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Matrices for Mono-Material Composites (MMC). The Case of Poly(ethylene terephthalate)

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Summary: The use of the same thermoplastic polymer for both the matrix and the filler in the preparation of composites is very attractive, because such composites are in principle fully recyclable. Recently it has been reported the preparation of a mono-material composite (MMC) made of polypropylene to be used in automobile parts. In this work we report on the preparation and characterization of matrices for quasi MMC made of poly(ethylene terephthalate) (PET). Particularly we found PET copolymers containing isophthalate (IPA) units adequate to be used as matrix.

Keywords: poly(ethylene terephthalate); mono-material; composite; matrices; polycondensation

Introduction

In recent years a large interest has been focused on the synthesis and processing technology of new polymeric materials using a more environment-friendly chemistry. This corresponds to have recyclable materials with enhanced durability. The first "performance" is very important because the wide use of polymeric materials leads to a constant increase of their over-all production.

In the case of thermosets, which are used in applications requiring good mechanical performance and dimensional stability, recycling is not possible. The use of recyclable materials with similar performance may contribute in decreasing environmental impact.

Recently it has been reported the preparation of a mono-material composite (MMC) made of

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polypropylene [1] to be used in automobile parts. The use of the same thermoplastic polymer for both the matrix and the filler in the preparation of composites is very attractive, because such composites are in principle fully recyclable.

In this work we will investigate the possibility of producing an MMC of poly(ethylene terephthalate) (PET) and its copolymers. Particularly, we will focus our attention on the preparation and characterization of matrices for this kind of MMC.

Experimental Part

Matrices synthesis

All reagents were used as obtained from Aldrich. High crystalline PET (η_{inh} = 0.6 dl/g) fibers, cut 18 mm long, were obtained from Montefibre (Italy). Matrices were synthesized following three different procedures a, b, and c.

(a) oligomers. The general procedure for the synthesis of oligomers is the following: 3 g of Bis(hydroxyethyl)terephthalate (BHET) are heated to 230°C in the molten state and Ti(IV) isopropoxide is added [0.020%w]. Different molecular weight oligomers can be obtained by regulating reaction time. For Trimer synthesis a different procedure has been used, due to the difficulty in obtaining such a low molecular weight with the previous method: 12g of BHET with 0.90ml of pyridine are dissolved in 100cc of *o*-diclorobenzene at 140°C. 1.00g of terephthaloyl chloride is dissolved in 10cc of o-diclorobenzene. The latter solution is added drop wise to the former one. After two hours, 150cc of *n*-heptane is added and the powder is collected by filtration. The white powder is washed with *n*-heptane and with ethanol. The powder is dried in oven at 120°C [T_m=196.7 °C, ΔH_m=109.49 J/g].

(b) PET hydrolysis. BHET is added to PET at 240°C until the whole mixture melts to a homogenous fluid. Two drops of $30\%_w$ sulfuric acid are added and the reaction is carried out for 10 minutes. No vacuum is applied. The viscous fluid is recovered by pouring on an aluminum pad.

(c) Copolymers. 20 g of BHET with the required amount of isophtalic acid (IPA) are placed in a vial at 200°C and Ti(IV) isopropoxide is added [0.020%w], then the temperature is raised under vacuum. The whole reaction is performed as resumed, for some matrices, in Table 1.

Table 1. PET Copolymers (calorimetric data referred to the first heating run).

