Reactive processing of poly(ethylene 2,6-naphthalene dicarboxylate)/poly(ethylene terephthalate) blends

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(Received 2 June 1992; revised 4 January 1993)

Extrusion of poly(ethylene terephthalate)/poly(ethylene 2,6-naphthalene dicarboxylate) blends results in transesterification reactions between the two polymers. In this study, the effects of blending time, temperature, blend composition and polyester catalyst on transesterification were determined using nuclear magnetic resonance, and rate constants and an activation energy for the process were determined. Over the ranges studied, the primary factors controlling the transesterification were the blending time and temperature, while the composition of the blend and the residual polyester catalysts had little or no effect on the interchange reactions. In addition, differential scanning calorimetry measurements demonstrated that transesterification led to the formation of a single amorphous phase.

(Keywords: polyesters; transesterification; blends)

INTRODUCTION

The ability to economically produce high barrier, single layer, recyclable, clear packages from poly(ethylene terephthalate) (PET) has led to its use in many food packaging applications. The use of PET in soft drink containers, for example, has grown in a relatively short time to rival that of glass and aluminium. Even though PET has found widespread acceptance, polymers with improved barrier properties are desired for extending product shelf-life and for packaging of some high-acid-content and oxygen-sensitive materials. One candidate for such applications is the analogue to PET based on 2,6-naphthalene dicarboxylic acid, poly(ethylene naphthalene 2,6-dicarboxylate) (PEN), which possesses an oxygen permeability of approximately one-quarter to one-fifth that of PET. PEN also has advantages over PET for packaging hot-filled products, since the glass transition temperature (T_g) of PEN is approximately 45 K higher than that of PET. Unfortunately PEN is also more expensive than PET and this has limited its use.

One potential approach for combining the attractive economics of PET with the better barrier and thermal properties of PEN is through blends of the polymers. Previous work in our laboratories demonstrated that stretch-blow-moulded bottles prepared from blends of PEN and PET, with 50–80 wt% PEN, had oxygen permeabilities of approximately half that of PET. However, the blends were often unacceptably hazy. Presumably the haze was due to immiscibility of PEN and PET, and clear bottles were obtained only when sufficient transesterification, or interchange, occurred during the processing to induce miscibility. Transesterification reactions in other blends containing polyesters and their effects on miscibility have been reported and reviewed by other researchers[1–32]. However, details of the process are not yet completely understood, and there is not complete agreement in the literature about the relative importance of the three possible mechanisms (alcoholysis, acidolysis or direct ester exchange)[14,19,21,23,25–28,31,32]. Whatever the mechanism, it is generally agreed that the interchange reactions lead to the formation of first block, then random copolymers, which enhance the miscibility of the blend[1,8,13,23,26]. Because of the changes in phase behaviour and the production of copolymer, it is very likely that the properties of the blend will vary as the interchange reactions proceed[6–12,15,25,27,32]. Thus, it is important to control transesterification in order to produce a consistent product. The objective of this work was to determine the effects of the parameters controlling the transesterification occurring during melt blending of PET and PEN, with the eventual goal of using this information in a rational control scheme.

EXPERIMENTAL

A balanced partial factorial experiment was performed to determine the effects of four factors — blending time, blending temperature, PEN content and PET catalyst — on the transesterification. The ranges of variables covered in the experiment are presented in *Table 1* and are representative of those that could be encountered in production of a PEN/PET blend. The trials and homopolymer controls were randomized and run in seven constant-temperature blocks of three to four samples each. A few additional experiments were also conducted at a later date to extend the temperature range studied. A summary of all experiments performed is presented in *Table 2*.

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0032-3861/93/194060–08

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Table 1 PEN/PET blends experimental design

Experimental factors	Range
Temperature (K)	568–588[a]
Time (min)	1.5–4.5
PEN content (wt%)	50–80
Ti catalyst level (ppm)[b]	0–20

[a] Additional experiments at 548 and 558 were also conducted
[b] In blends, all other catalysts were approximately constant

Table 2 Transesterification of PEN/PET blends

Composition PEN/PET (wt ratio)	PET type	Blending temperature (K)	Transesterification (%)		
			1st pass	2nd pass	3rd pass
80/20	PET0	578	10.9	21.3	31.6
80/20	PET20	568	8.4	15.6	22.5
80/20	PET20	588	16.5	32.5	45.4
80/20	PET40	578	10.1	21.1	34.5
65/35	PET0	568	8.3	16.4	20.2
65/35	PET0	588	12.6	25.5	33.0
65/35	PET20	578	8.2	21.2	30.9
65/35	PET20	578	8.8	18.2	30.8
65/35	PET20	578	8.6	19.5	28.9
65/35	PET40	568	9.4	14.3	21.7
65/35	PET40	588	12.1	25.8	38.7
50/50	PET0	578	7.8	20.2	26.6
50/50	PET20	568	5.8	12.4	21.3
50/50	PET20	578	7.6	18.6	27.7
50/50	PET20	588	13.8	28.0	38.3
50/50	PET40	578	12.0	20.0	29.3
70/30	PET20	558	7.1	12.3	14.8
50/50	PET20	558	5.0	12.7	16.5
70/30	PET20	548	3.5	4.5	7.8
50/50	PET20	548	2.4	6.1	9.5
100/0	–	568	–	–	–
100/0	–	588	–	–	–
0/100	PET0	568	–	–	–
0/100	PET0	588	–	–	–
0/100	PET20	578	–	–	–
0/100	PET40	568	–	–	–
0/100	PET40	588	–	–	–

