WATER-DISPERSIBLE, BIODEGRADABLE COPOLYESTERS FROM PET WASTES. I. INVESTIGATION OF HYDROPHILIC CHARACTER

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The paper presents results concerning copolyesters made from recycled poly(ethylene terephthalate) (PET) wastes, ethylene and diethylene glycol (EG and DEG), isosorbide (ISOS), adipic and succinic acid (AA and SA), and 1,3-dimethyl isophthalate 5-sodium sulfonate (DMIS). AA and AS are used to induce biodegradability, DMIS gives water dispersability, whereas ISOS significantly improves the physico-chemical and thermal properties of the copolyesters. In addition, ISOS derives from biomass that is a renewable source. The samples are characterized by ^{1}H-NMR, FTIR-ATR and UV-Vis proving the presence of aromatic and aliphatic protons, of ester and sulfonic groups, and of aromatic state. The copolyesters have good solubility in water, ethylene glycol and chloroform, and do not dissolve in alcohols, acetone and toluene. They give positive response to the qualitative test for surface active agents, but the surface tension measurements show only a feeble surfactant character. The reduced viscosity and turbidity data reveal that all the samples have polyelectrolyte features. These results demonstrate the hydrophilicity of the PET copolyesters, and recommend them as biodegradable, water-dispersible, film forming agents.

INTRODUCTION

Nowadays, the concept of environmental sustainability is increasingly used in connection with international standards enforcing to work and interact in ways that do not affect the living systems and the natural resources. The main components of the concept are elimination of wastes, removal of toxic emissions, and finding renewable sources opposed to classical feedstocks.

Poly(ethylene terephthalate) (PET) is an aromatic polyester with excellent thermal and mechanical resistance, outstanding chemical properties and transparency, which is mainly used for fibers and packagings. The world production of PET was of 13 million tons in 1997 and of 49 million tons in 2008.[1, 2] According to these figures, the world's total polyester production will exceed 55 million tons in 2010. More than one-third of this quantity is for bottles to packaging carbonated soft drinks, water, beer, juice, etc. However, PET is nonbiodegradable being a long term pollutant of the environment. This produces huge amounts of accumulated wastes, PET being one of the largest post-consumer plastic in landfills. Therefore, a key issue is nowadays the PET conversion into reusable products.[3] PET recycling is also important for conservation of oil resources, reduction of greenhouse effect, and energy preservation.[4] In this respect, a very recent release of PETCORE unveiled that European post-sorting PET collection was of 1.4 million tons in 2009.[5]

According to the principles of sustainable development, chemical recycling is the most acceptable technique for PET because it gives both parent raw materials and secondary value-added products.[6,7] Chemical recycling mainly includes: glycolysis, methanolysis, hydrolysis and aminolysis or ammonolysis.[3] Polyethylene terephthalate can be conclusively recycled using a wide spectrum of degrading agents eventually followed by (trans)esterification with mono- or dicarboxylic

saturated or unsaturated acids (or derivatives). This allows preparing precursor oligoesters for co-polymers with tailored properties.[1, 8, 9]

In the framework of friendly interaction with the environment, the development of ecologic products is becoming increasingly important. In recent years, there has been a great need for biodegradable polymeric materials, since waste polymers cause serious destruction of the environment.[10, 11] Many biodegradable polymers have been developed for biomedical applications,[12] packaging films and conteiners,[13] sheathing material for agricultural uses,[14] etc. At the same time, requirements regarding low emission of organic volatile compounds upon the environment have resulted in manufacturing various novel water dispersible or compatible polymers.[15, 16]

On the other hand, using renewable resources, as an alternative to standard petrochemicals, comes in the framework of more and more pregnant worldwide trend for manufacture of materials based on biological products.[17, 18] The chemical structure of PET backbone can be modified using suitable comonomers conferring to the resulted copolyesters targeted properties such as biodegradability,[19-21] water dispersibility[22] and thermal stability.[23]

This paper presents the synthesis and results obtained by investigating the hydrophilic character of several copolyesters developed by our team using PET wastes, different diols, isosorbide (ISOS) a product derived from biomass, aliphatic dicarboxylic acids (ADA) and 1,3-dimethyl isophthalate 5-sodium sulfonte (DMIS). ADA and DMIS were used to provide biodegradability, and to confer water dispersability to the copolyesters, whereas significant improvements of their physico-chemical properties were achieved by introducing the ISOS moieties along the polymer chain. The copolyesters were characterized by ^{1}H-NMR, FTIR-ATR and UV-Vis. Information about their hydrophilic character were obtained from solubility and qualitative tests of surfactant behavior, and from measurements of surface tension, viscosity and turbidity.

