Study of the Behavior of Polyester Concretes Containing Ionomers as Curing Agents

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ABSTRACT: Polyester concretes have been used in constructions for more than 20 years. This type of polymer concrete can advantageously replace traditional Portland concrete in situations that require fast consolidation of the material. Otherwise, polyester concretes are usually more expensive than Portland concretes. Part of the high cost of the polyester concretes is due to the fact that the aggregates used in the formulation of the concretes need to be dried prior to their incorporation into the polymer matrix. In this work, the use of different curing systems (methacrylic acid and maleic anhydride) was investigated to test the hypothesis that the introduction of acid functionalities into unsaturated polyesters based on isophthalic acid could both restrict the detrimental effect of moisture in the curing process and also improve interfacial interactions even in polyester concretes containing wet aggregates. In this work, as there was no search for ways to reduce cost of polyester concretes and also to contribute to the environmental preservation, unsaturated polyesters were synthesized from PET bottles and tested in the fabrication of concretes by reacting them with a conventional curing agent (styrene). Gel permeation chromatography, infrared spectroscopy, and electron microscopy were used to monitor and analyze the production of unsaturated polyester resins and concretes. Mechanical properties were also evaluated by compression tests. Results showed that methacrylic acid and maleic anhydride, when used as curing agents, led to the production of polyester concretes having higher mechanical properties in both dry and wet states than conventional polyester (based on isophthalic acid) concretes. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 2682–2690, 2008

Key words: polyester concretes; ionomers; recycling PET

INTRODUCTION

Polyester concretes are based on the combination of unsaturated polyester resins and inorganic aggregates. This type of concrete is frequently used as a construction material in special situations that require either fast consolidation or chemical resistance that are not achieved by standard Portland concretes.[1–6] On the other hand, polyester concretes are usually more expensive than Portland concretes. Moreover, since water can reduce both the efficiency of the curing process and adhesion between the polymer matrix and fillers, inorganic aggregates need to be dried before being mixed with the resin.

In this work, to possibly reduce the cost of polyester concrete preparation, styrene, a common curing agent for unsaturated polyester, was comparatively replaced by other monomers that have carboxylic acid functionalities. This type of functionality can potentially interact with inorganic surfaces by forming ionic bonds and/or hydrogen bonds in wet environments. Polymers that contain ionic functionalities (ionomers) combined with inorganic fillers have been used in dental applications as restorative materials.[7] In polymer concretes, these ionomers can potentially interact with wet inorganic aggregates to form strong interfacial bonds while keeping water molecules linked to the ionic bonds. Water molecules trapped inside ionic cages would then be less effective in interfering with the overall curing process. In this work, polyester concretes were also produced by replacing more conventional unsaturated polyester based on isophthalic acid with unsaturated polyester based on recycled PET. This approach is another interesting alternative to reduce cost of polyester concretes and also to contribute to the environment preservation. High molar mass PET chains can be reduced to oligomers by reacting PET with glycols (glycolysis).[8–11] A subsequent reaction of these oligomers with chemical species containing carbon double bonds can lead to the production of unsaturated polyester resins. Polyester concretes produced by using unsaturated polyester based on PET and
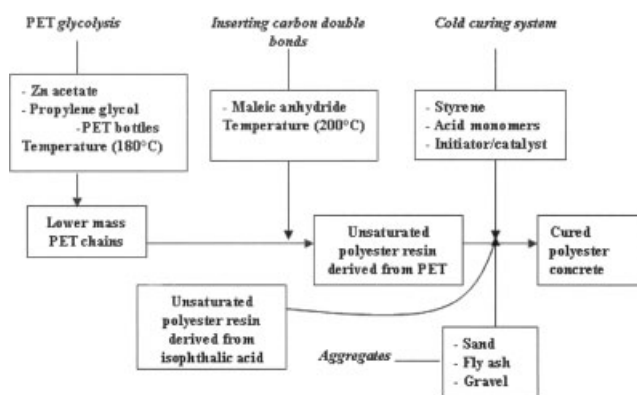
Figure 1 Experimental strategy used to produce polyester concretes in this work.

styrene (as curing agent) were tested and the results were also compared with other polyester concretes obtained by using ionomers as curing agents. Figure 1 illustrates the strategy of this work, in which both unsaturated polyester resins derived from isophthalic acid and PET were combined with different curing agents and aggregates to yield polyester concretes.

EXPERIMENTAL

Glycolysis of PET

The fabrication of unsaturated polyester resin from PET postconsumed bottles was performed in two steps: (1) conversion of PET high molar mass chains into lower molar mass species through glycolysis; (2) introduction of carbon double bonds by reacting PET oligomers with maleic anhydride.