The PET samples and the PEN used in most of the experiments were prepared by conventional melt-phase polymerization using antimony-based catalyst systems followed by solid-state polymerization. Previous researchers have concluded that titanium catalyst in the polyester has a major effect on transesterification kinetics[14,15,19,21,28]. Therefore, PET samples with different titanium levels were employed in this work. Two PETs, designated as PET0 and PET20, were used in many of the blends. PET0 contained no titanium while PET20 contained approximately 20 ppm. These concentrations were confirmed by X-ray fluorescence. Levels of other catalysts and inhibitors (Zn, Ga, Sn, Sb, Co, P, Mn and Ge) were roughly equivalent. Molecular weights, as determined by inherent viscosity, were also comparable. The inherent viscosities of the samples as measured at a concentration of 0.005 kg l^{-1} in a 60/40 phenol/tetrachloroethane solution at 298 K were approximately 71 l kg^{-1}. A third PET sample containing 40 ppm titanium, designated as PET40, was prepared by coating PET20 with a solution of titanium tetraisopropoxide in ethanol and evaporating the ethanol. As mentioned above, the PEN was also prepared by melt and solid-state polymerization. Its inherent viscosity was 66 l kg^{-1}.

Melt blends were prepared using a 19 mm Brabender single-screw extruder with an L/D ratio of 25/1. The extruder was equipped with a mixing screw with a 3:1 compression ratio and six rows of staggered pins near the nozzle. The melt-blending time was varied by extruding each sample three times, with samples retained after each extrusion. A screw speed of 90 rev min^{-1} was used in all experiments and previous work with similar materials on this equipment indicates that these conditions correspond to an average residence time of approximately 1.5 min per pass. As shown in *Table 2*, set-point temperatures of 548–588 K were investigated. At each temperature, a constant temperature profile was used, i.e. all control zones were set to the same set-point. In order to minimize hydrolysis, all samples were dried in dehumidified air at 423 K for at least 16 h prior to each extrusion. Neat PET and PEN controls were subjected to the same drying and extrusion protocols.

The extent of interchange of the blends was determined using the region of the ^{1}H n.m.r. spectrum corresponding to the ethylene moiety. However, a few comments concerning application of the technique are in order before describing the details of measurements. As expected, based on their structures, each of the two homopolymers exhibits one solution n.m.r. peak associated with the ethylenic protons. The peak for PEN occurs at approximately 4.9 ppm, while the peak for PET occurs at approximately 4.8 ppm. This region of the n.m.r. spectrum for a mixture of the two homopolymers prepared in solution (no transesterification) is shown in *Figure 1*. Only the two peaks associated with the homopolymers are present. This same region of the spectrum is shown for a random PEN–PET copolymer with 82 mol% PEN in *Figure 2*. In this spectrum a third peak with an intermediate chemical shift is apparent. This

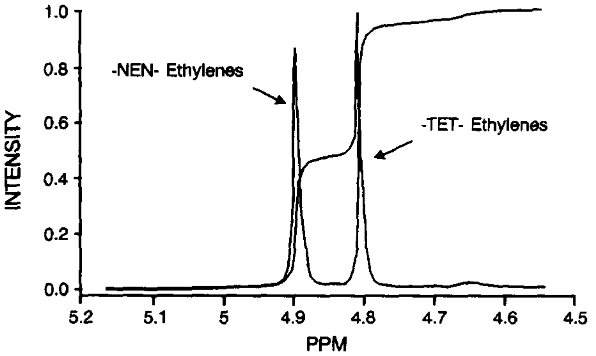

Figure 1 Proton n.m.r. spectrum of PEN and PET: ethylene region

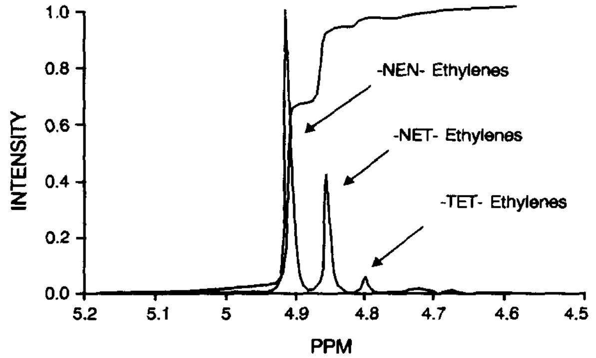

Figure 2 Proton n.m.r. spectrum of PEN–PET copolymer (82% PEN, 18% PET): ethylene region

new peak is due to ethylene protons which are between naphthalenic and terephthalic moieties in the backbone. This peak is also evident in melt blends of PEN and PET which have undergone transesterification reactions.

