

Synthesis and characterization of PET polymer resin for your application in concrete

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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 are 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.

I. 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 where possible in new products [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 called polyesters thermoplastics.

The 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 80s for bottling beverages mainly [4]. The Society of the Plastics Industry (SPI), the identifies with the 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 generates at the end of their use, a material with a chemical contaminate nature identical to the original; to be a difficult of degradation component (between 100 and 1000 years) therefore, it is important to reintegrate into a new cycle of use [5]. Because of this, currently we are working on finding techniques for recycling these plastics as alternatives to decrease the harmful effects caused on 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 representative, that after sorting, crushing, smelting and manufacturing, can be re-incorporated as a new material [8]. After this process, the 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 their properties. Being therefore necessary to establish the process that allows such application, this requires the study of thermal sequencing chemistry that enables generating said additive, thus enhancing the industrial application in the construction and especially in the use of concrete.

II. 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 the usual product [10].
2. Chemical reagents: Sodium Hydroxide (NaOH), propylene glycol (PG), Zinc Acetate (AZ), Maleic Anhydride (MA), Adipic Acid (AA), Bis-(2-

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HidroxiPropilTereftalato) (BHPT), dimethyl terephthalate (DMT) and styrene (all with 99% purity of the Aldrich brand).

III. Methodology

A. 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 study; after, was carried out a mechanical treatment for the reduction and homogenization of size, using an mill not standardized, with power five HP and equipped with scissor cutting knife (the process was performed twice, to afford flakes small, less than $\frac{1}{2}$ "); 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).

B. Process of Glycolysis

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

The chemical processes most 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. Which is based on the depolymerization of the components by chain scission of the polymer [13], which in the presence of a catalyst facilitates the attack of the glycol for possess free-radical (oxygen and glycol ester), thus causing a higher concentration of the electron density and an attraction between the carbonyl oxygen and, thus arriving to create a single bond with partial loads. Occurs after an electronic rearrangement in which again forms a double $\text{C}=\text{O}$ of ester caused by the electrostatic attraction between the O and H arises glycol, and thus producing the monomers plus a small remnant portion 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 resistant to temperatures between -40°C to 200°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.



Figure 1. Type reactor Vessel.

The process involves adding PET, solvent PG (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 was performed a sequence of increases in temperature (25°C every 20 minutes up to 200°C), 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 to semi-solid and opaque gray (BHET-R).

C. 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 to get the material in liquid form; which is the material feasible desired as a sustainable alternative application of PET in a densifying additive of the cementitious matrix of the concrete.

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

materials resulting from the primary reagents were appointed as BHET-P and R-P.

D. Characterization

For the comparative analysis of the polymeric materials created, was used Infrared Spectroscopy Fourier Transform (FT-IR) using spectrometer Nicolet 6700, 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 600-4000 cm^{-1} and a resolution of 4 cm^{-1} .

iv. Results

A. FT-IR Spectroscopy

The spectra of FT-IR were obtained of the study 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 cm^{-1} , 3435 cm^{-1} , 3098 cm^{-1} , 2958 cm^{-1} and 2885 cm^{-1} , respectively; bands of aromatic CH bending out of plane with a 1948 cm^{-1} ; a peak at 1710 cm^{-1} corresponding to C = O stretching carbonyl 1458 cm^{-1} and link $-\text{CH}_2-$ type in-plane bending; bonds to 1100 and 1017 cm^{-1} asymmetric CO ester, 870 cm^{-1} CH out of plane and 743 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 aforementioned and with no significant displacements; passes as well as (with reference to the frequency of 3500 cm^{-1}), which for the BHET-R peak is located at 3539 cm^{-1} being only sharper and distant than that of PET.