The glycolysis of PET was performed by reacting 1/1 in a weight basis of PET strips cut from bottles and propylene glycol. Acetic anhydride (0.5 wt %) was used as catalyst. The reaction was processed at 180°C in nitrogen atmosphere. Samples were collected each 2 h to check the evolution of the reaction by measuring the molar mass of the glycolyzed PET and the number of hydroxyl groups. The number of hydroxyl groups was measured by following the ASTM D 2849 standard. This method includes the preparation of a solution containing 30% in volume of acetic anhydride in pyridine. A glycolyzed PET sample with a known weight was immersed into to 10 mL of this solution. The mixture containing the glycolyzed PET was then heated up to the temperature in which the solution started to boil. After 10 min at this boiling temperature, the mixture was cooled down. The mixture was then titrated against a 1N potassium hydroxide (KOH) solution by using phenolphthalein (1% in pyridine) as the indicator. The number of hydroxyl groups (N_{OH}) that represents the mass (in mg) of KOH per gram of sample

was calculated by applying the measured values to the following equation:

$$N_{\mathrm{OH}} = \frac{56.1 \ (V_b - V_a)}{w} \quad (1)$$

V_b is the volume of the KOH solution required to titrate the solution without the glycolyzed PET sample; V_a is the volume of the KOH solution required to titrate the solution containing the glycolyzed PET sample; and w is the mass of the glycolyzed PET sample.

Synthesis of the polyester derived from PET

The synthesis of unsaturated polyester was carried out by introducing maleic anhydride into the reactor vessel together with the glycolyzed PET in a quantity based on the number of hydroxyl groups measured by titration. The polycondensation reaction was processed at 200°C until no more water was produced as a by product.

The molar mass of both glycolyzed PET and unsaturated polyester derived from PET was measured by gel permeation chromatography (GPC). For GPC analyses, samples were dissolved in tetrahydrofuran (THF) and inserted into polystyrene packed columns. Monodisperse polystyrene was used as the standard for GPC columns calibration.

Curing systems

Styrene is the traditional curing agent used in the commercial available unsaturated polyester resins. Besides styrene, the following comonomers were used in this work as curing agents: (1) 1/1 weight ratio of styrene and methacrylic acid; (2) 1/1 weight ratio of styrene and maleic anhydride. Both methacrylic acid and maleic anhydride can generate acid functionalities that can potentially interact with inorganic surfaces.

The final composition used in the formulation of the unsaturated polyester resins containing the curing agents and initiator/catalyst systems was typically: 68.5 wt % of unsaturated polyester resin; 30 wt % of curing agents; 1.0 wt % of methyl ethyl ketone peroxide (MEKP); and 0.5 wt % of cobalt naphtenate. MEKP and cobalt naphtenate are respectively, the initiator and the accelerator of the radical polymerization.

Production of polyester concretes

Two types of unsaturated polyester resins were used in the formulation of the concretes: (1) unsaturated polyester derived from glycolyzed PET; (2) traditional unsaturated polyester based on isophthalic acid.

The composition of the concretes included the following inorganic aggregates: 10 wt % of fly ash;

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TABLE I
Compositions of the Produced Polyester Concretes

</div>

| | Unsaturated polyester resin (12 wt %) | | | |
Sample	Polyester source (68.5 wt %)	Curing agent (30 wt %)	Initiator (1.0%)/catalyst (0.5%)	Aggregates: 88 wt % fly ash, sand, and gravel
1	PET	Styrene	MEKP/Co nap.	Dried
2	Isophthalic acid	Styrene	MEKP/Co nap.	Dried
3	Isophthalic acid	Styrene	MEKP/Co nap.	+5% wt of water
4	Isophthalic acid	Styrene/methacrylic acid	MEKP/Co nap.	Dried
5	Isophthalic acid	Styrene/maleic anhydride	MEKP/Co nap.	Dried
6	Isophthalic acid	Styrene/maleic anhydride	MEKP/Co nap.	+5% wt of water

35 wt % of sand (average particle size close to 0.3 mm); and 43 wt % of gravel (particle size equal to 5 mm). Table I reports the composition of the produced samples. After mixing all the components with the unsaturated polyester resin, cylindrical samples measuring 50 mm in diameter and 100 mm in height were produced by casting the mixture in metal molds.

The kinetics of cure

The curing rate of the polyester resins was measured by infrared spectroscopy (FTIR) by using a FTIR spectrometer (Perkim Elmer, Paragon 1000) with a horizontal ATR (attenuated total reflection) accessory. A 1-mm thick layer of unsaturated polyester containing the initiator, accelerator, and curing system was applied to the surface of a zinc selenide ATR crystal. Four scans were used each 30 s to monitor the polymerization.

The degree of conversion of carbon double bonds to single bonds during polymerization was calculated based on the ratio between the absorbance of the aliphatic C=C peak (1630 cm^{-1}) and the absorbance of the C=O peak (1715 cm^{-1}).[12] The degree of monomer conversion (DC) was calculated by subtracting the % C=C from 100%.

$$DC\,(\%) = 100 - \frac{[\text{Abs}(1630\text{ cm}^{-1})/\text{Abs}(1715\text{ cm}^{-1})]_{\text{polymer}}}{[\text{Abs}(1630\text{ cm}^{-1})/\text{Abs}(1715\text{ cm}^{-1})]_{\text{monomer}}} \times 100 \quad (2)$$

ASTM D-2471 standard was used to determine the gel time of the resins. This standard defines the time for gelation to occur as the moment in which no adhesion between a wood stick and the surface the sample undergoing polymerization could be observed.

