PROPERTIES OF PET-PEN BLENDS PRODUCED BY EXTRUSION AND INJECTION BLOW- MOLDING

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ABSTRACT

In this work, blends made of polyethylene terephthalate (PET) and polyethylene 2,6 naphthalene dicarboxylate (PEN) were prepared by melt extrusion processed at several temperatures and residence times. The blends with composition up to 20 wt % PEN were characterized with regard to their degree of transesterification and their rheological properties. Subsequently, bottles were produced by injection-stretch blow-molding and their mechanical properties were measured. It was found that improved PET-PEN blends were produced at 270°C with a PET content of 15 and 20 wt % and residence time processing of 4 minutes. Both blends present a low degree of transesterification, block conformations, high shear viscosity and improved tensile properties.

Keywords: PET-PEN blends, rheology, transesterification.

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INTRODUCTION

Polyethylene Terephthalate (PET) and Polyethylene Naphthalene 2,6 Dicarboxylate (PEN) form immiscible mixtures. Improved miscibility can be obtained by performing a transesterification reaction between both ingredients to produce copolyesters, which act as compatibilizers in the interface of the blend. This reaction, when is carried out in a melt extruder, depends strongly on temperature and residence time, in particular within 50-80 wt % PEN content /1/. Physical and mechanical properties of the resulting blend depend on the degree of transesterification and also on the resulting copolymer microstructure, i.e., whether it contains block or random substructures. Also, attention has been given to PET/PEN blends to elucidate the type of kinetics of the transesterification reaction, and in particular, reversible second-order kinetics has been found using model compounds in solution /2/, and after melt-extruded /3/. When the reaction is carried out in a mixing chamber the reaction kinetics is strongly affected by terminal hydroxyl groups /4/. In the same device, studies on the thermal, rheological and mechanical properties for blends with 25, 50 and 75 wt % of PEN content have also been reported /5/. Also, in a twin-screw extruder a block copolymer may be obtained via melt extrusion when the PEN content is 20 wt % /6/.

From the industrial point of view, PET-PEN blends are attractive in the production of bottles for carbonated liquids or for filling at high temperatures. PEN imparts the blend a higher resistance to gas diffusion, better mechanical properties and increased glass transition temperature (Tg) for high PEN contents (1). However, these benefits are partly offset by the cost of PEN, and for this reason PEN contents in the blend higher than 20 wt % are not viable. Besides, there are some problems in the production of these blends, since transesterification is promoted in systems with similar viscosities that leads to a high dispersion of small droplets and hence a larger contact area with the viscoelastic matrix /7/. Another problem is that agents which promote miscibility can only be processed at small concentrations, of the order of 2 wt %, otherwise, mechanical properties are negatively affected /8/. Furthermore, for certain concentrations of the ingredients in the blend, some properties increase (like tensile strength), but others decrease (like the Young's modulus) /9/. It seems that the full relationship between transesterification and mechanical properties is not well understood yet, due to the fact that in practice the behavior of the PET/PEN blends can be

554

affected by numerous factors, for example: the presence of abnormally-heated zones in the extruder, inefficient mixing, thermomechanical degradation, a wide molecular weight distribution, large differences in the viscosity of raw materials, residence times of the polymer in the extruder, processing temperatures, composition of the blends, materials incompatibility and so on. These factors affect strongly the transesterification kinetics and the subsequent production of bottles.

This work addresses the relationship between the properties of bottles made of PET-PEN produced by a two-step injection-stretch blow-molding operation and the properties of the blend after processing in a twin-screw extruder covering a range of processing variables, i.e., two residence times and three temperatures. The blends are characterized with regard to the degree of transesterification and microstructure with PEN contents up to 20 wt %. Their mechanical and rheological properties were measured while only the bottles were mechanically tested.

EXPERIMENTAL SECTION

Materials

PET (Eastapack 9921 from Eastman Chemical) had a density of 1.40 g/cm^3, melting temperature = 262°C, a glass transition temperature = 61.2° C and average molecular weight = 29,700 g/mol with polydispersity of 4.9. PEN (Kalidar X-70 from Dupont) had a melting point of 258°C, Tg = 112°C, average molecular weight = 108,700 g/mol and polydispersity of 3.6. No additives to prevent oxidation were used in compounding.

Equipment.

