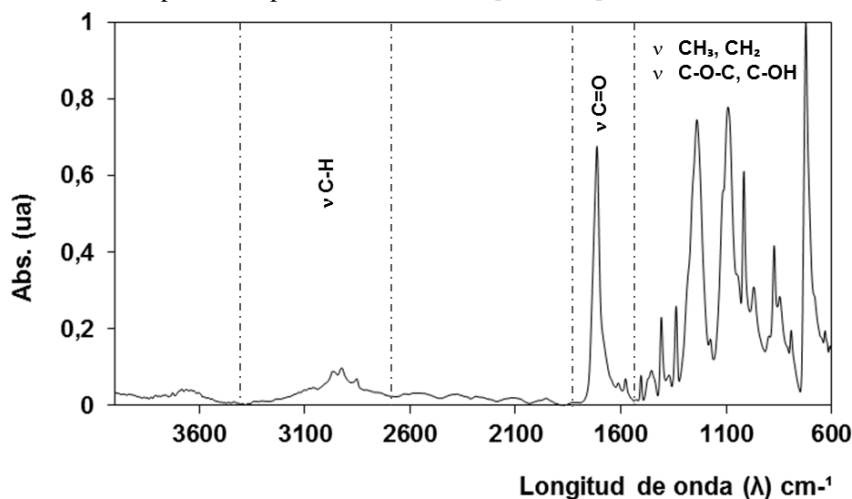
Figure 1.FT-IR-ATR Spectrum of the recycled Polyethylene Terephthalate shows the vibrational zones C=O, C-O-C, -CH$_2$, -CH.

3.1 Copolymerization PET-CEL

The real humidity of 76.70% of sugarcane bagasse,was removed[25]the raw material was reduced to a adjusted humidity of 5.31% for conditioning; since Palma [20]suggests that humidity of materials must be lower in natural matter because this allows the non-generation of water vapor inside the extruder and in this way homogeneity and pressure control is guaranteed inside the machine because this is one of the variables that must be controlled within the mass polymerization technique by the extrusion method. The copolymerization was carried out using the extrusion technology conditioning the samples in proportion between synthetic material (PET) and natural (Sugarcane Bagasse(BC)) for the evaluation of the properties of the final product in each of the relations, thus having a relevant evaluation in the behavior of the material at the different concentrations for each of the mixtures.

Fig. 2 shows the thermal characterization of the copolymer where the thermogram (TGA) of the material can be observed at the different percentages of polymerization of the obtained compound, in this way it can be seen how the curve of mixture A presents loss of weight at 290C compared to PET control that shows loss of mass at the temperature of 340C and mixtures B and C which register a weight loss at 350C, which is attributed to the evaporation of moisture present in the materials as well as the possible increase in the melting point of the copolymers (A, B, C,) in relation to the control whose temperature was 247.77C. For Moran et al.,[26] the thermal decomposition of cellulose as bagasse occurs between 200C and 400C. While for Palma [20]recycled PET presents decomposition at 390C. Observing in the different mixtures values similar to those observed in Palma[20] and Moran[26].

In this order of ideas it can be observed that the mixtures A, B and C maintain a similar behavior in weight loss throughout the test; observing an initial loss with a descending deviation in the curve at 350C, consecutively a remaining mass of 20% can be observed at the temperature of 599C respectively, which indicates the highest amount of mass loss and the maximum range of temperature for the thermal decomposition of the materials, which are in agreement with the control[20]. The differences in the temperature at the beginning of the decomposition could be due to an arrangement and union of the BC as size distribution, molecular weight, unions between the aromatic rings of PET and cellulose (BC), ordering of the structure and others[20,26]. On the other hand it can be concluded that the degradation at its maximum point of thermal decomposition is given to 810C inferring that most of the conversion of semisynthetic materials to ashes.
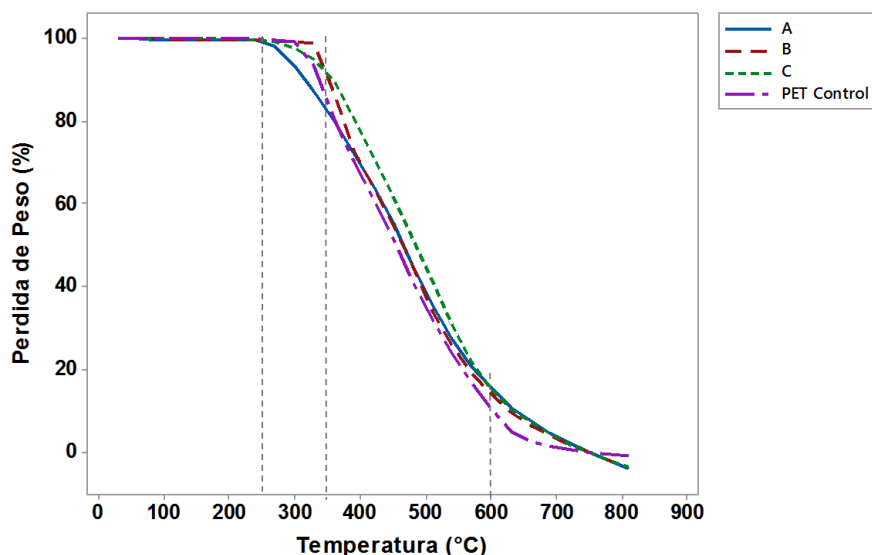

Figure 2. Thermogravimetric diagram of PET-BC Copolymers in mixtures A, B, C and PET-Control. The averages of n = 3 and the decomposition temperatures of the material are indicated.