The amount of transesterification in a mixture of PET and PEN can range from essentially no interchange to complete interchange. In this work, mixtures with no interchange will be designated as having 0% transesterification and the random copolymer will be designated as having 100% transesterification. For a random copolymer, the relative concentration of each type of ethylene link (NEN = between two naphthalene dicarboxylate groups; TET = between two terephthalate groups; and TEN = between one terephthalate and one naphthalene dicarboxylate group) can be calculated from the fraction of naphthalene dicarboxylate and terephthalate groups using Bernoullian statistics. This procedure was used to confirm that the area of the central peak in the spectrum presented in *Figure 2* corresponds to the fraction of TEN groups expected in a random copolymer. (An alternating copolymer would have a level of transesterification by this method of greater than 100%.) From the relative area of the three ethylene proton peaks it is possible to measure the actual level of interchange in a sample. This is then compared to the theoretical level of interchange for a random PEN–PET copolymer with the same overall ratio of naphthalate and terephthalate units to arrive at a value for mole per cent transesterification. While this n.m.r. method does not give any information about the distribution of the transesterified links along a single polymer chain or the proportion of molecules that contain TEN groups, it does provide a useful quantification of the average state of the sample.

The n.m.r. measurements were performed on samples dissolved in a 70/30 (by weight) mixture of deuterated chloroform and trifluoroacetic acid. The effect of different solvents on the results was not investigated for this system. However, the data are not expected to be significantly affected by the solvent as long as the solvent is suitable for n.m.r. measurements and does not degrade the polymers during the experiment. Two n.m.r. spectrometers were used: a Jeol model GX-400 n.m.r. spectrometer, operating at a field strength of 399.65 MHz for proton observation; and a Jeol model GX-270 n.m.r. spectrometer, operating at 270.05 MHz for proton observation. ^{1}H n.m.r. spectra were accumulated using 32 768 data points, 4000 Hz frequency window (400 MHz), 2700 Hz frequency window (270 MHz), 10 s relaxation delay, 16 transients with quadrature detection and a 60° pulse angle. The spectra were transformed and phased using Jeol PLEXUS operating software and transferred to a Digital Equipment computer cluster where optimum apodization was accomplished by a Lorenzian-to-Gaussian convolution program.

In order to investigate the accuracy of this technique, a series of samples with known transesterification ranging from 0 to 100% were prepared from solvent mixtures of PEN, PET and random PEN–PET copolymer. Each sample was run from four to 10 times to test the reproducibility of the method. At 400 MHz, the average standard deviation was 1.0% and 87.5% of the data points were within two standard deviations of the predicted value. At 270 MHz, the average standard deviation was 1.4% and 75% of the data points fell within two standard deviations of the predicted level. The lowest level of transesterification detected on both instruments was 4.6% with neither instrument detecting interchange in a sample containing 1.0% transesterification. Though the 400 MHz instrument was slightly more accurate, both spectrometers gave essentially equivalent results and were used interchangeably in this work.

Differential scanning calorimetry (d.s.c.) measurements were conducted on the samples from the partial factorial experiment and the homopolymer controls. These measurements were performed with a DuPont 912 d.s.c. at a scan rate of 20 K min^{-1} using a nitrogen purge. The glass transition temperature (T_g), temperature of the peak of the crystallization exotherm (T_{ch}) and temperature of the peak of the melting endotherm (T_m) on heating were determined. The samples were heated to approximately 593 K in the first cycle and then quenched in the d.s.c. using a nominal cooling rate of 593 K min^{-1}. Following the quench, a second heating cycle was conducted in which the T_g, T_{ch} and T_m were again measured.

RESULTS AND DISCUSSION

The n.m.r.-determined transesterification levels for all experiments are presented in *Table 2*. Apparently the interchange reactions proceed very rapidly in this system as all blends showed evidence of transesterification. The transesterification levels ranged from less than 5% for blends subjected to one pass through the extruder at 548 K to 45% for one sample subjected to three passes through the extruder at 588 K. The data for the various samples and blending conditions from the partial factorial experiment are presented as a function of blending time in *Figure 3*. Though the quantity of data and the number of independent variables make interpretation of this particular figure somewhat difficult, *Figure 3* illustrates that the transesterification level is primarily controlled by the temperature and total time of the blending operation. The other factors, PEN content and PET type, have a secondary influence. Further discussion of these results, which were also confirmed by statistical analysis of the data, follows.