EXPERIMENTAL

Materials

Post-consumer PET from recycled bottles was used for the degradation process. They were cut in flakes of 6-8 mm, washed with clean water and dried at 100 °C for 2 hours. The intrinsic viscosity determined according to ASTM D4603 was of 0.77 dL/g. Ethylene glycol (EG), diethylene glycol (DEG), isosorbide (ISOS), succinic anhydride (SA), adipic acid (AA), 1,3-dimethyl isophthalate 5-sodium sulfonate (DMIS) and titanium (IV) *iso*-propoxide (TTP) (catalyst) were of reagent grade and used as received. Solutions were prepared with ultrapure water obtained from a Millipore UV Simplicity apparatus.

Synthesis

PET solvolysis and esterification reactions were conducted in a stainless steel reactor of 1L, equipped with anchor agitator, reflux condenser, nitrogen inlet, and vacuum system for evacuation of the esterification by-products. The reactor was heated by means of an electrical mantle connected to an automatic controller by a thermo-couple linked to a temperature regulation device.

Degradative transesterification

PET wastes were depolymerized in the presence of oligo-esters of the aromatic and aliphatic diacids with different diols, previously or in situ obtained, at mole ratios DMIS/total acids in the range of 0.08-0.1, aliphatic dicarboxylic acid/total acids in the range of 0.2-0.3, and EG/DEG/ISOS in the range of 35-90/10-50/0-21, using 0.1 % wt, based on the weight of PET, TTP as transesterification catalyst. The reactions took place at atmospheric pressure under nitrogen, at 190-240 °C, during 4-5 hours, and were controlled by the evolved amount of stoichiometric by-products.

Polycondensation

The solvolysis products of PET were subjected to polycondensation, at 240-280 °C and under 3-5 mm col. Hg vacuum, during 3-4 hours. Some glycols distilled off, as a result of polymer chain growth.

Apparatus and methods

The final products and intermediates were analyzed using various analytical techniques. The melting temperature range, T_m, was measured using a Boetius apparatus. Acid and hydroxyl numbers were obtained by chemical titration. Intrinsic viscosity [η] was determined with Ubbelohde viscometer, using phenol/tetrachloroethane 1:1 (wt/wt) as solvent. The relative viscosities were measured with an Ostwald apparatus having a flow time for water higher than 100 s. In both cases, the measurements were done at 25 °C with an error of ± 0.1 s. DSC analysis was performed under nitrogen with a Netzsch DSC 204 F1 Phoenix apparatus, in the temperature range -50 ÷ 200 °C, at a heating rate of 10 °C/min.

^{1}H-NMR spectra were recorded on a Varian Gemini spectrometer operating at 300 MHz, with supraconductive magnet, using $CDCl_3$ as solvent. FTIR measurements were done on a Nicolet iZ10 FT-IR module, Thermo Scientific spectrophotometer equipped with crystal diamond. The spectra were processed by ATR correction and by introducing proper baselines. The OMNIC spectroscopic software was used for data handing. Thirty-two scans were collected at a resolution of 4 cm^{-1}, from 4000 to 650 cm^{-1}. The UV-Vis measurements were carried out with the aid of a Varian-Cary 100 Bio apparatus using 1 cm quartz cells. The spectra were recorded in the 200-800 nm range. The turbidities were measured on the same apparatus at 610 nm.

Surface tensions were measured by the ring method. The data were collected from a K11, Krüss apparatus. The error of measurement was of ± 0.08 %.

The test for surfactant behavior of modified PET samples was done according to Reid et al.[24]

The main physico-chemical characteristics of the copolyesters synthesized from recycled PET are shown in Table 1.