Blends were prepared in a 30 mm diameter co-rotating twin-screw extruder (Werner & Pfleiderer ZSK30) with a general-purpose screw configuration including two rows of kneading elements (15 elements by row and 5 mm width each) and L/D = 30. The extrusion residence time was measured by recording the traveling time of a colored trace inside the extruder. It was found that the screw speed of 40 RPM corresponds to a residence time of 4 minutes, and 50 RPM corresponds to 2 minutes. Three temperature profiles along the extruder were considered for the feeder and die sections, respectively: (a)- 262-265-269-267 and 270°C, (b)- 270-281-278-

282 and 280°C, (c)- 273-291-290-290 and 290°C. The extruder was equipped with a volumetric band feeder working under nitrogen atmosphere to prevent moisture absorption and consequent hydrolysis or chemical degradation of the polyesters. Moisture determinations were carried out in a Moisture Analyzer Omnimark Mark2. Bottles were produced in a two-step injection-stretch blow-molding machine AOKI with a temperature profile of 275°C at the feeder and 320°C at the injection nozzle, with pre-form temperature of 112°C and blow mold temperature of 16°C. Low blow and high blow nitrogen pressures were 75 and 250 psi, respectively. Rheological properties were measured in a TA-Instruments AR 1000-N controlled stress rheometer with parallel plates of 25 mm diameter and 0.75 mm gap. ^{1}H-NMR determinations were performed in a Varian Unity Plus 300 Spectrometer using a solution of deuterated chloroform and trifluoroacetic acid (60:40) as the solvent for the PET-PEN blends. Determination of the tensile mechanical properties was made in an Instron-1125 following ASTM 638 specifications with a strain rate of 50 mm/min. The injection process to produce the pre-forms requires a re-crystallization step prior to processing. As mentioned, the blend is produced in a twin-screw extruder followed by pelletization. The threads of polymer exiting the extruder are cooled immediately at 15°C. Pellets are then re-crystallized before the injection molding operation to produce the bottles.

It is necessary to point out that the PET/PEN blends were produced for the injection-stretch blow-molding operation. According to the properties of materials, a high PEN content leads to better physical properties of the bottles, but also increases the melt viscosity and costs.

Block conformations of the co-polyester produced in the transesterification reaction lead to better properties than those with random copolymers. Compatibilizer concentrations more than 2 % and hence high conversions are not recommended for good blend properties.

RESULTS AND DISCUSSION.

^{1}H-NMR characterization

The degree of transesterification was measured by ^{1}H-NMR in samples that were not re-crystallized. Chemical shifts are reported taking as a reference the chemical shift position of chloroform with respect to TMS using a spectral window of 4000 Hz. The extent of transesterification

(fraction of naphthalene-ethylene-terephthalate blocks, NET), the percentage of terephthalate-ethylene-terephthalate blocks (TET) and naphthalene-ethylene-naphthalene blocks (NEN) were derived from the peaks corresponding to different types of ethylene groups by spectral deconvolution. In the ethylene region of the ^{1}H-NMR spectra of blends, peaks at 4.9 ppm NEN, 4.8 ppm TET and 4.85 ppm NET (peak due to transesterification) are measured. The degree of transesterification can be determined from the integrals of those peaks as follows:

$$\% \text{ Transesterification} = I_{NET} / (I_{TET} + I_{NEN} + I_{NET})$$

where, for example, I_{NET} is the integral for ethylene units in a NET sequence. In the same manner, the following quantities are defined:

$$P_{NT} = (I_{TEN}/2) / (I_{TEN}/2 + I_{NEN})$$
$$P_{TN} = (I_{TEN}/2) / (I_{TEN}/2 + I_{TET})$$
$$B = P_{NT} + P_{TN}$$
$$\text{Extent of Reaction} = (I_{TEN}/2) / (I_{TEN}/2 + I_{\text{bigger peak}})$$

where P_{NT} is the probability that the ethylene naphthalene group (EN) reacts with the ethylene terephthalate group (ET) in the PEN chain. P_{TN} is the probability that the ET group reacts with the EN group in the PET chain. B is the degree of randomness, which takes the value of one if the copolymer is random, and zero if the copolymer has a block structure. The extent of reaction deals with the reacted ratio of the major component for each composition /10/.

In this work it was found that for some combinations of the processing parameters (temperature, residence time and mix composition) lead to results that are sometimes different from what is usually expected. For example, NET percentages at 270°C and 4 min residence time are lower than those determined at the same temperature but with 2 min residence time (see Table 1).