Synthesis	Thermal treatment			T_g/T_m [a]	ΔH_m [b]	M_w [c] $(x10^4)$	η^* x 10^3 [d]
	T (°C)	Time (min)	vacuum				
A(24)	200	10	No	68/ -	-	63	0.66
	200	70	Yes				
16.7 $\%_w$ IPA	240	50	Yes				
	260	45	Yes				
	280	50	Yes				
A(25)	200	60	No	74 / 232.2	37.5	35	/
	240	60	Yes				
9.09 $\%_w$ IPA	280	60	Yes				
A(26)	200	60	No	69 / 212.4	26.4		/
	240	180	Yes				
13.0 % IPA							
A(27)	200	60	No	67 / 197.7	7.2		0.034
	240	180	Yes				
16.7 $\%_w$ IPA							for reology see <u>Figures 9</u>
A(28)	200	60	No	68 / -	-		1.24
	240	60	Yes				
16.7 $\%_w$ IPA	280	120	Yes				for reology see <u>Figure 8</u>
A(29)	200	10	No	68 / -	-		
	200	50	Yes				
16.7 $\%_w$ IPA	240	60	Yes				
	260	45	Yes				
	280	50	Yes				
A(30)	200	60	No	68/-	-		
	240	60	Yes				
28.6 $\%_w$ IPA							
A(43)	230	60	No	71/215	-		
	240	80	Yes				
9.09 $\%_w$ IPA	280	70	Yes				
A(44)	230	60	No	72/226	-		
	240	35	Yes				
4.86$\%_w$ IPA	260	45	Yes				
	280	120					

[a] T_g,T_m /°C, glass transition and melting temperature, respectively; [b] $\Delta H_m/Jg^{-1}$, melting enthalpy; [c] M_w / g mol^{-1}, average molecular weight; [d] η^* / Pa s, viscosity measured at 200°C with 5% strain at 10 rad/s.

<u>Composites preparation</u>

Matrix **A(30)**, previously dried at 120°C under vacuum for one night, is heated up to 200°C. Short crystalline fibers are added in the required amount and mechanically mixed with matrix for two minutes at 200°C. Then the mixture is pressed at 200°C for 30 seconds between two Teflon foils and quenched in a water bath. Composites using a PET fabric as filler were prepared in the same way with matrices **A(43)** and **A(44)**.

Characterization

Thermal measurements were carried out using a DSC-7 Perkin Elmer calorimeter under nitrogen flow at 10°C/min rate.

Polarized optical microscopy was performed using a Jenapol microscope.

Fiber diffraction spectra were recorded by means of a flat camera with a sample-to-film distance of 70.0 mm and the X-ray beam direction perpendicular to the fiber axis (Ni-filtered Cu-Kα radiation). The Fujifilm MS 2025 imaging plate and a Fuji Bio-imaging Analyzer System, mod. BAS-1800, were used for digitizing the diffraction patterns.

A Waters 150-C ALC/GPC instrument was used for GPC analysis, equipped with three columns PSS SDV from Polymer Standard Service (Gmbh) (PSS 100 Å- PSS 10^4 Å- PSS 10^5 Å).and a Jasco 875 UV detector operating at 254 nm . Polystyrene as standard and chloroform as solvent (samples previously dissolved in 1,1,1,3,3,3-hexa fluoro-2-propanol) at 1 ml/min and 30°C.

Dynamic mechanical tensile analysis (Single Cantilever) was carried out by means of a Perkin Elmer DMA 7 analyzer, at 5°C/min heating rate under nitrogen flow. Frequency was set at 1 Hz. Sample size is 18.0x8.4x0.3 mm.

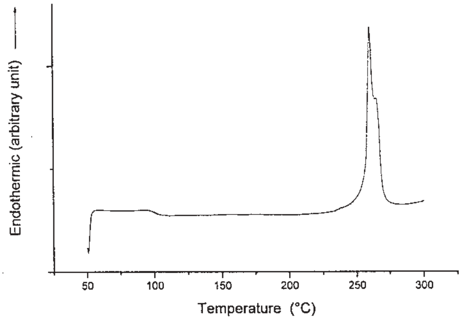
The dynamic flow properties of the molten materials were measured with an ARES rheometer (Rheometrics, Inc.) using a parallel plates geometry (plate radius=12.5 mm, gap=1 mm). The samples for testing were dried at 105°C in a vacuum oven for 16 hrs and analyzed under a nitrogen gas purge in order to minimize thermo-oxidative degradation phenomena. Temperature sweep tests were carried out in the temperature range of 220÷180°C at a constant stress amplitude. Frequency sweep tests (0.1÷100 rad/s) were made at 200°C at constant strain amplitudes (5%, 10% and 20% strain).