Morphological and mechanical analyses

Mechanical tests were used to determine the strength of the polyester concretes in compression. Mechanical tests were all performed a week after the preparation of the samples. At least five samples were tested. The ABNT NBR 5759 standard was used to measure the mechanical strength of the polyester concretes. This standard is usually used to measure the mechanical strength of both polyester concretes and Portland concretes and defines the size of the samples and conditions of the test. The mechanical tests were performed in a Universal Testing Machine Dinateste having a 20 ton load cell.

Scanning electron microscopy (SEM) was used to investigate the morphological features of the fracture surface of the concretes. The fracture surfaces were coated with gold before SEM analysis.
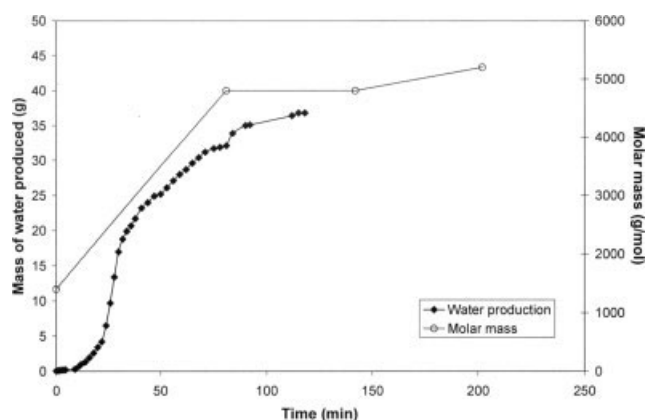
RESULTS AND DISCUSSION

Figure 2 shows GPC results of samples collected during the PET glycolysis. It can be seen that, in less than 2 h of reaction, PET molar mass was reduced to values close to 1800 g/mol. By extending the reaction longer, a more pronounced reduction in molar could be observed that finally had a trend to level up after 10 h. A reduction in the molar mass of PET to values lower than 1500 g/mol is import in the manufacture of the unsaturated polyester due to two basic factors: (1) these low molar mass species display lower values of viscosity; (2) the presence of these oligomers ensures a high degree of homogeneity in the distribution of the unsaturated groups throughout the polyester molecules.[9]

The synthesis of unsaturated polyester based on PET oligomers was also monitored by GPC. Results are displayed in Figure 3. Also in Figure 3, the rate of evolution of water during the reaction between PET oligomers and maleic anhydride is shown. The results revealed that, by starting with PET oligomers having molar mass close to 1400 g/mol, unsaturated polyester molecules with values of molar mass of 5000 g/mol could be obtained after 2 h of reaction. The highest rates of reaction were seen during the first 30 min of the reaction. The same result could be observed by checking the formation of water during the polycondensation reaction.
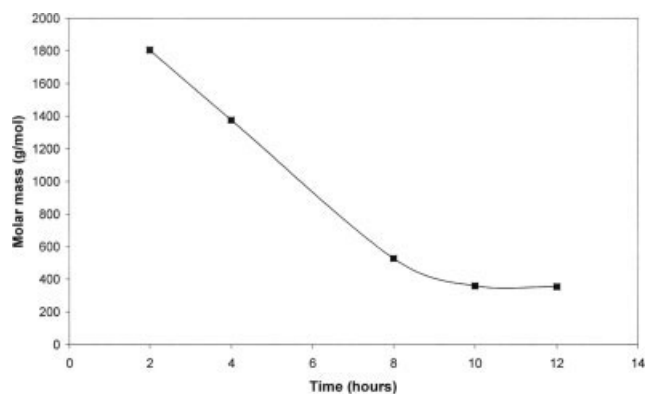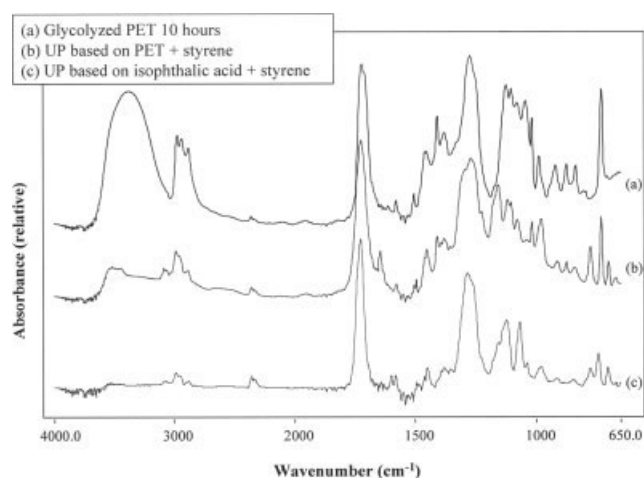
Figure 2 Kinetics of PET glycolysis monitored by GPC.