^{1}H-NMR measures the degree of transesterification that represents the NET content in the blend. This content results from the reaction that is reversible at the processing conditions including thermo-mechanical work and degradation of the polymer chains. In the previous example, a lower NET content obtained with 4 min residence time means that the breakage of NET bonds is higher with this residence time than with 2 min residence time. The

same situation occurs at 280°C, for which the NET content is larger with residence time of 2 min than with 4 min. However, at 290°C the situation reverses. In this case, the degree of transesterification increases with residence time. This result is in agreement with previous works which show that the reaction rate constants are four times higher at this temperature /2,3/.

According to values of the parameter B, at 270 and 280°C, upon increasing the residence time leads to higher block contents. However, at 290°C, increasing the residence time and the PEN content leads to lower block compositions. In general, increasing the transesterification degree leads to more random structures.

To illustrate better the data shown in Table 1, in Figure 1 the degree of transesterification is plotted as a function of PEN content. At 270°C, transesterification is negatively affected by residence time, since the NET percentage (and extent of reaction) decreases when the residence time increases. At 280°C the NET group percentage increases with PEN content, but once again the residence time affects negatively the NET percentage. At this temperature, data produced with 4 minutes residence time lie below those data corresponding to two minutes residence time. On the contrary, at 290°C, the % NET increases with residence time and PEN content. An increase in temperature leads to enhancement of the reaction rate facilitating copolymer production and hence compatibilization. Each blend depicts a particular combination of transesterification temperature and extrusion residence time. Tharmapuram *et al.* /7/, predicted transesterification processing temperatures using reaction kinetics for a wide range of compositions.

Shear Viscosity

Figure 2 shows the shear viscosity data of the polyesters as they are received (in pellets). Rheological measurements were made at 270°C. The first Newtonian viscosity of PEN is about ten times that of PET, and the shear-thinning region of the former starts at 2 s^{-1} while that of PET begins at higher shear rates (around 20 s^{-1}). Shear viscosities of PET-PEN blends processed at 270°C with 2 min residence time are shown in Figure 3. The viscosity tends to a plateau for lower shear rates (first Newtonian viscosity) and shear thins for shear rates larger than 10 s^{-1}.

Table 1

Properties of PET-PEN blends for several compositions and processing conditions.