Table 1

Main data of copolyesters obtained from recycled PET

	Co-monomers used for PET modification							Physico-chemical characteristics				
	Acid, % mol/total acid component				Diol, % mol/total diol component			Melting range, °C	T_g, °C	I_A, mg KOH/g	I_{OH}, mg KOH/g	$[\eta]$, dL/g
	AT	AS	DMIS	AA	EG	DEG	ISOS					
CO-PET3	65	-	10	25	40	60	-	75 - 132	15	2.8	12.5	0.39
CO-PET6	70	-	10	20	15	70	15	86 - 152	33	1.4	11.9	0.38
CO-PET7	72	20	8	-	15	70	15	122 - 172	34	3.9	9.6	0.42
CO-PET8	67	25	8	-	10	70	20	120 - 176	36	2.3	6.8	0.48
CO-PET12	70	-	8	22	30	50	20	85 - 118	36	3.0	10.9	0.35

RESULTS AND DISCUSSION

The copolyester samples were characterized by ^{1}H-NMR, FTIR and UV-Vis. The characterization cycle also included determinations of solubility in water and in organic solvents, and the qualitative test for anionic surfactants. They were completed with surface tension, viscosity and turbidity measurements on water solutions. The obtained results are presented in the following sections.

^{1}H-NMR

The chemical structure of all co-polyester samples was proved by ^{1}H-NMR analysis. The spectra show the characteristic signals and chemical shifts. Two symmetrical multiplets at 1.6 and 2.3 ppm were attributed to eight protons from adipic acid. Broad singlets corresponding to succinic acid and to OH appear at 2.6 ppm and 2.5 ppm, respectively. The glycolic protons from EG and DEG are present in the 3.6-4.7 ppm range. The most deshielded signal at 4.69 ppm corresponds to intrachain EG groups. The two large signals at 3.9 and 4.5 ppm belong to the protons of intrachain DEG units and the signals from 3.70 to 4.42 ppm belong to DEG end chain. The broad signals in the 4.80-5.50 ppm range correspond to four protons, assigned to the four metin groups in the isosorbide moiety. Around 8.0 ppm are four aromatic protons. The signal is splitted due to non-equivalence of the terephthalic acid in the polymer. The broad signal centered at 8.3 ppm is of the aromatic protons in DMIS.

FTIR

FTIR spectroscopy is a powerful method for the structural and conformational characterization of polymers because the molecular vibrations are sensitive to bond strengths and configurations. The obtained FTIR-ATR spectra shown in Fig. 1 present an intense band at 1335-1375 cm^{-1}, which proves the presence of sulfonate groups in the synthesized PET copolyester samples. At the same time, the 700-1500 cm^{-1} region of the FTIR spectra, which is the finger print and individualizes the samples, reveals characteristic bands of the groups present in copolyesters. The bands that appear in the 1245-1270 cm^{-1} range are due to the single carbon-oxygen bonds. The most intense bands are in between 1710-1720 cm^{-1}, being characteristic to the carbonyl groups. The observed shift is generated by the different ratio between the terephthalate and the glycols in the samples. The spectra also have bands of medium intensity in the 2850-2960 cm^{-1} range, which belongs to the carbon-hydrogen bonds. Those of higher frequency are linked to the aliphatic bonds. The C-H aromatic bands appear at lower frequencies as shoulders of the aliphatics. The broad and very weak bands form 3300 to 3600 cm^{-1} are due to OH groups from residual glycols and water present into the samples.
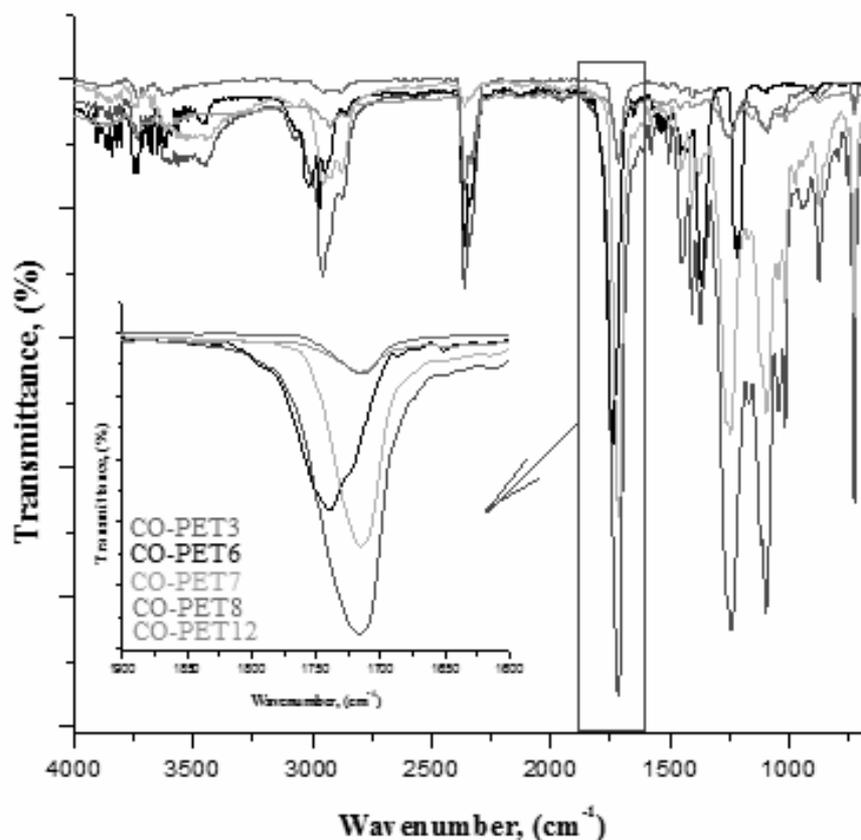
Fig. 1 – FTIR-ATR spectra of copolyester samples.