The formation of unsaturated polyester derived from the reaction between glycolyzed PET and maleic anhydride was also monitored by FTIR. Figure 4(a) shows FTIR spectrum of a PET sample after 10 h of glycolysis that exhibits clearly the presence of typical IR (infrared) bands due to PET molecular structure, such as the 1720 cm^{-1} absorption band associated with the carbonyl group and the 1270 cm^{-1} absorption band that can be related to the C—O bond.[13] Major IR assignments for the components used in this work are described in Table II. In Figure 4(b), the spectrum of the unsaturated polyester, produced by the condensation reaction between glycolyzed PET and maleic anhydride and containing styrene, is shown. In this spectrum, a reduction in the intensity of the 3400 cm^{-1} IR band due to OH groups indicates that the condensation reaction between anhydride and hydroxyl groups had been processed, leading to the formation of the unsaturated polyester. IR bands assigned to aliphatic C=C bonds (1630 cm^{-1}) derived from both styrene and unsaturated polyester can be observed together with other bands typical of styrene, such as 756 and 698 cm^{-1} (Table II) in Figure 4(b,c) (spectrum of the

Figure 4 FTIR spectra of PET oligomers (a), unsaturated polyester (UP) derived from PET containing styrene (b) and unsaturated polyester derived from isophthalic acid containing styrene (c).

unsaturated polyester derived from isophthalic acid containing styrene).

FTIR spectra of unsaturated polyesters (based on isophthalic acid) having different curing systems are shown in Figure 5. Among the spectral differences observed in Figure 5, the presence of more intense absorption bands at 3400 cm^{-1} for the unsaturated polyester systems containing methacrylic acid [Fig. 5(b)] and maleic anhydride [Fig. 5(c)] demonstrates the incorporation of OH groups derived from acid functionalities in the systems when compared with the spectrum of more traditional unsaturated polyester having styrene as curing agent [Fig. 5(a)]. These functionalities were introduced to enable the formation of strong linkages between the components of unsaturated concretes, such through ionic bonds. In the FTIR spectrum of unsaturated polyester containing maleic anhydride [Fig. 5(c)], absorption bands at 1840 cm^{-1} and 1790 cm^{-1}, due to C=O stretching

Figure 3 Kinetics of the production of unsaturated polyesters based on the reaction between PET oligomers and maleic anhydride.

TABLE II
Major IR Absorption Bands Observed in the Components Used in this Work

| Wavenumber (cm^{-1})	Assignment
3400	OH stretching
3060	Aromatic C—H stretching
2960, 2880	Aliphatic C—H stretching
1840, 1790	C=O stretching in maleic anhydride groups
1713	C=O stretching in maleic acid groups
1740–1720	C=O stretching in ester and carboxylic acid groups
1630	Aliphatic C=C stretching
1465	—CH$_2$— deformation band
1270	C—O stretching in ester bonds
1070	C—H bending vibration of ring in plane
756	C—H out-of-plane bending vibration of ring
698	C—H out-of-plane bending vibration of ring
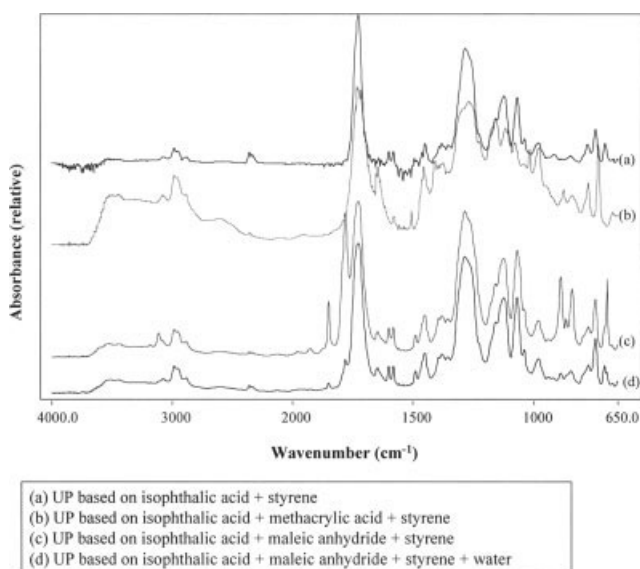
Figure 5 FTIR spectra of unsaturated polyesters (UP) containing different curing systems.

vibrations, show that anhydride functionalities were incorporated into the system.[14] These functionalities were effectively converted to acid functionalities by adding 5% of water to the unsaturated resins, as observed in the FTIR spectrum shown in Figure 5(d), in which no absorption bands in the 1840–1790 cm^{-1} range were detected. It is known that anhydride functionalities are usually instable and readily converted to acid functionalities. This type of conversion will possibly occur when unsaturated polyester resin containing maleic anhydride as curing agent would interact with inorganic aggregates that naturally have high levels of humidity. The formation of acid functionalities is important since one of the goals of this work involves the incorporation of ionic linkages among the components of polyester concretes.

