

## NEW CONCRETE ADDITIVE BY CHEMICAL RECYCLING OF PET

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### ABSTRACT

Due to the problem that represents the accelerated production of waste from the consumption of polyethylene terephthalate (PET), it becomes necessary to look for alternative solutions; chemical recycling is a suitable method for conversion into a material with potential application in concrete additive, such as unsaturated polyester resins; with the above improvements and conservation of non-renewable raw materials can reduce the environmental impact. This investigation was focused on obtaining the synthesis of a polymeric resin by the method of glycolysis, and their characterization by Infrared Spectroscopy (FT-IR); the results show that the recycled materials (PET and its processing) are similar to reagents made from primary materials so that it is considered feasible to use in the intended application.

**Keywords:** concrete admixtures, glycolysis, polymeric resins, polyethylene terephthalate.

## INTRODUCTION

As a globalization in today's lifestyle, and looking for new adaptations in the environment, perception and the archetypes of society are adapting; among these, new consumer behaviors are generating waste with significant figures, especially in the domestic scope. Inadequate treatment of these, partly caused by the lack of awareness on correct production, consumption, waste and responsible use; and secondly, by little or no social system oriented environmental conservation, require actions to foster this waste minimization, incorporating in new products, where possible [1].

One of the residues with significant representation in our society, with a generation of 13 MT/year [7], is PET, which belongs to the group of polyesters called thermoplastics.

PET is a polymer derived from a combination of two monomers: dimethyl terephthalate (DMT) and ethylene glycol (EG) whose molecules are configured in long chains of organic elements, such as carbon (C), oxygen (O) and hydrogen (H); and which was patented for the purpose of manufacture of fibers, by Whinfield and Dickson (1941) [2]; this material has been in use with wide dissemination throughout the world since the 80's, mainly for bottling beverages [4]. The Society of the Plastics Industry (SPI) identifies the material with a logo of the three arrows in the center and the number one (100% recyclable) or the acronym PET (PETE English) in the bottom of containers made of this material [3].

The benefits of its various uses are countless, however, the material with a chemical contamination, identical to the original, at the end of PET use, is difficult in degradation (between 100 and

1000 years), therefore, it is important to reintegrate PET into a new cycle of use [5]. Because of this, we are currently working on finding techniques for recycling these plastics as alternatives to decrease the harmful effects to the environment, and likewise also reducing consumption and extraction of non-renewable raw materials for your manufacturing [6, 7].

In 1977, PET was recycled and used as the basis for a new bottle; today much of European and American cities have a protocol for collection and recovery of recyclables; generally plastics being one of the most popular representative, which after sorting, crushing, smelting and manufacturing, can be re-incorporated as a new material [8]. After this process, waste PET may become modified to produce different materials; including unsaturated polyester resins [9] relevant to this work for the feasibility of implementation as an additive to the polymer-modified concrete, in order to improve its properties. As it is necessary to establish the process that allows such an application, this requires the study of thermal sequencing chemistry that enables generating the said additive, thus enhancing the industrial application in the construction and especially in the use of concrete.

## MATERIALS

The materials used for the development of the experimental phase were:

1. Study base materials: PET bottles used: transparent color, origin of waste and beverage containers of different capacities. Their characteristics and properties are typical [10].
2. Chemical reagents: Sodium Hydroxide (NaOH), propylene glycol (PG), Zinc Acetate (AZ), Maleic Anhydride (MA), Adipic Acid (AA), Bis-(2-HidroxiPropilTereftalato) (BHPT), dimethyl terephthalate (DMT) and styrene (all with 99% purity of the Aldrich brand).

## METHODOLOGY

### Obtaining recycled PET flakes

As a preliminary step to the chemical recycling of PET requires the collection and segregation at colors and other solids present; then the

bottle labels and rings were removed to avoid contamination to include other polymeric materials, other than the studied; after that a mechanical treatment for the reduction and homogenization of size was carried out, using a not standardized mill, with five HP power and equipped with a scissor cutting knife (the process was performed twice, to obtain small flakes, smaller than than 1/2"); in order to remove impurities, the flakes were washed with a solution of sodium hydroxide and 50% water; and finally, the resulting product was dried in an oven at 60 °C for 8 hours to remove any moisture present therein (prevent unwanted chemical reactions).