Discussion

Preliminary investigation

In order to set matrix performances, filler (PET fibers) response to thermal treatment should be investigated first. Composite preparation will require the insertion of fibers in a molten matrix with a suitable viscosity to allow processing. Processing temperature should be as lower as possible to save tensile properties of fibers.

In Figures 1 and 2, DSC and DMA traces of a fiber sample of PET are shown, respectively. At temperature higher than the glass transition temperature (T_g), tensile modulus decreases reaching a plateau at 150°C. Finally, at temperature close to 250°C fibers collapse. Annealing at a temperature lower than 230°C-240°C does not significantly affect fiber orientation degree as confirmed by the X-ray diffraction pattern of fiber samples (see Figure 3). For practical purpose, we take 220°C as the upper limit of the over-all processing.



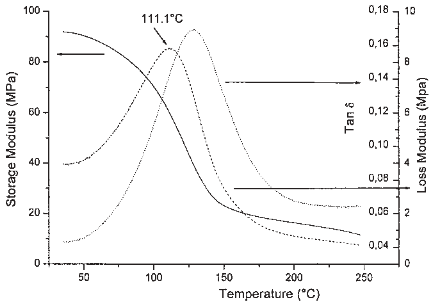


Figure 1. 1st heating run for a high oriented and high crystalline fiber sample of PET

Figure 2. DMA traces for a high oriented and high crystalline fiber sample of PET (same sample of Figure 1) (Storage and Loss Modulus are given in arbitrary units)

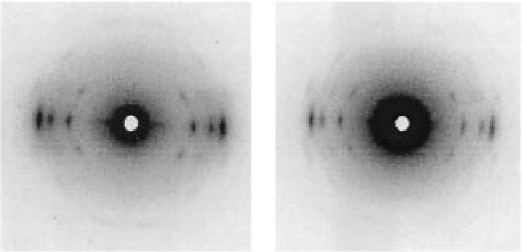


Figure 3. X-ray diffraction patterns of a fiber sample of PET (same sample of Figure 1) (right) as made and (left) after annealing at 220°C for 3 h

Matrix preparation

According to the experimental section, we synthesized matrices following three different approaches:

(a) Oligomers

In principle, fibers may be covered by a solid layer of oligomers taking advantage of the lower melting temperature (T_m) compared to polymer. Subsequent annealing at the appropriate temperature should increase molecular weight of matrix by solid state polycondensation, Ti(IV) as catalyst [2-6]. To avoid matrices desegregation due to glycol diffusion, oligomers with quite high molecular weight, but with low T_m, should be used. Unfortunately, this is not the case of PET oligomers. In fact, melting temperature increases suddenly with molecular weight as shown in Figure 4 (Figure 4 shows only a qualitative trend, low molecular weight compounds being out of the linearity range of GPC). For example, trimer has T_m=197°C and a mixture of oligomers with an average weight molecular weight (M_w) of 1.12 x 10^3 g/mol (see GPC in Figure 5) has T_m=248°C. Thus only very short oligomers (a mixture from trimer to pentamer) can be used as matrix but in this case the amount of glycol produced during polycondensation is too high. Consequently, trails with low melting oligomers ensure good covering of fibers but matrix desegregates during annealing at 180°C-200°C.

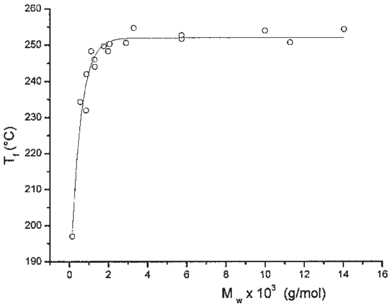


Figure 4. Melting temperature *vs.* molecular weight M_w (temperature referred to the second heating run)