FTIR was also useful in this work to determine the rates of cure of the different unsaturated polyesters. By monitoring the evolution of the IR band associated with the C=C bond, it was possible to follow the kinetics of polyester cure. As an example, Figure 6 shows FTIR spectra between 1600 and 1800 cm^{-1} of an unsaturated polyester sample derived from isophthalic acid during polymerization. In this figure, it is shown that the height (absorbance) of the 1630 cm^{-1} absorption band decreases as a function of time. Reduction on the 1630 cm^{-1} peak height is an evidence of the consumption of C=C bonds during free radical polymerization. Data provided by spectra in Figure 6 was used to calculate the degree of monomer conversion using eq. (2).

The degree of conversion obtained from FTIR measurements is plotted as a function of time in Figure 7(a) for polyesters containing different curing
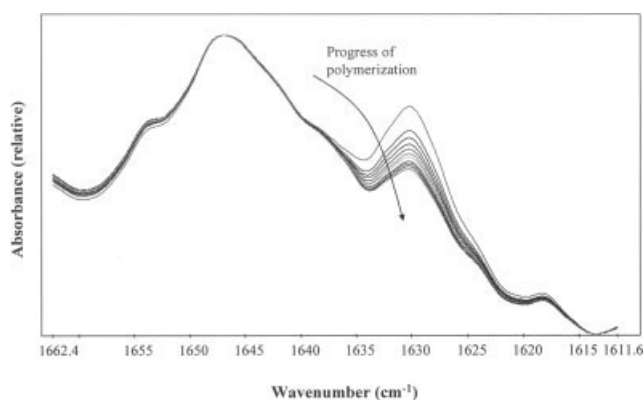
Figure 6 Evolution of the polymerization of unsaturated polyesters monitored by real time FTIR.

systems: (a) polyester derived from isophthalic acid containing styrene as a curing agent; (b) polyester derived from PET containing styrene as a curing

(a) Polyester derived from isophthalic acid + styrene
(b) Polyester derived from PET + styrene
(c) Polyester derived from isophthalic acid + styrene + methacrylic acid
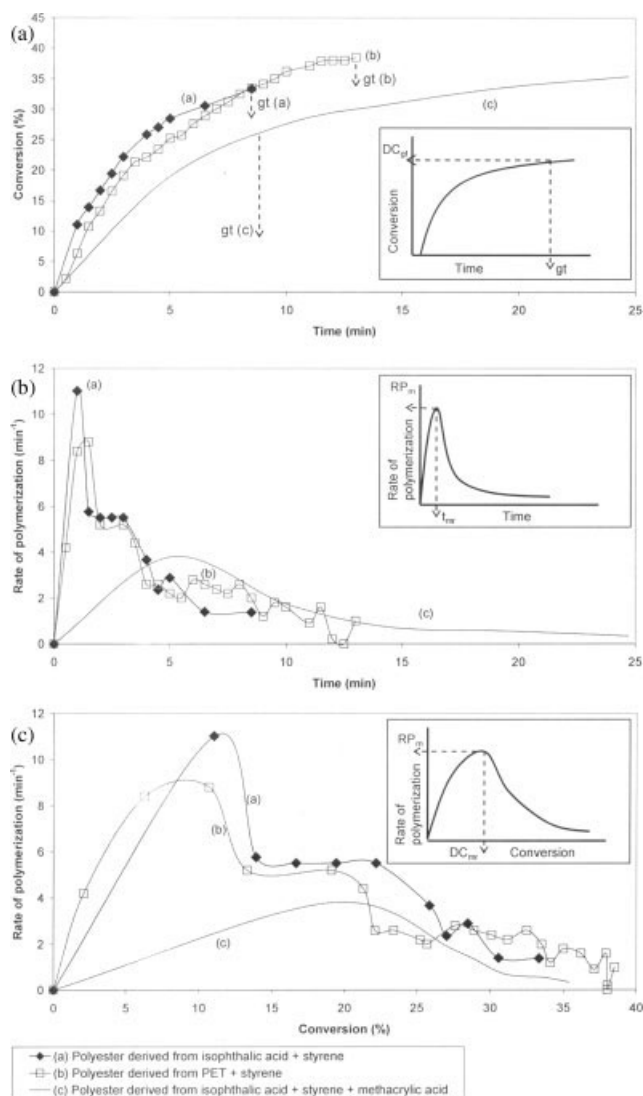
Figure 7 Kinetic curves obtained from FTIR real time measurements.