UV-Vis

Electronic transitions responsible for the UV-Vis spectra generally give information about the unsaturated groups present in the sample molecules. For example, olefins absorb in UV near 220 nm, aromatics in the 260 – 280 nm range, poly-nuclear aromatics from 260 to 500 nm, etc.[25] Any colored material will absorb in visible, the intensity being proportional to the number of chromophores giving rise to the absorption band. Although the UV-Vis is not as productive in information as FTIR, the method is very useful in identification of compounds bearing chromophores as well as in assessing their concentration.

We applied this technique to our copolyester samples. Fig. 2 shows the spectrum of CO-PET3 in water, ethylene glycol and chloroform. The spectra of the other copolyesters are similar and are not shown. No matter the solvent, the spectra reveal transparency of the samples in the near ultraviolet region, and have a sharp increase of the absorption at about 310 nm. The first absorption band of the CO-PET3 sample, which is the lowest energy band, displays a vibronic structure having maxima at 283 nm and 293 nm in water, at 291 nm and 297 nm in ethylene glycol, and at 281 nm and 294 nm in chloroform. This band belongs to the $n \rightarrow \pi^*$ transition, where a non-bonded electron of oxygen lone pair of the carbonyl group is excited to the corresponding antibonding π^* orbital. One may observe that peaks resulting from this transition are blue shifted with increasing solvent polarity. This arises from increased solvation of the lone pair which lowers the energy of the n orbital. The second absorption band appears at 240 nm in water, at 241 nm in ethylene glycol and at 253 nm in chloroform. For water and ethylene glycol these values are fairly similar with those mentioned in the literature, and are usually attributed due to the electronic $\pi \rightarrow \pi^*$ transition in the terephthalate chromophore.[26, 27] This transition describes the promotion of an electron from a bonding π orbital to an antibonding π^* orbital. In chloroform this transition is red shifted. It is caused by attractive polarization forces between the solvent and the absorber, which lowers the energy levels of excitated and unexcitated states.
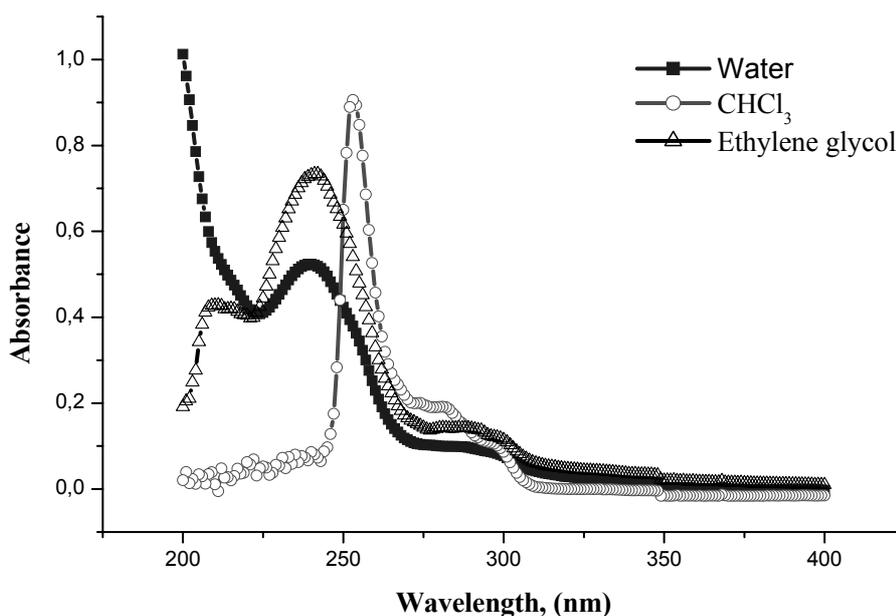
Fig. 2 – UV-Vis spectrum of CO-PET3 sample in various solvents.