| PEN conc.	Extruder Processing Temperature	Extruder Residence Time	NET	B	Extent of reaction	Tensile Strength	Elastic Modulus	Shear Viscosity $(1\ s^{-1})$
%	°C	min	%			MPa	MPa	Pa.s
0	270	2	*****	*****	*****	50	1296	218
5	270	2	ND	******	*****	118	2307	306
10	270	2	1.7	0.12	0.92	120	2182	441
15	270	2	8.7	0.39	4.98	140	2583	596
20	270	2	11.1	0.45	6.48	71	1758	685
5	270	4	0.2	0.03	0.10	70	1885	392
10	270	4	0.4	0.03	0.22	93	1810	522
15	270	4	1.7	0.08	0.97	182	3042	540
20	270	4	1.3	0.05	0.78	185	2842	454
5	280	2	0.8	0.08	0.42	59	1561	334
10	280	2	2.4	0.23	1.26	50	1296	305
15	280	2	6.1	0.67	3.20	142	2458	397
20	280	2	19	0.99	10.66	168	2921	496
5	280	4	ND	******	*****	56	1529	396
10	280	4	0.5	0.04	0.27	62	1721	324
15	280	4	4.2	0.2	2.39	131	2508	233
20	280	4	14.4	0.64	8.27	130	2229	661
5	290	2	1.1	0.18	0.57	113	2478	276
10	290	2	4.5	0.35	2.42	97	2282	350
15	290	2	5	0.24	2.83	128	2811	412
20	290	2	5.8	0.23	3.42	128	2624	459
5	290	4	1.1	0.16	0.57	90	2162	265
10	290	4	8.1	0.62	4.35	126	2732	395
15	290	4	11.2	0.62	6.22	118	2571	415
20	290	4	19.6	0.96	11.07	135	2734	451
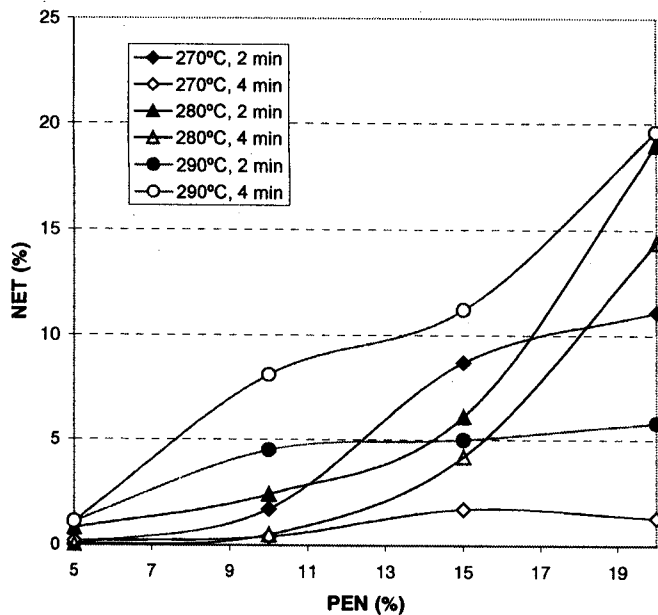
Fig. 1: Degree of transesterification or NET groups percentage as a function
of PEN content, for blends prepared by melt extrusion at various
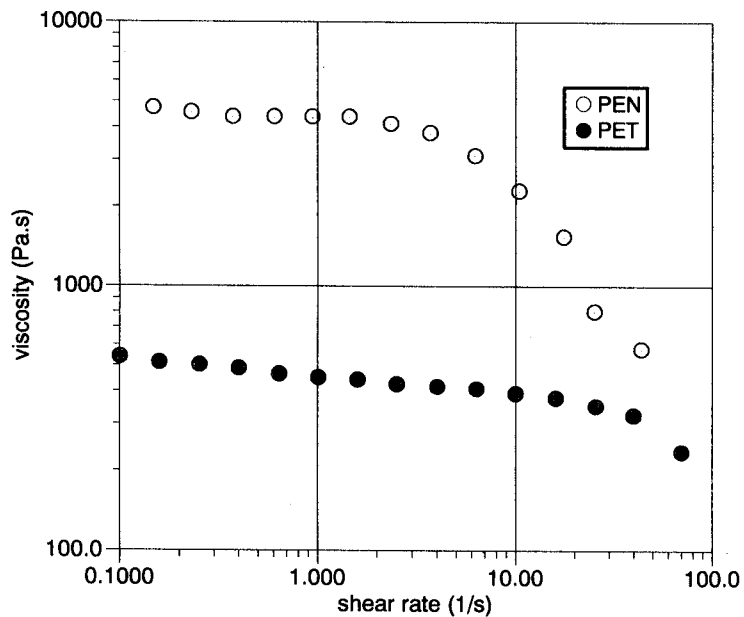processing conditions.

Fig. 2: Shear viscosity as a function of shear rate for PET and PEN polymers.
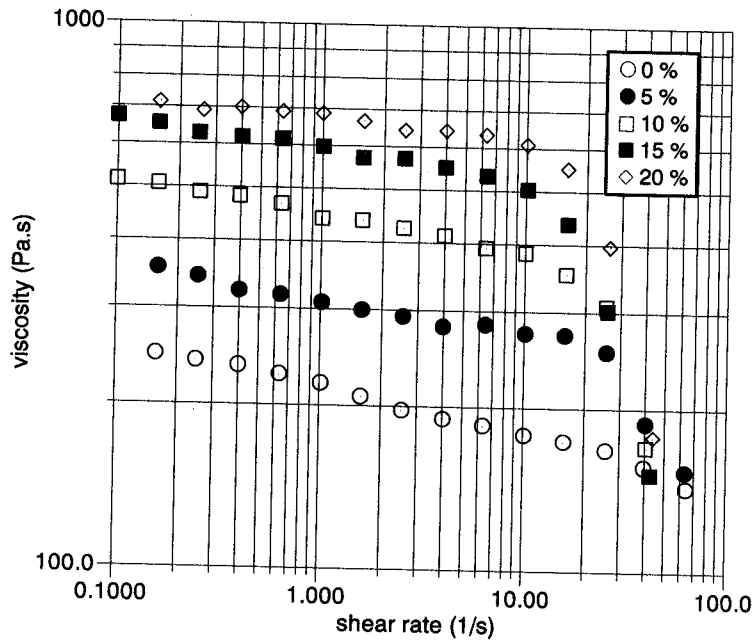
Fig. 3: Shear viscosity as a function of shear rate for blends of various compositions prepared by melt extrusion at the conditions indicated.
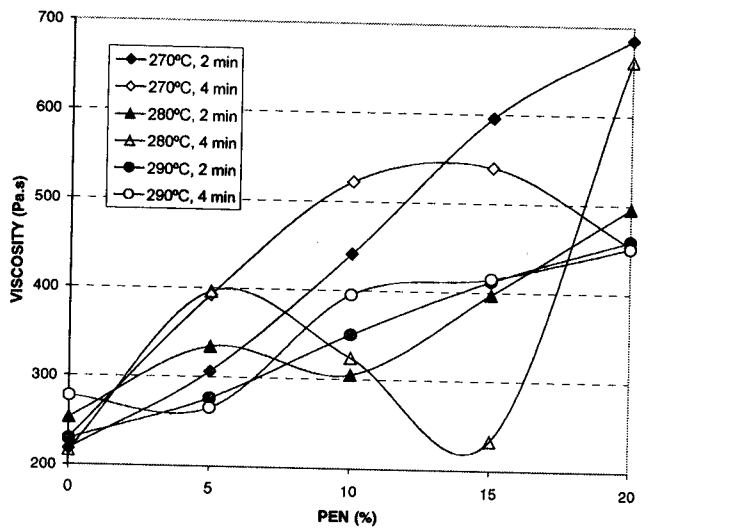