The effects of time and temperature on the transesterification of PEN/PET blends are emphasized in *Figure 4*, in which the average values for all samples (including the samples blended at 548 and 558 K) with a given blending time and temperature are presented. These results clearly demonstrate the significant increases in transesterification which accompany increases in time or temperature. The level of transesterification at a given temperature is, to a first approximation, a linear function of blending time. In addition, the rate at 588 K is approximately 4.5 times the rate observed at 548 K.

A similar analysis is presented in *Figure 5* for the effect of PEN content on the interchange observed. In this figure, the average values for the samples from the designed experiment with a given PEN content are presented as a function of blending time. These data indicate that there may be a slight effect of overall blend composition on the level of transesterification achieved. However, any effect is of secondary importance compared to the effects of time and temperature described above. The specific PET used has even less effect. This is demonstrated in *Figure 6*, in which the average values for samples from the designed experiment with a given blending time and PET type are presented. As these data

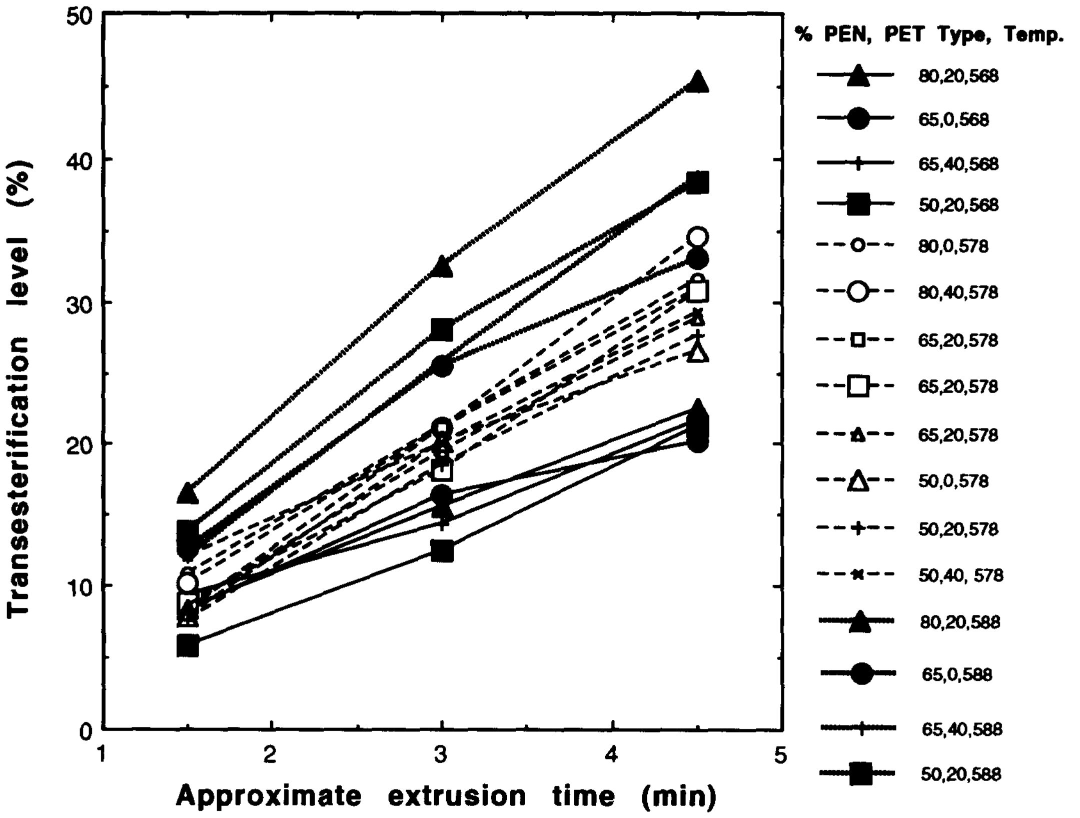

Figure 3 Effect of extrusion time on the transesterification of PEN/PET blends

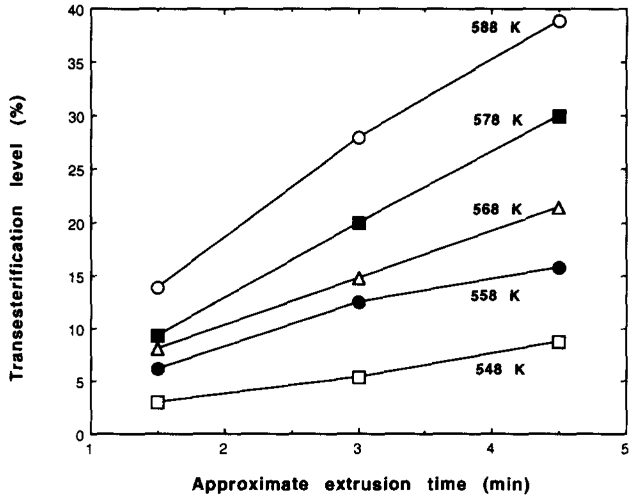

Figure 4 Effects of temperature and time on the transesterification of PEN/PET blends