TABLE III
Kinetic Parameters Obtained from FTIR Experiments

Types of polyesters		Kinetic parameters				
Polyester source	Curing agent	DC_{gt} (%)	RP_m (% min^{-1})	DC_{mr} (%)	t_{mr} (min)	gt (min)
Isophthalic acid	Styrene	30.0	11.2	11.5	1.0	7
PET	Styrene	38.5	8.7	9.1	1.5	13
Isophthalic acid	Styrene/methacrylic acid	27.6	3.9	19.8	5.2	9

agent; (c) polyester derived from isophthalic acid containing styrene and methacrylic acid as curing agents. The kinetic data obtained from FTIR experiments (Fig. 6) were also converted into polymerization rate by taking the first derivative of the time versus conversion curves [Fig. 7(b)]. Conversion was also plotted against the rate of polymerization in Figure 7(c). Important kinetic parameters were obtained from the curves for each material,[15,16] such as: (1) the degree of conversion at the gel time (DC_{gt}); (2) the maximum rate of polymerization (RP_m); (3) the degree of conversion at the maximum rate of polymerization (DC_{mr}); (4) time during the polymerization that led to the maximum reaction rate (t_{mr}). As described in the Experimental Section of this work, the gel time (gt) was measured by applying the ASTM D-2471 standard. These parameters are reported in Table III.

The overall shape of the kinetic curves in Figure 7(a,b) is useful to identify typical stages of polymerization based on free radical chain polymerization.[15] It is possible to observe that all curves display the so called auto acceleration phenomenon at low degrees of conversion. This behavior is due to the difference between the propagation and the termination steps of the chain polymerization and also due to the extremely high viscosities of concentrated polymer systems. At low conversion, termination requires the reaction between one long and one short macroradical. Microradicals and macroradicals are active chains of different sizes that can grow by incorporating nearby monomer molecules. As conversion increases, the mobility of macroradicals becomes progressively more restricted as a consequence of the increase in viscosity, reduction in the free volume, formation of microgels, macrogels, and entanglements. This series of factors lowers the effective termination rate constant, and the net effect is to increase the rate of polymerization. Auto acceleration stops when the polymer system becomes rigid enough, i.e., when the glass transition temperature of the monomer-polymer blend becomes higher than the temperature of the reaction (vitrification). At this point, the chains become essentially immobile and even the propagation reaction starts to be diffusion limited and, hence, the overall rate of polymerization decreases.

The maximum rate of polymerization (RP_m), shown in both Figure 7(b) and Table III, represents the magnitude of the auto acceleration process. For the three resins studied using FTIR real time measurements, the results showed that auto acceleration was more pronounced for polyester derived from isophthalic acid having styrene as curing agent, possibly due to the fact that this resin has a lower viscosity that can enhance molecular interactions and improve reactivity. On the other hand, a low value of the maximum reaction rate was observed for the polyester system containing methacrylic acid, as a possibly evidence that polar species can reduce the effectiveness of free radical generation and propagation. It is also possible to observe in Figure 7(b) that some rate versus time curves display bimodal profiles in which there are shoulders after the polymerization rate maxima. Bimodal kinetic profiles have been also observed by other authors while studying the kinetics of polymerization.[15] A possible mechanism to explain this behavior involves the fact that monomers react initially through primary cyclization instead of forming crosslinks. The formation of these microgels would then delay the onset of the diffusion limitation and auto acceleration. Microgels entrap unreacted double bonds and radicals. As the polymerization proceeds, microgels would then merge together to form macrogels that can release entrapped radicals and monomers to improve the polymerization rate.

In Table III, the time in which the maximum polymerization rate (t_{mr}) occurred is shown for the polyesters studied by FTIR. This parameter can indicate the window of time available for the macroradicals to grow until the formation of a too rigid polymer structure (vitrification) that freezes all the system, reduces the polymerization rate and restricts the ability of the macromolecules to flow to relieve stress derived from the polymerization shrinkage. Results showed that vitrification was very fast for all the analyzed systems. Only for the polyester system containing methacrylic acid, the time for vitrification to occur (t_{mr}) was a little longer, possibly, due to the presence of hydrophilic molecules that reduces the overall curing rate.

The degrees of conversion at the maximum rate of polymerization (DC_{mr}) are also reported in Table III.

TABLE IV
Mechanical Properties and Gel Time of the Different Types of Unsaturated
Polyester Concretes and Portland Concretes

		Sample	State of aggregates	Gel time (min)	Compressive strength (MPa)
1	PET	Styrene	Dried	20	52.2 ± 3.7
2	Isophthalic acid	Styrene	Dried	10	46.5 ± 2.0
3	Isophthalic acid	Styrene	+ 5% wt of water	ND[a]	0.0 ± 0.0
4	Isophthalic acid	Styrene/methacrylic acid	Dried	13.5	62.6 ± 1.2
5	Isophthalic acid	Styrene/maleic anhydride	Dried	5	46.9 ± 1.0
6	Isophthalic acid	Styrene/maleic anhydride	+ 5% wt of water	15	27.0 ± 1.0
7	Portland cement[b]	Aggregates: sand/gravel (30/45 wt %)	Dried	2880	35

For Samples 1–6: Polyester source (68.5 wt %) and Curing agent (30 wt %); for Sample 7: Portland Cement and Aggregates: Sand/gravel (wt %).
[a] ND = not detected.
[b] Data from Ref. 9.