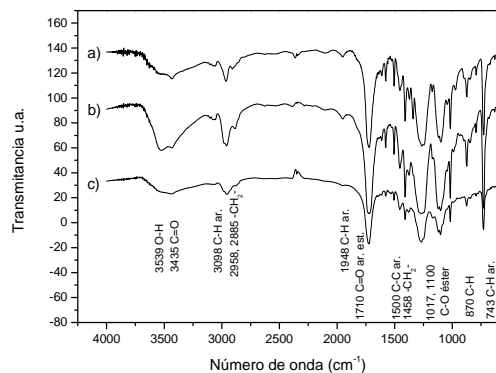


Figure 2. Spectrum FT-IR: a) PET, b) BHET-R and c) R-R

Likewise, analyzing the polymeric materials obtained with the primary reagents (BHET-P and R-P), the Figure 3, indicates that the band at 3529 cm^{-1} corresponds to bonds the glycol O-H, the 3420 cm^{-1} is C=O of ester carbonyl, the 3055 cm^{-1} is C-H aromatic ring and the 2960 cm^{-1} and 2875 cm^{-1} is $-\text{CH}_2-$ bonds, all the above of stretching vibration, likewise, the band 1955 cm^{-1} is aromatic C-H bending out of plane with the 1718 cm^{-1} C=O aromatic aliphatic ester carbonyl stretching a 1500 cm^{-1} , stretching of C-C on the aromatic ring, the 1450 cm^{-1} $-\text{CH}_2-$ bending in the plane, 1100 and 1017 cm^{-1} ester C-O bonds, the 873 cm^{-1} C-H out of plane, and 735 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 cm^{-1} band of C-H and 2958 cm^{-1} $-\text{CH}_2-$, moving a negligible extent, and varying intensity.

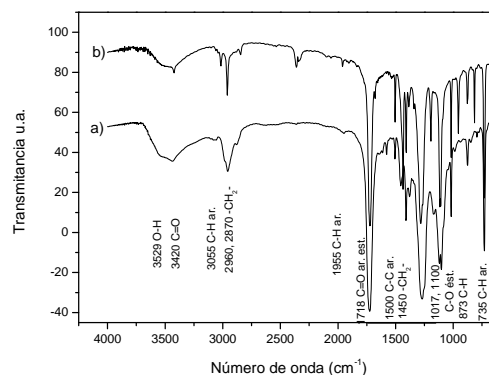


Figure 3. Spectrum FT-IR: a) R-P and b) BHET-P

When compared the spectra of BHET-P (Fig. 4a) and BHET-R (Fig. 4-b) were detected the following small variations of bands: 3539 cm^{-1} , 3435 cm^{-1} and 3098 cm^{-1} (BHET-R) and 3529 cm^{-1} , 3420 cm^{-1} and 3055 cm^{-1} (BHET-P), on the other hand also shows that the bands 2960 cm^{-1} and 2870 cm^{-1} are slightly wider to BHET-R. This must be interpreted as not significant given that their displacement and intensity are reduced and attributed to the change of the chemical environment of the reaction and small differences in the molecular weight of them.

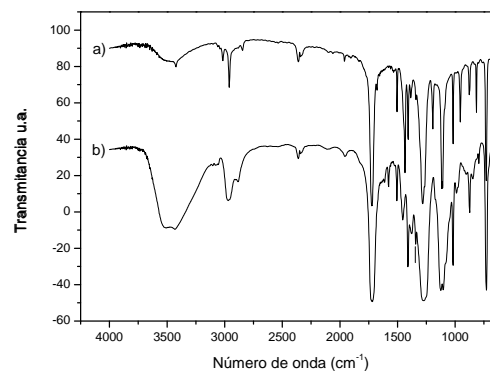


Figure 4. Spectrum FT-IR: a) BHET-P and b) BHET-R

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 cm^{-1} is

shifted to 1115 cm^{-1} of the R-R; while in the latter, a band 1955 cm^{-1} disappears. Furthermore, bands are also shown in 1115 cm^{-1} and 1090 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].

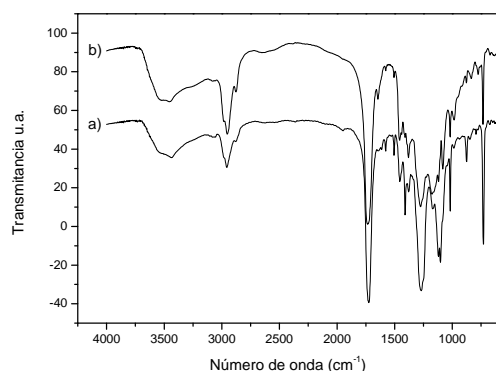


Figure 5. Spectrum FT-IR: a) R-P and b) R-R

v. Conclusions

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

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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