Solubility test

Solubility of polymers depends on their chemical structure and on that of the solvent. Usually, it increases when the solubility parameters of polymer and solvent are similar. Besides the chemical structure, the physical state of the polymer is very important, the crystalline polymers being less soluble than the amorphous counterparts.[28]

The solubility of our copolyesters was tested in water as well as in organic solvents, and the results are presented in Table 2. It has to be noticed that all copolyesters are soluble in water at room temperature. In the tested organic solvents, our copolyesters dissolve in chloroform and ethylene glycol and are insoluble in methanol, isopropanol, acetone and toluene. Since all the samples are slightly soluble in chloroform this accounts for the lack of crystallinity of our copolyesters.[29]

Testing for anionic surfactant

Sulfonation of PET introduces ionic groups into the polymer and promotes solubility in water.[30] Because our copolyesters contain the 1,3-dimethyl isophthalate-5-sulfonate, it is important to test if they have surfactant character. The examination is done by titrating in acidic medium the aqueous copolyester solutions with a standard solution of cationic surfactant in water.[24] The appearance of precipitate indicates that the sample has surfactant features. All samples gave positive test, and one may affirm that the copolyesters belong to anionic surface active agents. However, this test is only qualitative and has to be confirmed by a specific method, like surface tension. The results of these measurements are presented in the following section.

Table 2

Solubility of copolyesters at 25 °C

Solute	Solvents						
	Water	Methanol	Isopropanol	Chloroform	Toluene	Acetone	Ethylene glycol
CO-PET3	s	i	i	s	i	i	s
CO-PET6	s	i	i	s	i	i	s
CO-PET7	s	i	i	s	i	i	s
CO-PET8	s	i	i	s	i	i	s
CO-PET12	s	i	i	s	i	i	s

s-soluble, i-insoluble.

Surface tension

Fig. 3 illustrates the dependence of surface tension on concentration of the aqueous copolyester solutions. The obtained graph has two parts connected by a break point. In the first, the surface tension decreases steeply with concentration, and is almost constant in the second. In the case of surfactants, the break point marks their aggregation into solution.[31] The phenomenon is explained by the fact that when dissolved in water, materials that contain a hydrophilic group distort the solvent structure and increase the free energy of the system. Surfactants do concentrate at the surface and orient the hydrophobic groups away from the solvent thereby minimizing the free energy of the system. The free energy of solution can be also reduced by aggregation when the surface active molecules form clusters such as micelles. In micelles, the hydrophobic groups of the surfactants are directed towards the interior whereas the hydrophilic parts are oriented to the solvent. If the distortion of the solvent structure by the hydrophobic groups is small, there is little tendency for micellization to occur. This is often the case of short-chain alkyl surfactants in water or of genuine surfactants in nonaqueous solvents. On the other hand, the surfactant molecules may experience some loss of freedom by confining into micelle. In the case of ionic surfactants, the loss of freedom comes from electrostatic repulsion with other similarly charged molecules in the micelle. These forces increase the free energy of the system and oppose to micellization. Whether micellization occurs in a particular system and at what concentration of monomeric surfactant only depends on the balance between the factors promoting and opposing to it.