3.2 Analysis FT-IR-ATR Copolymer

Figure 3 shows the vibrational bands of the FT-IR-ATR spectrum of the PET-BC mix (A, B and C), the PET Control in the medium infrared of 4000 to 600 cm^{-1}, where the interaction of the functional groups of the organic compounds that compose them, showing similarity between them, varying the intensity of the vibration of the -OH, -CH bands in the PET-BC copolymer with respect to the PET-control. While the areas of C=O, C-O-C, -COO, CH$_3$ and CH$_2$ are observed overlapping each other.
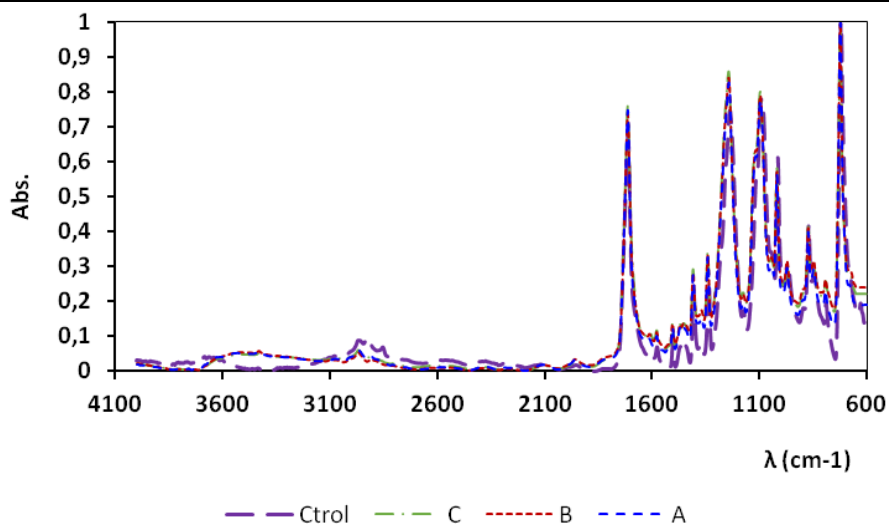
Figure 3.FT-IR-ATR spectrum of the PET-BC A, B, C mixture and its control by mass polymerization in a thermal extruder.

Table 2 shows the mechanical tests such as charpy impact (ICh) and rockwell hardness (DR). In the row of the ICh, the formation of three groups can be observed with significant differences between the mixtures and the control, where the mixtures B and C do not present significant differences among themselves, but with the control, being the mixture A with the least strength to the impact, this behavior can be due to the presence of bubbles in the matrix of the material when not leaving totally being incorporated into its preparation[27] (Ramos, 2008). It should be noted that for Matos[28], the materials after the initial impact the halves of the test piece were expelled in the opposite direction to the direction of the impact made that is related to the unstable crack propagation, action that was evidenced in this study. While in row DR four significantly different groups can be observed between the mixtures and the control, mixture A for presenting greater amount of PET presents the highest DR with respect to B and C but smaller with respect to the control, for Gallego et al.,[29] decreasing in the hardness of the mixtures is due to several factors such as the size of the PET phase and the degree of mobility of the chains, make them less harsh. Another factor that could intervene is the miscibility between the components that cause the mixtures to have intermediate to low properties with respect to the control[29]. It should be noted that the PET-BC copolymer, due to its less mechanical behavior than PET without modification, does not reduce its application and uses to be used in the packaging industry, to mention some.

Ensayo	A	B	C	Ctrol
Impacto Charpy (KJ/m^2)	0.25± 0,005b	0.45±0,005a	0.40± 0,005a	2± 0,007c
Dureza Rockwell (N/mm^2)	96,75±1,75a	59,0±4,0b	46,5±4,0c	170±0,03d

Table 2.*Mechanical properties of PET-BC mixtures and their control. The mean of n = 3 and its standard deviation is shown. The concentrations of the mixtures of PET-BC A: 95: 5, B: 90:10, C: 85:15.*

IV. Conclusions
- The physicochemical characteristics of the PET as melting point, moisture and ash were consistent with the initial conditioning for the formation of the reformed material.
- The analysis of FT-IR-ATR and thermogravimetry where a favorable thermal and vibrational behavior was obtained since the formation of the new material could be verified, detecting the functional groups such as the bands of C=O, COC, C=C and CH_2. In the thermogram it was possible to observe the decomposition of the material obtained at 290, 350, and 600C, thus observing a change in relation to the decomposition temperatures of the PET control.

- As for the mechanical properties of the copolymer as ICh and DR were lower in the three mixtures with respect to the control, however the mixture A showed significant differences in relation to the control being more fragile than the PET.

V. Acknowledgments

VI. BibliographicReferences

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