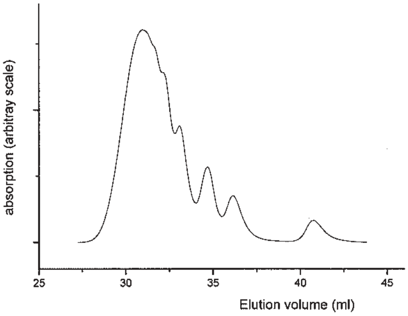


Figure 5. GPC curve for a PET oligomer with T_m = 248.3°C and M_w = 1.12 x 10^3 g mol^{-1}

(b) PET hydrolysis

Another way to decrease melting temperature is to introduce disorder along the molecular chain by inserting comonomers. This approach will be discussed in this and in the next paragraph, following two different procedures. Strictly speaking this does not correspond to have a pure PET matrix for preparing a real MMC, but the approach can be acceptable provided that composition differs as less as possible.

Here comonomers will be generated starting directly from PET by hydrolysis. In fact, hydrolysis, catalyzed by diluite sulfuric acid, is expected to cause: *i*) chain scission, generating carboxyl units; *ii*) vinyl units formation by dehydration of glycol; and *iii*) diethylenglycol (DEG) formation by etherification of two glycol terminal groups [7]. The first two cases produce a lower molecular weight polymer whilst the last one leads to a copolymer: in this case melting temperature depression depends on the amount of DEG. Unfortunately this corresponds to have also a decrease of glass transition temperature that has a negative effect on the tensile performance of matrix. The relative trend of T_m and T_g should be tested for different reaction conditions.

In order to decrease the temperature at which hydrolysis is carried out we prepare a mixture of PET/BHET by dissolving PET in BHET in the molten state. In this way, melting temperature decreases and hydrolysis can be performed at temperature ranging from 220°C to 240 °C.

Melting temperature *vs*. composition for hydrolyzed samples are reported in Figure 6 and Table 2. In spite of the different nature of the two components (high molecular weight PET and low molecular weight monomer BHET) the GPC curve consists of a single peak (see Figure 7). Then 10 minutes hydrolysis is enough to ensure, in terms of molecular weight, an homogenous matrix. Unfortunately , according to Figure 6 and Table 2, melting temperature is still too high. Increasing reaction time would decrease much more molecular weight thus acid hydrolysis seems to be not a suitable way for preparing matrices.

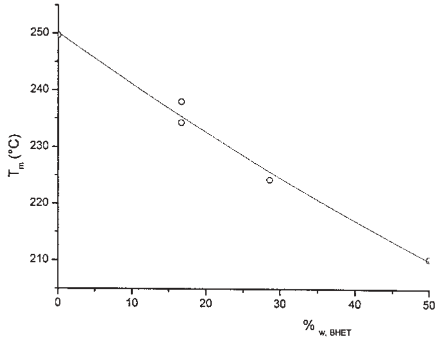


Figure 6. Melting temperature *vs*. composition of PET/BHET mixtures (temperature referred to the second heating run)

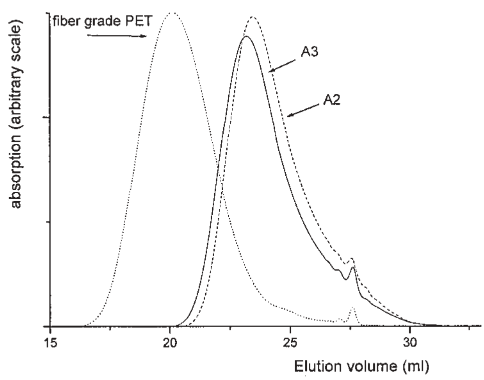


Figure 7. GPC elution curves of (a) **A(2)** [M_w = 6.8 x 10^3 g mol^{-1}], (b) **A(3)** matrix [M_w = 8.8 x 10^3 g mol^{-1}], and (c) fiber grade PET [M_w = 77 x 10^3 g mol^{-1}]

Table 2. PET hydrolysis (calorimetric data referred to the second heating run).