A detailed inspection of data in Fig. 3 allowed us to extract the concentration and the surface tension values corresponding to the break point of copolyester solutions. The obtained values are summarized in Table 3. They reveal surface tension depressions of no more than 15 mN/m with respect to water, which are very small in comparison with those of the surfactants that amounts to 30-40 mN/m.[32, 33] This result shows that the synthesized copolyesters are not real surface active agents, in spite of their positive response to the surfactant test.
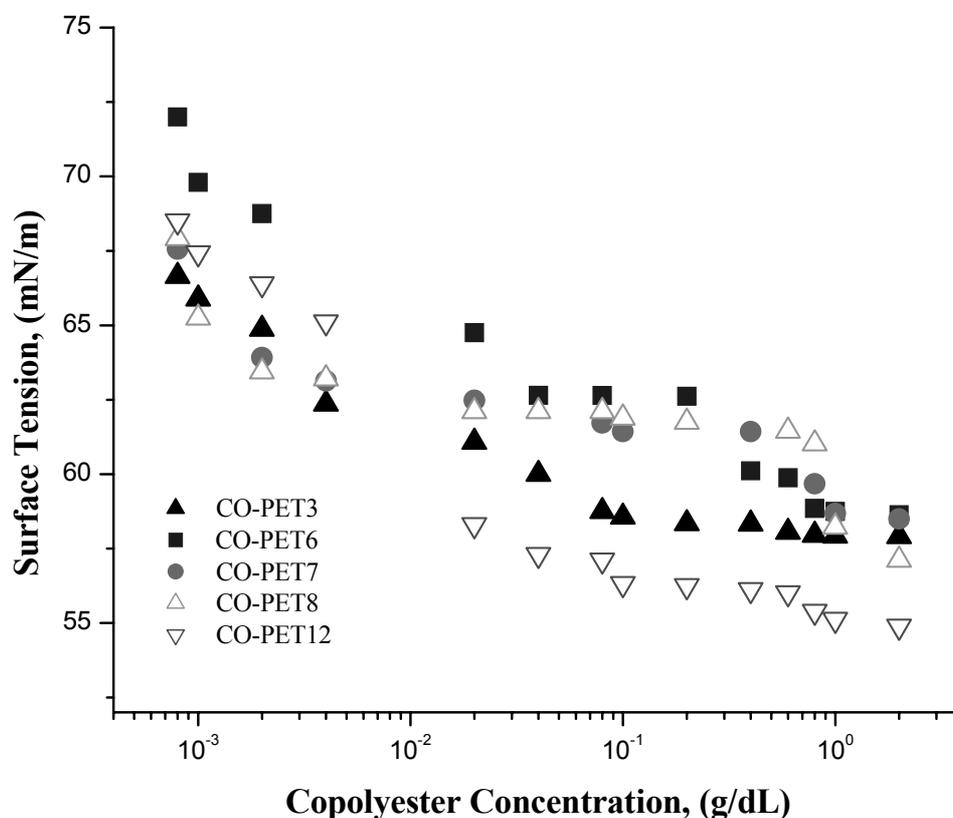

Fig. 3 – Surface tension isotherm of copolyester samples.

Surface tensions and aggregation concentrations of copolyesters in water

Copolyester	Surface tension at break point, (mN/m)	Aggregation concentration, (g/dL)
CO-PET3	58	1×10^{-1}
CO-PET6	62	5×10^{-2}
CO-PET7	62	2×10^{-2}
CO-PET8	62	2×10^{-2}
CO-PET12	57	4×10^{-2}

Viscosity

Viscosity is a convenient method to characterize polymers in solution. This can be done by measuring the efflux time of the solution, t, flowing through a capillary viscometer and comparing it to the corresponding time of the solvent, t_0. The viscosity is proportional with the efflux time multiplied through the densities of the liquids. Because the density of dilute solutions can be taken equal to that of the solvent, one can define the relative viscosity, η_{rel}, as the t/t_0 ratio. More insight about the behavior of copolyester samples in solution is given by the specific viscosity, η_{sp}. This parameter expresses the incremental viscosity