### Process of Glycolysis

In accordance with the principles of sustainable development for the choice of the most appropriate recycling technique, chemical recycling is optimal [11]; it consists of complete or partial depolymerization of PET to degradation into its monomers or oligomers; its main virtue is that basic raw materials that could be re-used for the production of PET or other materials are obtained (such as polymeric resins). The process may represent a saving of up to 50–60% energy, when compared with manufacturing the same product, but on the basis of laboratory reagents [7, 12].

The chemical processes used are: methanolysis, hydrolysis and glycolysis, the first two are carried out under conditions of pressure and temperature higher than the third; and the hydrolysis can generate environmental problems due to acidic or basic conditions requiring process [3, 12], therefore, glycolysis was selected as the most suitable method for this research. It is based on the depolymerization of the components by chain scission of the polymer [13], which in the presence of a catalyst facilitates the fission of the glycol possessing free radicals (oxygen and glycol ester), thus causing a higher concentration of electron density and an attraction between the carbonyl oxygen and, thus arriving to create a single bond with partial loads. This occurs after an electronic rearrangement in which again forms a double C = O of ester, caused by the electrostatic attraction between the O and H gives glycol, and thus producing the monomers plus a small remnant portion of glycol [13].

The glycolysis process is carried out in a vessel type reactor (Fig. 1); which consists of the following elements: a glass cup double layer resis-



tant to temperatures between  $-40\text{ }^{\circ}\text{C}$  to  $200\text{ }^{\circ}\text{C}$ , a motor with a digital display for the control of agitation and a system for recirculating the fluid (silicone) with passageways allowing deposit and maintain temperature.

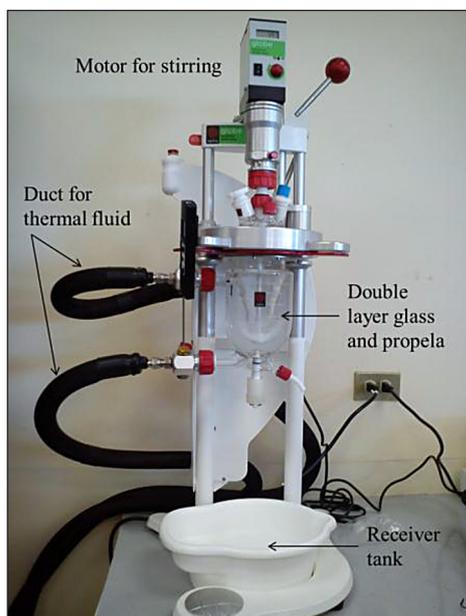


Fig. 1. Type reactor Vessel

The process involves adding PET, PG solvent (50% by weight of PET) and AZ catalyst (0.5% by weight of PET); the latter being essential in the process of degradation, which allows the breaking of the polymer chain.

Then a sequence of increases in temperature ( $25\text{ }^{\circ}\text{C}$  every 20 minutes up to  $200\text{ }^{\circ}\text{C}$ ) was performed, keeping in agitation (165 rpm) for eight hours. The material resulting from this process showed a viscous consistency and transparent gray color, which upon reaching room temperature passed into semi-solid and opaque gray (BHET-R).

### Synthesis of the Resin

In the synthesis of the resin (R-R) BHET-R, AM and AA were used at a molar ratio of 1.1:0.5:0.5, these compounds were dosed by weight and were introduced them into the reactor; which followed the same programming sequence of temperature and duration as the previous process. The resulting product showed a viscous consistency and a gray color, which at room temperature became semi-solid and amber. Finally, a curing process, which consisted of dissolving the RR (40%) styrene (60%) until obtaining the material in liquid form, which is a desired material

as a sustainable alternative application of PET in a densifying additive of the cementitious matrix of concrete.

To make a comparison between the obtained materials (BHET-R and R-R), comparable products were synthesized from primary reagents (BHPT and DMT). The synthesis procedures and required equipment for this new process were the same as the ones used for the preparation of the R-R; these new materials resulting from the primary reagents were appointed as BHET-P and R-P.

### Characterization

For the comparative analysis of the polymeric materials created, Infrared Spectroscopy Fourier Transform (FT-IR) using spectrometer Nicolet 6700 was used, comprising an information processor and screen for viewing and manipulating the spectra. Solid samples were prepared by the compressed method with potassium bromide (KBr) [15], which comprises milling the polymeric material over the portion of KBr. The obtained material was introduced into metal capsules and was placed in the press, in order to make the tablet, and form a thin wafer; which is introduced into the spectrometer for evaluation, after calibration using reference test (blank test) only with a KBr pellet. The samples were analyzed after of 32 scans wavenumber in the range of  $600\text{--}4000\text{ cm}^{-1}$  and a resolution of  $4\text{ cm}^{-1}$ .