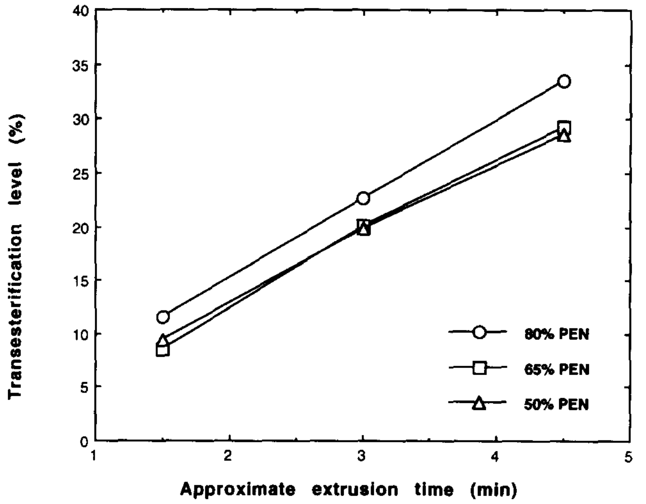

Figure 5 Effects of composition and time on the transesterification of PEN/PET blends

demonstrate, there is little if any effect of PET type on the transesterification observed. Thus, varying the amount of titanium in the PET from 0 to 40 ppm appears to have practically no effect on the interchange. As mentioned previously, the relative insensitivity of transesterification to the PET used and the PEN content of the blend were also confirmed by the statistical treatment of the data.

It is informative to compare the present results for transesterification of PEN/PET blends with those for other blends containing polyesters, and the work of Joyce and Berzinis[13] provides a particularly useful point to begin the comparison. They performed a study in which they prepared polycarbonate (PC)/poly(butylene terephthalate) (PBT) melt blends in a Haake Buchler System 90 torque rheometer and monitored the interchange using both *F*Ti.r. and n.m.r. As in the present work, they found that the amount of interchange observed was a strong function of blending time and temperature. Several other groups have also noted one or both of these effects for various blends containing polyesters[5,10,12,14,19,21–25]. Contrary to the results reported here for PEN and PET, however, Joyce and Berzinis determined that the composition of the blend had a major effect on the interchange observed in PC-rich blends. In addition, they found that the residual polymerization catalysts in the polyester did not produce significant transesterification in a convenient time-scale and that the transesterification rate was significantly increased by the addition of titanium catalyst. Earlier, other researchers had also found titanium catalysts to be important for ester interchange reactions during melt blending of polyesters with PC[14,15,19,21]. Godard *et al.*[21], for example, reported that transesterification rates were not measurable in a PET/PC blend without titanium and that the rate varied with the titanium concentration to the power of 1.85. Similarly, Devaux *et al.*[19] reported that the transesterification rate of PBT/PC blends varied with the titanium concentration to the power of 2.5. In the PEN/PET system, however, it appears that residual polyester catalysts that do not include titanium are adequate for promoting rapid interchange and that the reaction kinetics are relatively insensitive to the level of titanium catalyst over the range investigated. Thus, while there are similarities between the behaviour of polyester/PC and PEN/PET systems, it also appears that there are some significant differences. The fact that both the PEN and PET possess other residual polymerization catalysts and hydroxyl and carboxyl end-groups may account for some of the differences noted. But transesterification in other polyester/polyester blends without titanium catalysts[22–25,31] has also been reported, and it may be that rapid interchange in the absence of titanium catalyst is a general phenomenon for polyester/polyester blends, but not for polyester/PC blends. If this is true, it is not obvious why there would be a difference between the effect of titanium catalyst in polyester/polyester and polyester/PC blends. Perhaps it is an indication that there is a difference in the controlling mechanism (alcoholysis, acidolysis or direct interchange) for polyester/polyester and polyester/PC blends, particularly in the absence of titanium. However, this is only speculation.