due to the presence of polymer in solution. By normalizing η_{sp} to concentration one obtains the reduced viscosity, η_{rel}/c, which is the incremental viscosity per unit concentration of polymer. The plot of reduced viscosity versus the polymer concentration is normally a straight line, and its extrapolation to zero concentration gives the intrinsic viscosity, $[\eta]$. $[\eta]$ is a very important parameter being a characteristic of each polymer. It is independent of polymer concentration but depends on the solvent used to measure the viscosity. Intrinsic viscosity also depends on the molecular weight of the polymer, and is a means to obtain the viscosity average molecular weight.
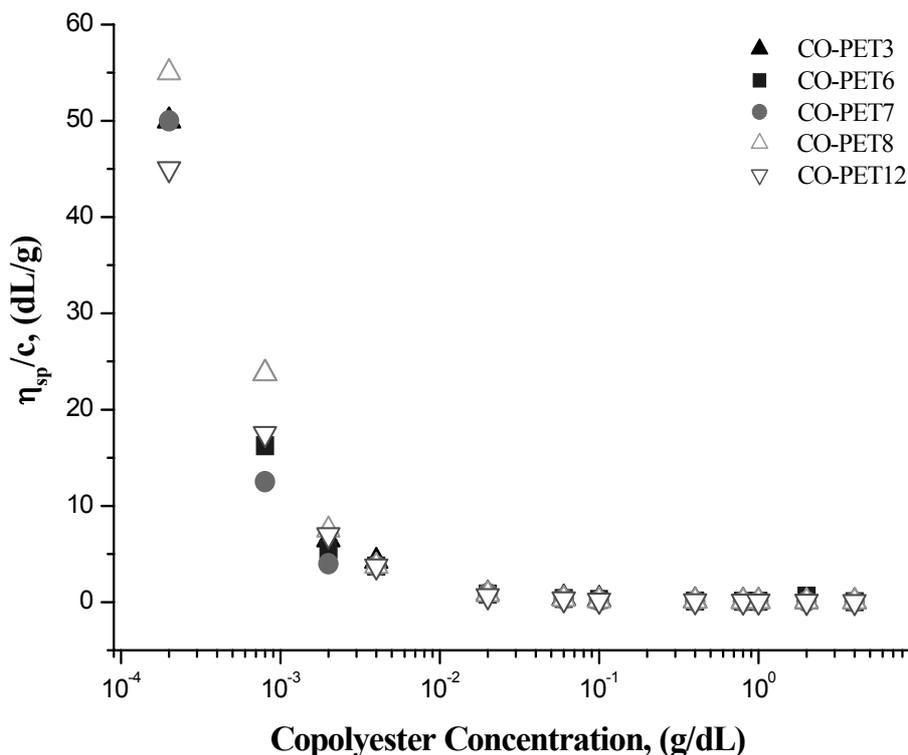

Fig. 4 – The change of reduced viscosity with copolyester concentration.

Fig. 4 is a plot of our reduced viscosity data versus the polymer concentration. Instead of straight lines, it unveils curves. The curves almost parallel the concentration axis at polymer

concentrations higher than 0.01 g/dL but increase steeply below 0.001 g/dL. This behavior is typical to polyelectrolytes, and is due to dissociation of the ionizable groups resulting charged polyions and an

equivalent number of counterions.[34,35] The phenomenon can be explained by the fact that the decrease of concentration produces in polyelectrolytes the increase of dissociation that is accompanied by increased coulombic repulsions between the ionic groups of the polyelectrolyte. These phenomena entail expansion of the polymer chain and lead to the observed increase of viscosity. Addition of low-molecular salt to the polyelectrolyte solution compensates the effect of the coulomb forces by shielding the dissociated ionic groups. This allows for extrapolation to zero concentration and determination of intrinsic viscosity. Unfortunately, attempts of dissolving the samples in 0.1 M NaCl were unsuccessfully because of phase separation. However, one has to mention that the intrinsic viscosities of polyester samples measured in a phenol/tetrachloroethane 1:1 solvent mixture (See Table 1) are lower as compared to the initial value of the non-modified PET ([η] = 0.77 dL/g, See Experimental). This is a consequence of either the introduction of the aliphatic units in the macromolecular chain or the diminishing of the molecular weight through solvolisis and copolycondensation.