## RESULTS

### FT-IR Spectroscopy

The spectra of FT-IR were obtained in the studied materials: PET, BHET-R and RR.

In Figure 2-a (PET spectrum), the following bands are reported: OH glycol stretching, C = O of carbonyl, CH of aromatic ring, type bonds  $-\text{CH}_2-$ , at frequencies of  $3539\text{ cm}^{-1}$ ,  $3435\text{ cm}^{-1}$ ,  $3098\text{ cm}^{-1}$ ,  $2958\text{ cm}^{-1}$  and  $2885\text{ cm}^{-1}$ , respectively; bands of aromatic CH bending out of plane with a  $1948\text{ cm}^{-1}$ ; a peak at  $1710\text{ cm}^{-1}$  corresponding to C = O stretching carbonyl  $1458\text{ cm}^{-1}$  and link  $-\text{CH}_2-$  type in-plane bending; bonds to  $1100$  and  $1017\text{ cm}^{-1}$  asymmetric CO ester,  $870\text{ cm}^{-1}$  CH out of plane and  $743\text{ cm}^{-1}$  aromatic CH symmetric stretch. In Figures 2-b and 2-c, corresponding to BHPT-R and RR, can be observed very similar spectra to that of PET, since the same bands appear with no significant displacements; passes as

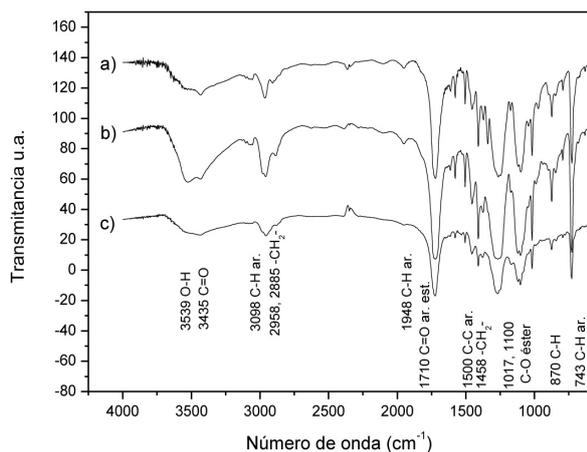


Fig. 2. Spectrum FT-IR: a) PET, b) BHET-R, c) R-R

well as (with reference to the frequency of 3500  $\text{cm}^{-1}$ ), which for the BHET-R peak is located at 3539  $\text{cm}^{-1}$  being only sharper and more distant than that of PET.

Likewise, analyzing the polymeric materials obtained with the primary reagents (BHET-P and R-P), the Figure 3, indicates that the band at 3529  $\text{cm}^{-1}$  corresponds to bonds of glycol O-H, the 3420  $\text{cm}^{-1}$  is C=O of ester carbonyl, the 3055  $\text{cm}^{-1}$  is C-H aromatic ring and the 2960  $\text{cm}^{-1}$  and 2870  $\text{cm}^{-1}$  is  $-\text{CH}_2-$  bonds, all the above of stretching vibration, likewise, the band 1955  $\text{cm}^{-1}$  is aromatic C-H bending out of plane with the 1718  $\text{cm}^{-1}$  C=O aromatic aliphatic ester carbonyl stretching a 1500  $\text{cm}^{-1}$ , stretching of C-C on the aromatic ring, the 1450  $\text{cm}^{-1}$   $-\text{CH}_2-$  bending in the plane, 1100 and 1017  $\text{cm}^{-1}$  ester C-O bonds, the 873  $\text{cm}^{-1}$  C-H out of plane, and 735  $\text{cm}^{-1}$  symmetric stretch aromatic C-H. With respect to Figure 3-b (BHPT-P), has similar spectrum bands, with only small differences, as is the case of the 3098  $\text{cm}^{-1}$  band of C-H and 2958  $\text{cm}^{-1}$   $-\text{CH}_2-$ , moving a negligible extent, and varying intensity.