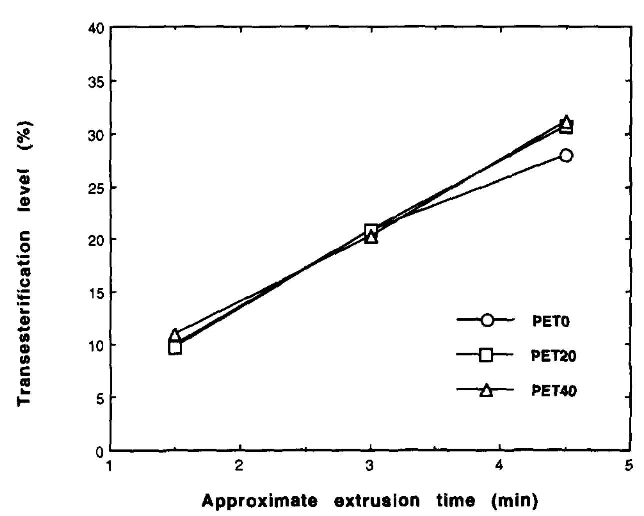

Figure 6 Effects of PET type and time on the transesterification of PEN/PET blends

Transesterification kinetics may be modelled as a first-order approach to equilibrium and first-order reaction-rate constants (k) were determined for PEN/PET blends using the approach developed by Devaux *et al.*[19]. The results of this analysis are presented in *Table 3*. As shown, the reaction-rate constant increases approximately five-fold as the temperature increases from 548 to 588 K. This corresponds to an activation energy (E_a) of 110 kJ mol^{-1} (26 300 cal mol^{-1}) (coefficient of determination, $R^2 = 0.974$). The rate constants and activation energy are similar to those previously reported for other polyester blends[13,19,21–23,25,31]. This is illustrated in *Figure 7*, in which the kinetics of transesterification for PEN/PET blends are compared with those reported for interchange of several other

Table 3 First-order rate constants for the transesterification of PEN and PET

Temperature (K)	k (1/min)	R^2
548	0.0195	0.95
558	0.0400	0.97
568	0.0535	0.98
578	0.0770	0.97
588	0.109	0.95

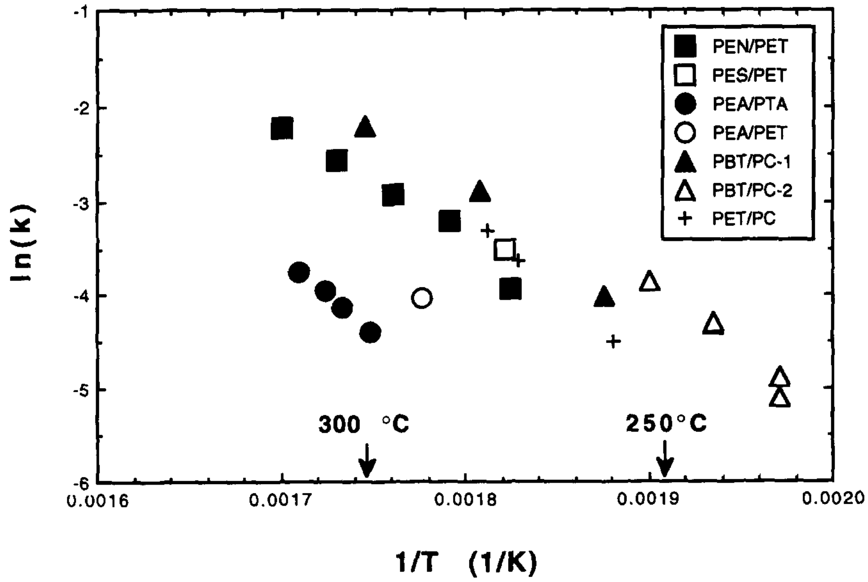

Figure 7 Comparison of transesterification kinetics for blends containing polyesters: PEN/PET from this work; poly(ethylene sebacate) (PES)/PET from data in Table 1 of reference 22; poly(ethylene adipate) (PEA)/poly(trimethylene adipate) (PTA) from data in Figure 2 and Table 1 of reference 25; PEA/PET from data in Table IV of reference 23; PBT/PC-1 from Figure 6 of reference 13; PBT/PC-2 from Table 1 of reference 19; PET/PC values for 50/50 blends with 1.70×10^{-6} mol catalyst g^{-1} polymer from Table 2 of reference 21

blends containing polyesters. In *Figure 7*, the data are presented using an Arrhenius plot in order to facilitate the comparison, since the various sets of data cover different temperature ranges. The results for the PEN/PET blends include samples with and without titanium, but none of the other polyester/polyester blends represented in *Figure 7* contain titanium. The data for the polyester/PC systems, on the other hand, are for blends that do have significant levels of titanium. As described above, rates for polyester/PC blends without titanium catalyst are very much lower. Except for the difference in the effect of titanium catalyst between the polyester/polyester and the polyester/PC blends, the agreement among the various sets of data is quite good, especially the agreement in E_a (slope). This agreement is particularly satisfying given that the reaction times for the PEN/PET blends were all based on a single value of the approximate residence time per pass, even though the extrusion temperature, sample molecular weight and sample composition could affect the actual residence time distribution. In any event, the results for PEN/PET blends appear to be in general agreement with those for other polyester blends.