Turbidity

Fig. 5 shows the optical transmittance as a function of surfactant concentration for the CO-PET aqueous solutions. In the diluted regime, the samples are clear, having a very high and almost constant transmittance. Above a concentration of copolyester of about 2×10^{-3} g/dL the solutions become hazy. The cloudiness steeply rises by increasing the concentration and the systems become completely opaque above a copolyester concentration of 4×10^{-1} g/dL. The transmittance decreases because the turbidity of the systems increase, and the concentrations corresponding to the maximum of turbidity match very well the points of viscosity rising. The shape of the curve describing the change of transmittance with copolyester concentration is also connected with the physical aspect of the systems. During the preparation of samples, modifications of their aspect and consistency are observed. For example, by increasing the copolyester concentration, the samples become more turbid, the color are more and more intense and change from pale yellow to dark-brown.
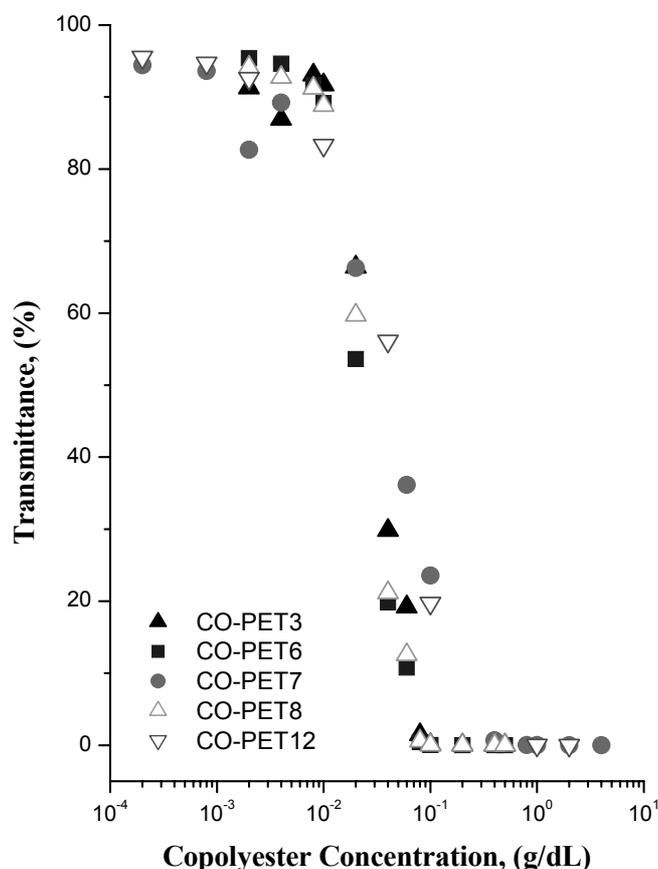

Fig. 5 – The variation of transmittance with copolyester concentration.

CONCLUSIONS

The results presented in the previous sections allow us to draw the following conclusions: copolyesters are obtained by using recycled PET from soft-drink bottles together with ethylene and diethylene glycol, isosorbide, adipic and succinic acid and 1,3-dimethyl isophtalate 5-sodium sulfonate. Diethylene glycol is used because it confers more flexibility to the macromolecular chain in comparison to ethylene glycol. Isosorbide is selected since it increases the glass transition temperature of the copolymers. Moreover, it comes from biomass which is a regenerable source opposed to petrochemicals. The aliphatic dicarboxylic acids are employed to confer biodegradability, whereas 1,3-dimethyl isophtalate 5-sodium sulfonate provides water dispersability and film-forming properties to the copolyesters. The characterization by ^{1}H-NMR and FTIR-ATR shows that the obtained copolyesters contain aromatic and aliphatic protons, and ester and sulfonic groups. UV-Vis spectra have absorption peaks from the aromatic $\pi \rightarrow \pi^*$ transition and from $n \rightarrow \pi^*$ transition, the latter belonging to the carbonyl group. Both transitions depend on polarity of the solvent. The $n \rightarrow \pi^*$ transition is blue shifted with increasing solvent polarity, and the $\pi \rightarrow \pi^*$ transition is red shifted with decreasing solvent polarity. The copolyesters are soluble in water, ethylene glycol and chloroform, and insoluble in alcohols, acetone and toluene. They give positive response to the qualitative test for surface active agents. However, their surfactant properties are weak as demonstrated by the surface tension measurements. The viscosity and turbidity results attest the polyelectrolytic character of all the samples. These results demonstrate that the obtained PET copolyesters have hydrophilic properties and suggest their use as biodegradable, water-dispersible, and film forming agents.

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