Fig. 4: Shear viscosity measured at a shear rate of $1\ s^{-1}$ (Newtonian plateau) as a function of PEN composition. Blends were prepared by melt extrusion at the indicated processing conditions.

561

Shear viscosity data of the blends processed at 270, 280 and 290°C for various compositions and two residence times were taken at shear rate of 1 s^{-1} (within the first Newtonian region) and they are shown in Figure 4. Viscosity should increase with PEN content, although an anomalous behavior is observed at 270°C with 20% PEN and 4 min residence time and at 280°C with 15% PEN and 4 min residence time, where the viscosity goes through a minimum. A relatively low viscosity is convenient for the processing of the pre-form and during the stretch blow-molding operation

In the case of 2 min residence time at 270°C, viscosity increases monotonically with PEN content, reaching a very large value for large PEN contents. According to Table 1, the extent of reaction for these blends attains one of the highest values, as well as the % NET (transesterification degree). This is also shown in Figure 4. Notice that the shape of the viscosity versus composition curve for the 270-2 blend in Figure 4 is similar to the shape of the curve of % NET versus composition in Figure 1. When the residence time is 4 min for blends processed at 270°C, the viscosity does not increase monotonically with composition and presents a maximum at 15 wt % PEN content. This maximum is also observed in the extent of the reaction for 15 wt % PEN (0.97) and in the transesterification degree (1.7). Once again, shapes of the viscosity-composition curve and % NET-composition curve are similar (see Figures 1 and 4). It is noteworthy that the blend processed at 270°C with 4 min residence time presents the lowest % NET and reaction extent (with block structure). It is apparent that viscosity scales with extent of reaction and transesterification degree.

Viscosity of the blend produced at 280°C with 2 min processing time increases gradually with PEN content (see Figure 4) in accordance with the monotonic increase in the extent of reaction and transesterification degree (see Figure 1). But the blend produced with 4 min of processing time at same temperature presents a sigmoidal shape with a minimum located at 15 wt % PEN and a drastic increase in the viscosity up to 20 wt % PEN (661 Pa·s). This steep increase is associated to the jump in more than three-fold in the transesterification degree and in the extent of reaction, i.e. from 4.2 to 14.4 and from 2.4 to 8.3, respectively, also shown in Figure 1.

Blends produced at 290°C with two residence times show a monotonic increase of the viscosity with PEN content, also in accordance to the monotonic increase in the % NET and in the extent of reaction. Once again, the viscosity scales with % NET and extent of reaction.
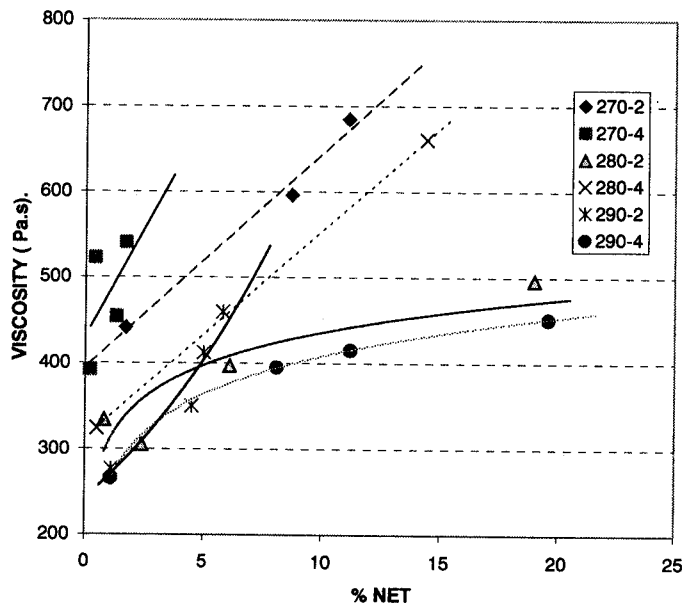
562

Fig. 5: Shear viscosity as a function of degree of transesterification (% NET) for the indicated temperatures and residence times.