Sample	$\%_{w, BHET}$	T_m [a]	T_c [b]	ΔH_m [c]	M_w [d] ($x10^3$)
PET (pellets)	0	249.7°C	169.3°C	28.3	53.4
A(2)	50.0	210.3	158.7	26.2	6.8
A(3)	28.6	224.3	170.7	37.2	8.8
A(4)	16.7	238	190.0	39.1	
A(6)	16.7	234.3	184.0	39.9	

[a] T_m /°C, melting temperature; [b] T_c /°C, crystallisation temperature; [c] $\Delta H_m/Jg^{-1}$, melting enthalpy; [d] $M_w/g\ mol^{-1}$, average molecular weight

(c) Copolymers

The last procedure to be tested is the synthesis of copolymers made of terephthaloyl and isophthaloyl units. It is well known that the insertion of conformationally rigid comonomers in the chain does not affect too much the glass transition temperature of PET. Moreover bend shaped monomer placed along the chain inhibits crystallization making lateral chain-to-chain register less favorite. This correspond to have a lower melting temperature. Isophathalic acid is one of these comonomers. The problem is to find out a matrix with good performances and a composition as close as possible to pure PET sample. Of course the insertion of more than two rigid bend comonomers might improve performances of matrix, even decreasing the total comonomers content.

In principle, there are several parameters which influence final matrix performances: composition, reaction temperature, reaction time, pressure, catalyst content, and so on. To reduce the number of variables we report on copolymers made of two monomers only, BHET and IPA, and some of reaction parameters fixed according to Table 1.

After several runs, we observed that:

i) at 200°C, IPA is not completely soluble in the molten BHET and a white suspension is obtained. After 60 min. suspension is still present; it disappears slowly only at higher temperature (230°C). If vacuum is applied, clarification of fluid is accompanied by sublimation of part of IPA, so that matrix composition is not well controlled;

ii) in the preliminary treatment at 200°C vacuum is not really necessary. Indeed atmospheric pressure is to be preferred because it avoids IPA and low molecular monomers sublimation;

iii) thermal treatment at 280°C brings to yellow and highly viscous matrix, thus lower temperature and longer reaction time should be imposed. The obtained matrices show viscoelastic behavior (see Figure 8) with the two G’ and G’’ curves quite superimposed. The obtained matrices show a non-Newtonian flow behavior (see

Figure 8): the complex viscosity curve is highly shear thinning in the whole frequency range examined and the two G' and G'' curves are quite superimposed in the lowest frequency region (ω = 0.1-5 rad/s);

iv) 60 minutes at 240°C were found adequate for having transparent colorless matrices with low viscosity (see Figure 9). Matrices with adequate viscosity might be prepared by regulating reaction time;

v) glass temperature transition is quite unaffected by IPA content (see dynamic tensile moduli in Figure 10).

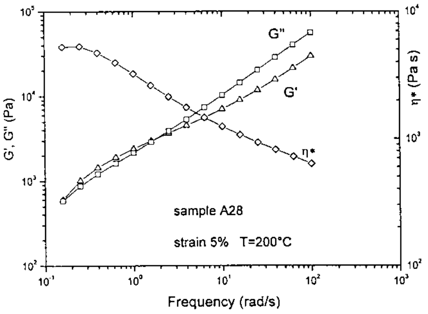


Figure 8. Dynamic flow properties of the molten **A(28)** sample (strain 5%)

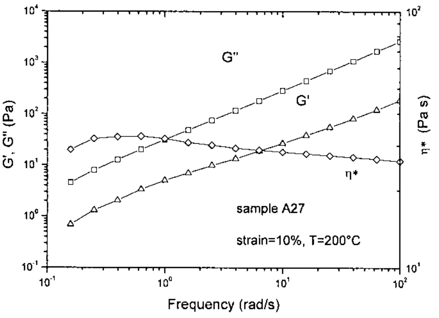


Figure 9. Dynamic flow properties of the molten **A(27)** sample (strain 10%)