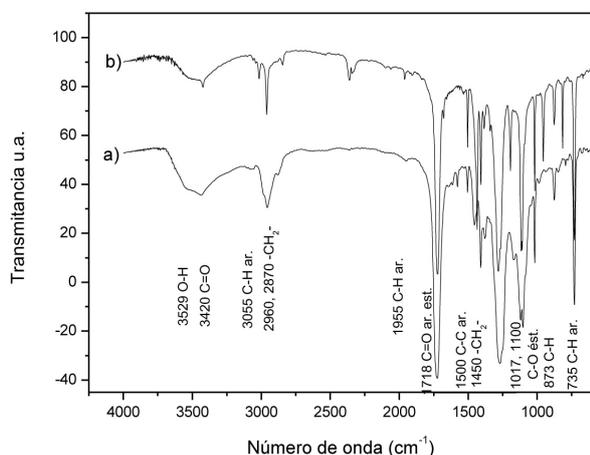


Fig. 3. Spectrum FT-IR: a) R-P and b) BHET-P

When compared the spectra of BHET-P (Fig. 4a) and BHET-R (Fig. 4-b) the following small variations of bands: 3539  $\text{cm}^{-1}$ , 3435  $\text{cm}^{-1}$  and 3098  $\text{cm}^{-1}$  (BHET-R) and 3529  $\text{cm}^{-1}$ , 3420  $\text{cm}^{-1}$  and 3055  $\text{cm}^{-1}$  (BHET-P) were detected, on the other hand, also shows that the bands 2960  $\text{cm}^{-1}$  and 2870  $\text{cm}^{-1}$  are slightly wider to BHET-R. This must be interpreted as insignificant, given that their displacement and intensity are reduced and attributed to the change of the chemical environment of the reaction and small differences in their molecular weight.

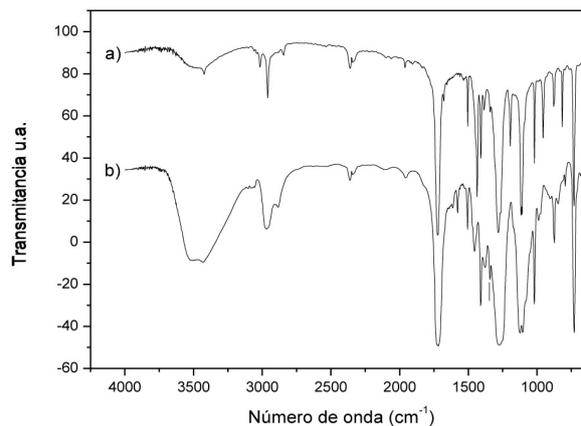


Fig. 4. Spectrum FT-IR: a) BHET-P and b) BHET-R

Comparing R-P (Fig. 5-a) and R-R (Fig. 5-b), one can see the following differences: for R-P the band at 1109  $\text{cm}^{-1}$  is shifted to 1115  $\text{cm}^{-1}$  of the R-R; while in the latter, a band 1955  $\text{cm}^{-1}$  disappears. Furthermore, bands are also shown in 1115  $\text{cm}^{-1}$  and 1090  $\text{cm}^{-1}$  respectively, which are displaced between them slightly. The change is related to the fact that wider bands are shown in the higher molecular weight materials.

The FT-IR results shown above are consistent with those reported in similar studies by other authors [13–16].

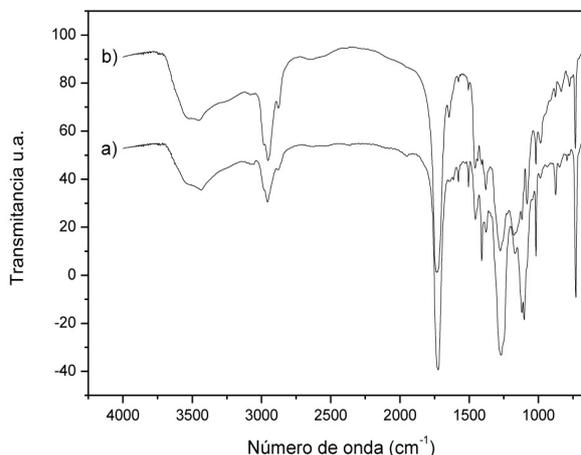


Fig. 5. Spectrum FT-IR: a) R-P and b) R-R



## CONCLUSIONS

The features found in the FT-IR technique in the studied materials, both PET product origin and the primary reagents, revealed the same typical bands; and therefore, the trends are similar and well defined there.

By FT-IR technique is feasible define the molecular structure of each polymeric material from the chemical recycling, showed no significant difference in the reference material (primary reagents); therefore considered feasible the processing of the R-R for use as an additive for making CMP with sustainable uses. However, it will require further research in the mechanical and durability performance in these CMP.

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