Similarities in behavior of the blends illustrated in Figures 1 and 4 lead to the conclusion that the variation of the rheological functions can be clearly depicted as a function of the relevant parameter, which is the % NET. This is shown in Figure 5, where the viscosity is plotted with extent of transesterification (% NET). At low temperature (270°C) a rapid growth in the viscosity with % NET is observed, the slope of which is larger as the residence time increases. This rise in the viscosity is attained at relatively low % NET. Similar results are observed as the temperature increases to 280°C, although the curves are shifted to higher values of % NET and the growth in the viscosity is substantially lower with % NET. In contrast, at the highest temperature (290°C) a rapid growth in the viscosity is observed at low values of % NET for short residence times. Enhanced residence times lower the viscosity and its growth at this temperature.

Results shown in Figure 5 for the viscosity are also observed in the variation of the elastic modulus with extent of transesterification (% NET), following similar trends. For this reason these are not shown.

The presence of copolymer at the interface of the blends, even in a small

proportion, induces compatibility, which influences the viscosity behavior of the system. The minimum in the viscosity observed in Figure 4 for the 280-4 blend has also been reported in other works /11-14/. Utracki *et al.* pointed out that negative deviations from additivity are observed in immiscible blend systems, although Aharoni /15/ observed negative deviations in compatible systems (PET and polyester carbonate). This apparent contradiction exists because copolymers formed during the transesterification reaction are the source of a different viscosity-structure relationship. Ausin *et al.* /14/ stated that for systems where the morphology changes with composition and processing conditions (i.e. temperature or residence time), not only the viscosity but also the activation energy of flow versus composition should either exhibit a maxima or minima depending on the structure of the copolymers /11/. Since temperature and residence time control the transesterification reaction, in the case of PET/PEN it is readily expected that the morphology of the blends change with both composition and extrusion conditions. Furthermore, Jabarin *et al.* /11/ hypothesized that the minimum occurs because at low PEN contents, a naphthalate linkage causes disruption in the PET monomer sequence, acting as a diluent for PET. As the PEN content increases, naphthalate units increase the chain rigidity and hence the viscosity.

Storage Modulus.

In Figure 6, the storage modulus is plotted with frequency for blends with 15-20 wt % PEN content processed at two temperatures (280°C and 290°C) with 4 min residence time. As a reference, measurements of PET processed at two temperatures (270°C and 290°C) with 4 min residence time are also plotted. Data for PET processed at these two temperatures coincide over most frequencies. The blend with PEN content of 20% processed at 280°C shows a remarkable increase (more than a decade) of the elastic modulus over that of PET. As shown in Figure 4, this blend reaches one of the highest viscosities, which corresponds to a large % NET for this composition (see Figure 1). In fact, at this processing temperature, viscosity increases strongly with PEN content, and as the PEN content increases the microstructure changes from block to random conformation.

A decrease in the elastic modulus is observed as the processing temperature increases to 290°C, for two PEN contents (15 and 20 wt %) as shown in Figure 6. This drop coincides with a large drop in the viscosity