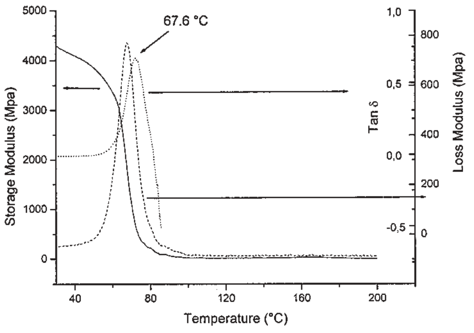


Figure 10. Dynamic tensile measurements for **A(24)** sample

Composites

Matrices **A(27)** and **A(30)** in Table 1 have been used for preparing PET composites at 200°C. In the case of **A(27)**, test was unsuccessful due to the partial crystallization of matrix occurring during thermal treatment at 200°C. Thus it was necessary to increase temperature up to 240°C, but at this temperature dissolution of fibers in the matrix occurs. In the case of **A(30)**, test was successful. In fact at 200°C **A(30)** is fluid and fibers can be easily added. Mixtures with different compositions were prepared and pressed at 200°C. At the present stage, we were not able to prepare homogenous composites, which are necessary for a correct analysis of tensile and mechanical performances, but we obtained only very preliminary samples. They were tested for analyzing fibers morphology: by X-ray diffraction analysis, fibers result to be still oriented and locally aligned (see Figure 11) and in the calorimetric traces the endothermic melting peak of fibers is visible (see Figure 12).

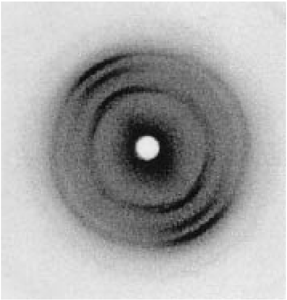


Figure 11. X-ray diffraction patterns of composite made of PET fibers as filler and **A(30)** sample as matrix

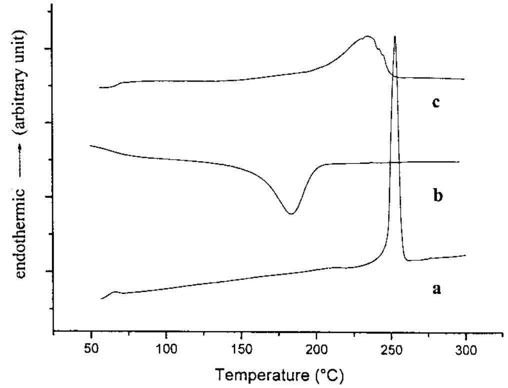


Figure 12. Calorimetric traces of a composite sample made of PET fibers as filler and **A(30)** sample as matrix: (a) first heating run, (b) first cooling run, and (c) second heating run

Conclusion

BHET/IPA copolymers are suitable to be used as matrices for PET composites.

We prepared a composite using matrix **A(30)**, but at the present stage of investigation we are not able to control homogeneity of final sample. Further work is necessary in order to prepare quite large samples with homogeneous distribution of fibers as filler. The amount of IPA should be reduced as much as possible by testing the synergic effect of different comonomers or crosslinking agents in order to have a quasi pure MMC. Moreover the effects of reaction temperature in the range 240°C-280°C and reaction time on matrices performances need a deeper investigation.

[1] E. Johannboeke and G. Popp, *Kunststoffe*, 89, (1999), p.77.
[2] J. Otton et al., *J. Polym. Sci.*, 26, (1988), p. 2199.
[3] T.H. Shah, J.I. Bhathy, G.A. Gamlen and D. Dollimore, *Polymer*, 25, (1984), p. 1333.
[4] B. Huang and J.J. Walsh, *Polymer*, 39, (1998), p. 6991.
[5] F.K. Mallon and W.H. Ray, *J. Appl. Polym. Sci.*, 69, (1988), p.1775.
[6] I. Devotta and R.A. Mashelkar, *Chem. Eng. Sci.*, 48, (1993), p. 1859.
[7] N. Halacheva and P. Novakov, *Polymer*, 36, (1995), p. 867.