In many applications, polymer clarity is a key property. The appearance of a blend can also be used as one piece of evidence in determining its miscibility. Therefore, a rough assessment of the effect of interchange on the clarity of PEN/PET blends was performed and the results are presented in *Figure 8*. All samples were qualitatively classified as either clear or hazy by visual inspection of the extruded sample. This is a simplification of the actual situation as the samples exhibited a continuous range of clarity from very hazy to quite clear. However, it proved to be adequate for our purposes. As shown in the figure, samples with greater than 10% transesterification were relatively clear, while all samples with less than 8% transesterification were relatively hazy. Between approximately 8 and 10% transesterification, mixed results were obtained. Some of the blends also contained low levels of crystallinity as determined by d.s.c., but there was no direct correlation between crystallinity and clarity. In fact, most of the neat PET samples contained higher crystalline contents than any of the PEN/PET blends and all of the PET homopolymer samples were clear. Thus it appears that levels of interchange of 10% or more are necessary to produce clear blends. Even at these levels, however, it may still be possible, through the use of different thermal treatments, to develop sufficient levels of large crystallites to affect the clarity. However, this complication was not investigated in this work.

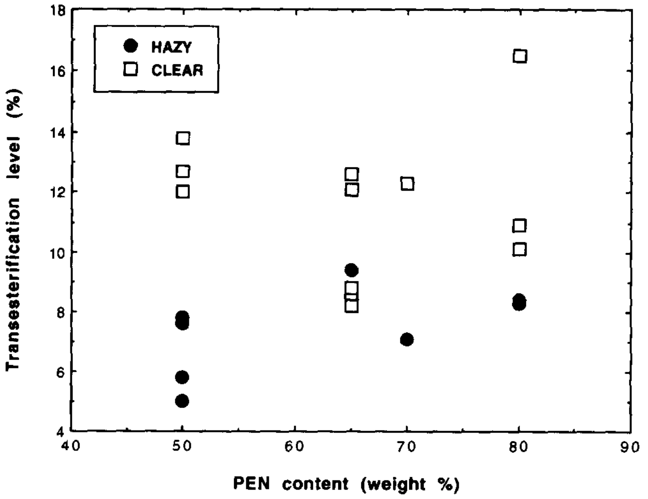

Figure 8 Relative clarity of PEN/PET blends

Results of the first and second heating cycle d.s.c. measurements for the T_gs of the blends of the designed experiment and the homopolymer controls subjected to one pass through the extruder are presented in *Table 4*. The data are also presented in *Figure 9* as a function of blend composition. For a given d.s.c. scan, each sample exhibited a single T_g which varied with the composition of the sample and was intermediate between the T_gs of PEN and PET. This behaviour is typical of a miscible system. In some cases, there was a definite broadening of the T_g region (these samples are indicated by an asterisk in *Table 4*), but none of these samples, not even those that were relatively hazy, exhibited multiple T_gs. This is somewhat surprising since haziness is often an indication of immiscibility and immiscibility would lead one to expect multiple T_gs. This apparent contradiction is probably due to a lack of sensitivity of the d.s.c. measurement which limits the resolution of the T_gs. As mentioned above, there was definite broadening of the T_g region for some samples. Also, some of the first cycle d.s.c. traces were complicated and difficult to interpret. As will be shown, it is likely that the samples with low levels of interchange are partially miscible, i.e. they do not possess a single phase but there is significant solubility of both components in each phase. This partial miscibility could account for both the broad T_gs and the haziness. Comparison of the T_gs measured on the first and second heating cycles provides one indication that PEN and PET are partially miscible. The values of the T_gs for the second cycle fall within a narrower temperature range for a given composition. This is most likely due to two effects. First, the d.s.c. measurement exposes the sample to an additional heating step which removes any ageing effects on the d.s.c. response. But most importantly, the additional heat history experienced during the measurement protocol allows the interchange reaction to proceed, thereby promoting miscibility and narrowing the T_g region.

In order to further investigate the effects of the d.s.c. measurement on the state of the sample, a 50/50 blend of PEN and PET with no transesterification was prepared by dissolving the polyesters in a 70/30 hexafluoroisopropanol/methylene chloride solution and then recovering the blend by precipitation with methanol. D.s.c. measurements were performed on this sample using the procedure described above, except that it was only heated to 578 K and then immediately removed from the instrument and quenched by placing it on a block of metal in contact with dry ice. This protocol was selected to minimize transesterification during the d.s.c. measurement. A second heating scan was then conducted. A broad, complicated T_g region, with a central point of 364 K, was observed in the first heating cycle. On the second cycle, however, two distinct T_gs were readily apparent at 356 and 390 K. Interestingly, if the sample was held in the melt for approximately 1 min at 578 K following the first heating cycle, the second cycle T_gs shifted to 360 and 383 K and began to merge. These phenomena are clear evidence that the samples with low levels of interchange are partially miscible and that the samples react during the d.s.c. measurement[8].