shown in Figure 4. In this case, the microstructure is mostly random. Comparing the data at these two processing temperatures is evident that both share a high extent of the reaction and % NET (see Figure 1), but the decrease in the viscosity and elastic modulus can be ascribed to degradation induced at higher processing temperatures, i.e., at 290°C.
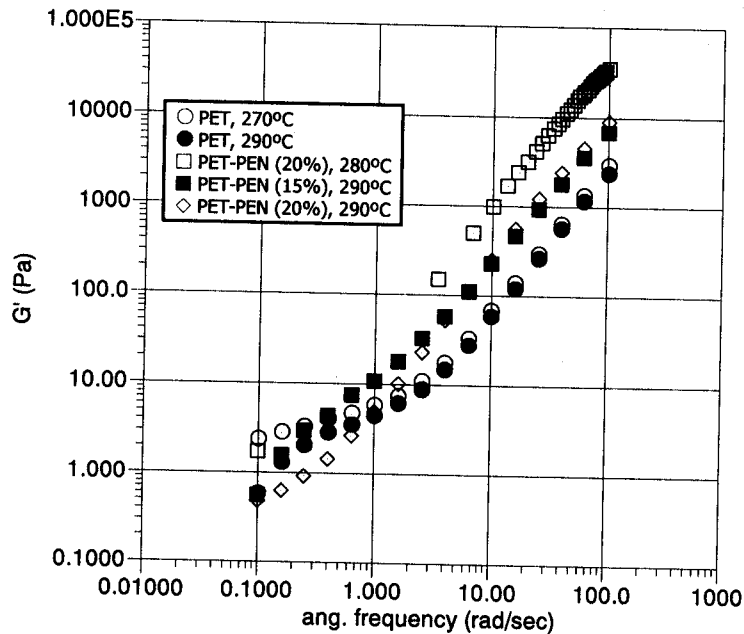

Fig. 6: Elastic modulus as a function of frequency for several compositions and temperatures with 4 min of processing time.

Mechanical properties of the resulting bottles depend strongly on the compatibility of the blends produced in the extrusion process. A method to evaluate the degree of compatibility of the blends was proposed by Hsiao-Ken *et al.* /16/. This method suggests that correlation of data into a master plot of G' versus G" indicates compatibility. As an example, Figures 7 and 8 show the master plots for the blend processed at 270°C with 2 min and 4 min residence times, respectively. As observed, a very good correlation is obtained for G" values exceeding 1000 Pa, as the PEN composition is varied. For lower G" values, and low residence time (2 min), scatter of data is associated to the presence of additional relaxation modes in the low frequency range of the spectrum (see Figure 8). It is interesting that a single

master curve, with better correlation, is obtained in the blends processed at higher temperatures (not shown), which suggests that the same degree of compatibility of blends is attained at the three temperatures and two residence times /16,17/. To corroborate the miscibility degree of the blends, measurements of Tg with DSC were made in blends with 5 to 20 wt % PEN composition at two residence times (2 and 4 minutes) and 270°C processing temperature. Miscibility defined in terms of a unique Tg for all blends is depicted in the thermograms. Results are shown in Table 2.
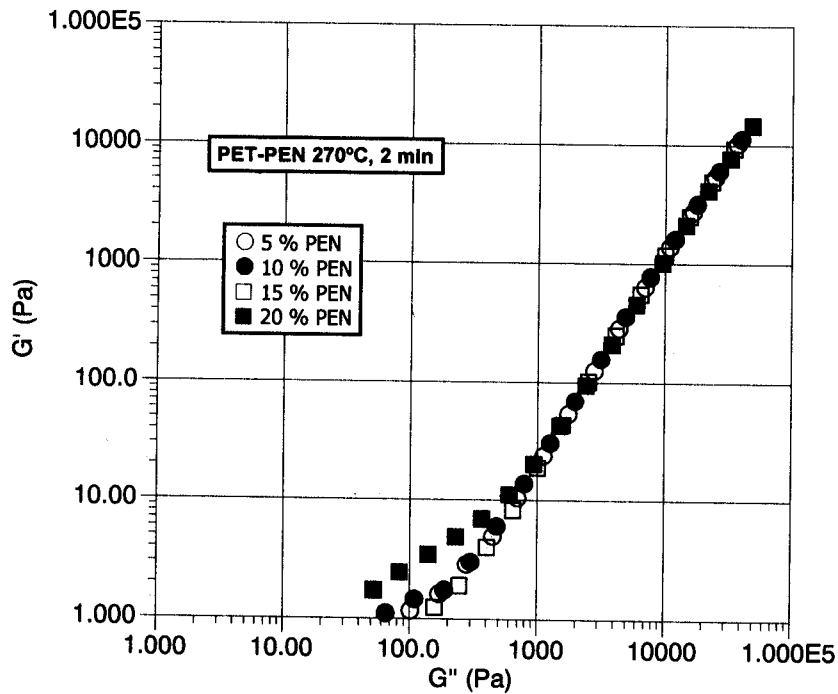
Fig. 7: Elastic modulus as a function of the loss modulus for various compositions. Process temperature of 270°C and 2 min of processing time.
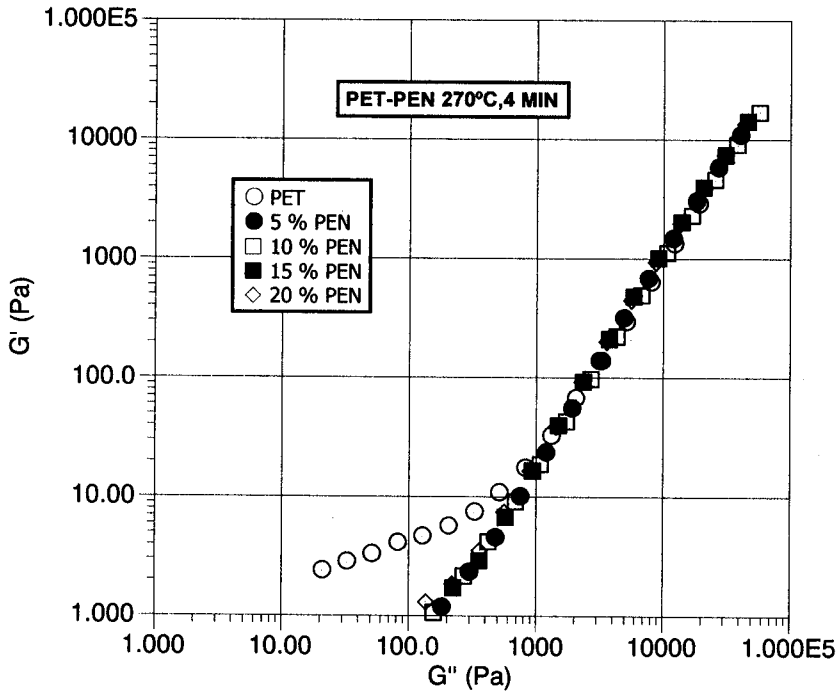
Fig. 8: Same as Figure 7. Processing time of 4 min.