These results, combined with the gel time measured using the ASTM D-2471 standard, demonstrated that vitrification at lower degrees of conversion enlarged the time for gelation (gt) to occur, i.e., the formation of the polymer network through crosslink bonds is delayed because of the low mobility of the macroradicals locked inside the vitrified system. The polyester system based on PET vitrified at the lowest conversion of all the analyzed systems and also had the longest gel time. This result may be related to the fact that PET based polyesters have a more rigid chain backbone (derived from terephthalic acid) that can be responsible for higher viscosities and a faster increase in the glass transition temperature during polymerization. For all the investigated polyester systems, conversion at the gel time (DC_{gt}) had values close to 30%. Therefore, roughly one third of the carbon double bonds were required to be broken to produce the three dimensional polymer networks. In unsaturated polyester systems, although slowly, polymerization should proceed even after gelation and should result in conversion higher than 65%. The magnitude of the autoacceleration process (RP_m) did not seem to affect the conversion at the gel point, since systems with either high or low values of maximum polymerization rate had conversions close to 30% at gelation. This result indicates that, although the rigidity of the network reached at the end of the auto acceleration step reduces dramatically the rate of polymerization, it does not eliminate the possibility of a slower reaction rate that progressively improves conversion. Fast vitrification that occurs at high rates of polymerization can create a temporary excess of free volume that allows molecules to have enough mobility to still interact at lower rates.[16] On the other hand, delayed gelation also enables molecules and radicals to react more successfully for longer periods of time at conditions of lower viscosities.

Table IV reports the gel time and the compressive strength of the concretes obtained by mixing the dif-

ferent types of resins with aggregates as described also in Table I. The measured gel times for the concretes correlated well with the overall kinetics of polymerization studied by FTIR. The values of gel time for the concretes were on average 30% higher than those observed for the pure resins, as an indication that the inorganic aggregates can affect the polymerization rate by providing surfaces for monomer and macroradicals to adsorb. Adsorption onto surfaces reduces the overall diffusion rate of the species that consequently would reduce molecular interactions and the polymerization rate.

Concretes derived from unsaturated polyester based on PET and having styrene as curing agent showed slight higher values of mechanical strength than concretes obtained from unsaturated polyester based on isophthalic resins containing also styrene. This result is due to the fact that terephthalic acid units derived from PET have para linkages that contribute to the enhancement of chain orientation and packing efficiency and consequently to higher mechanical properties. The introduction of methacrylic acid together with styrene in the formulation of the curing system for isophthalic acid derived polyester resulted in a major increase (35%) in mechanical strength of the concretes when compared to the same polyester but containing only styrene as curing agent. This fact may mean that acid functionalities due to the presence of the methacrylic acid repeat unit could have allowed the formation of stronger interactions between chains and between them and the hydrophilic surfaces of the aggregates. The use of maleic anhydride combined with styrene as the curing agent for unsaturated polyesters led to the production of concretes with comparable strength of polyesters containing only styrene. Although in this case acid functionalities again could have been generated, the fast observed gelation could have restricted densification of this type of concrete, leading consequently to a less homogeneous and less dense
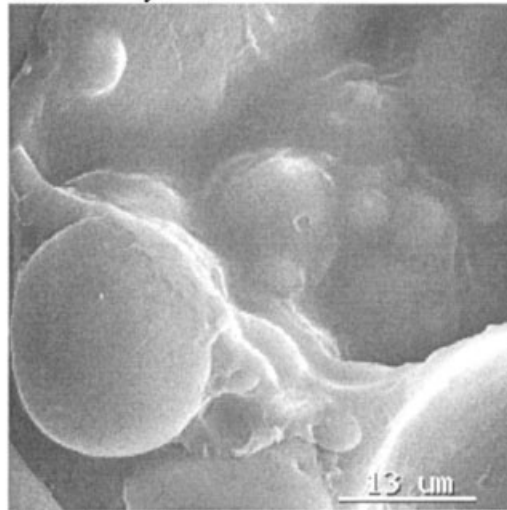
(a) Polyester concrete derived from isophthalic acid containing styrene
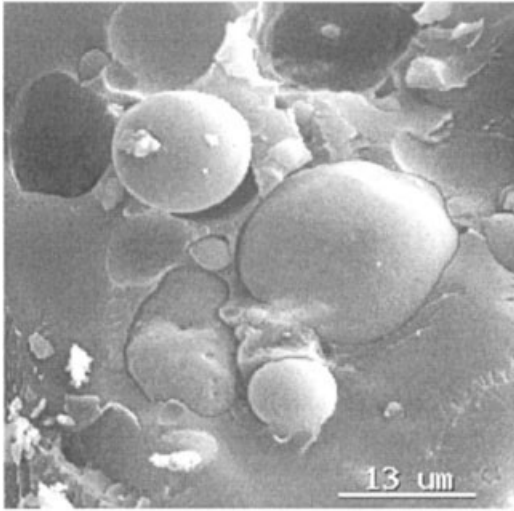
(b) Polyester concrete derived from isophthalic acid containing styrene and maleic anhydride
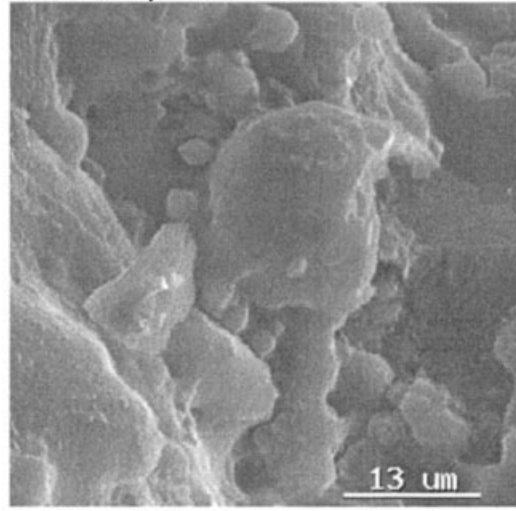
(c) Polyester concrete derived from isophthalic acid containing styrene, maleic anhydride and water