Table 2

Glass transition temperatures of PET-PEN blends processed at 270°C.

Sample	Residence time (min)	Tg (°C)
PEN pellets as received		111.7
PET pellets as received		69.6
PET extruded once		61.2
PET- PEN 5%	2	72.1
PET-PEN 10%	2	73.3
PET-PEN 15%	2	67.0
PET-PEN 20%	2	69.2
PET-PEN 5%	4	73.4
PET-PEN 10%	4	72.2
PET-PEN 15%	4	66.7
PET-PEN 20%	4	68.4

Tensile mechanical properties.

Mechanical tests were made on samples taken from the bottles wall in the longitudinal direction. The blends for the bottle production were prepared by melt extrusion following the same preparation procedure for all blends.

It was found that those bottles with better mechanical properties were prepared at 270°C with 4 min processing time and PEN contents of 15-20%, as shown in Table 1. In fact, the largest value is obtained for 15 wt % of PET content. Bottles made from this blend had a tensile strength which reaches 2.6 times that of PEN (70 MPa) alone and 3.6 times that of PET (50 MPa). Also, Young's modulus attains a maximum when the PEN content is 15 wt %, corresponding to 2.3 times that of PET (1300) and 1.6 times that of PEN (1,900 MPa).

Those systems with high viscosity and high PEN contents present better mechanical properties. On the other hand, better mechanical properties were obtained with the block microstructure and low % NET.

CONCLUSIONS

According to the experimental data, at mixing temperatures of 270 and 280°C the kinetics of the reaction is different to that obtained at 290°C.

In this work, the influence of processing temperature and residence time in the extruder upon the transesterification reaction carried out between PET and PEN was studied. Bottles produced in the blow molding operation were tensile-tested. It was found that the processing variables (temperature and residence time in the extruder) and the complexity of the reaction affect the properties of the blend considerably. With regard to the tensile tests, properties are affected mostly by PEN content. With a small degree of transesterification, mechanical properties of the bottles exhibit considerable increases over those of PET.

It is important to remark that within a range of 30°C NET molecules are obtained in either block or random microstructure and with % transesterification from zero up to 20%.

Apparent compatibility is predicted in the blends, as suggested by the G' versus G" master-plots. In the low frequency range of the master-plots, scatter reflects relaxation due to branching or entanglements produced by degradation reactions. Slopes lower than two in the low frequency region of

the elastic modulus manifest the presence of an elastic network.

Bottles produced at 270°C with 4 min residence time when the PEN contents are 15 and 20 wt % are transparent and present the best properties under tensile test with low transesterification, NET block conformation and high viscosity.

ACKNOWLEDGEMENTS

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