Figure 8 Scanning electron micrographs of the fracture surfaces of polyester concretes containing different curing systems.

material that would not have ability to show any major enhancement in mechanical properties.

Table IV shows also that wet aggregates restricted the gelation of the polyester concrete containing only styrene as the curing agent. Otherwise, when maleic anhydride was used together with styrene not only gelation occurred but also concretes with low but reasonable mechanical properties were obtained. This result can be explained by considering that acid functionalities inserted into the polymer network can generate ionic cages when combined with cations (Ca^{2+}, Al^{3+}) leached from the aggregates that can trap water molecules, reducing their abilities towards restricting both the curing process and the

formation of strong interchain and interfacial interactions. In terms of the application of polyester concretes, the possibility of using aggregates with some content of humidity means that costs related to drying can be reduced leading to the production of a less expensive material that can replace in both properties and cost conventional Portland concretes.

Portland concretes can display a wide range of values of mechanical strength depending on their composition and processing. However, it is expected that a conventional Portland concrete (water/cement ratio = 0.5) would display a compressive strength of 35 MPa after 28 days of processing.[10] This value is also reported in Table IV only to give an idea of me-

chanical properties of Portland concretes when compared to the polyester concretes produced in this work. By using this value of mechanical strength of a Portland concrete as a reference, it would be possible to say that the polyester concretes developed in this work have comparable or higher values of strength in respect with Portland concretes. Even the ''wet'' polyester concrete displayed mechanical properties close to this reference value (indicating that this condition of processing may still yield valuable products).

Figure 8 shows SEM micrographs of the fracture surfaces of some of the investigated polyester concretes. In Figure 8(a), fly ash particles inserted into a polyester resin derived from isophthalic acid and styrene can be clearly observed. The presence of well-defined interfaces and detachment of particles is an evidence of a low degree of interaction between inorganics and the polymer matrix. Lower levels of particle detachment can be seen in the micrograph shown in Figure 8(b) that can indicate higher levels of adhesion between polymer and inorganic particles in the system consisted of the same polyester derived from isophthalic acid and maleic anhydride. Even higher levels of adhesion can be suggested by the micrograph in Figure 8(c) (polyester concrete derived from isophthalic acid containing styrene, maleic anhydride, and water), in which polymer films cover partially the surfaces of the inorganic particles, indicating that the interfacial strength was high enough to force the crack to propagate thorough the polymer matrix. This result can be attributed to the formation of stronger electrostatic interactions between polymer and inorganic surfaces due to the presence of acid functionalities derived from the conversion of maleic anhydride to maleic acid in the presence of water.

CONCLUSIONS

In this work, monomers containing acid functionalities, such as methacrylic acid and maleic anhydride, were incorporated into polyester concretes. The polyester concretes containing these acid monomers demonstrated to yield materials with higher mechanical properties than polyester concretes containing only styrene. It was also observed that polyester con-

cretes containing acid monomers, such as maleic anhydride, were successfully polymerized even in the presence of water (introduced to simulate the use of wet aggregates), yielding concretes with lower but reasonable mechanical properties.

Polyester concretes were also obtained by replacing more traditional unsaturated polyesters based on isophthalic acid with unsaturated polyesters derived from PET bottles. Oligomers obtained by the glycolysis of PET bottles were successfully reacted with maleic anhydride to yield unsaturated polyesters resins to be used in the production of polyester concretes. Polyester concretes obtained by using glycolyzed PET had values of compressive strength higher than polyester derived from isophthalic acid.

Results of this work showed that polyester concretes derived from recycled PET and containing acid functionalities can expand the use of this material by improving properties and reducing cost (through the use of less expensive recycled raw materials and by enabling the use of wet aggregates) when compared to more traditional polyester concrete formulations.

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