Most of the samples tested exhibited one crystallization

Table 4 D.s.c. results for PEN/PET blends after one pass through the extruder

Composition PEN/PET (wt ratio)	PET type	Blending temperature (K)	T_g 1st cycle[a] (K)	T_g 2nd cycle (K)	T_{ch} 1st cycle (K)	T_m 1st cycle (K)	T_{ch} 2nd cycle (K)	T_m 2nd cycle (K)
80/20	PET0	578	385	386	480	535	491	523
80/20	PET20	568	387	386	478	536	492	523
80/20	PET20	588	384	387	495	531	491	521
80/20	PET40	578	386	386	478	537	488	523
65/35	PET0	568	386*	381	484	533	–	–
65/35	PET0	588	376	377	487	529	–	–
65/35	PET20	578	379*	377	484	531	–	–
65/35	PET20	578	376	378	473	535	–	–
65/35	PET20	578	376	380	475	534	–	–
65/35	PET40	568	382	379	485	532	–	–
65/35	PET40	588	377	378	475	532	481[b]	514[b]
50/50	PET0	578	360*	372	469	523/533	–	–
50/50	PET20	568	366*	373	450/470	521/531	–	–
50/50	PET20	578	382*	372	465	521/533	–	–
50/50	PET20	588	368	372	487	527	–	–
50/50	PET40	578	372	374	490	529	–	–
100/0	–	568	399	398	499	537	491	538
100/0	–	588	396	400	491	540	485	541
0/100	PET0	568	352	351	418	525	418	525
0/100	PET0	588	351	351	415	525	418	526
0/100	PET20	578	351	352	412	525	426	524
0/100	PET40	568	350	350	414	524	421	526
0/100	PET40	588	348	350	410	526	418	525

[a] Asterisk indicates a very broad T_g region

[b] Small peak

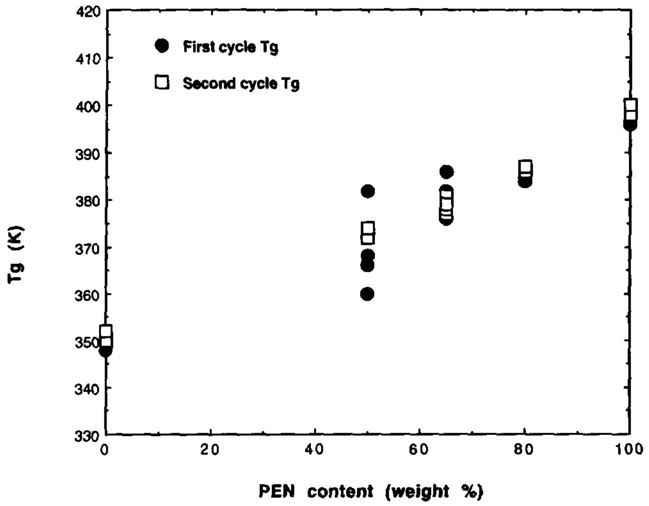

Figure 9 Glass transition temperatures of PEN/PET melt blends

peak and one melting peak in the first heating cycle. However, the three samples from the partial factorial experiment with the lowest levels of interchange displayed two melting peaks upon heating in the d.s.c. and the sample with the lowest level of transesterification also exhibited two crystallization peaks on heating. In addition, the blend precipitated from solution possessed multiple crystallization and melting peaks (first cycle: T_{ch} at 462 K, T_ms at 524 and 536 K; second cycle T_{ch}s at 441 and 489 K, T_ms at 523 and 531 K). While the majority of samples did not exhibit second-cycle crystallization or melting peaks, the samples with 20% PET did have a measurable T_{ch} and T_m on the second heating cycle. In general, the second-cycle T_{ch} for these samples was at a higher temperature than the first cycle T_{ch} and, conversely, the second cycle T_m was at a lower temperature than the first cycle T_m. One other melt-blended sample exhibited small crystallization and melting peaks on the second heating cycle, and these were also slightly shifted. These shifts in crystallization and melting temperatures, the lack of multiple crystallization and melting peaks for most of the samples, and the complete absence of crystallinity in many samples during the second heating cycles are all further evidence of the interchange reactions which lead to the formation of copolymer and induce miscibility in the PEN/PET blends[9–12].

SUMMARY

Melt blending of PEN and PET results in transesterification reactions between the two polymers which can be conveniently followed by ^1H n.m.r. Over the ranges studied, the amount of interchange is determined primarily by the blending time and temperature. The composition of the blend and the residual polyester catalysts, on the other hand, have little effect on the degree of transesterification achieved during the blending. The interchange reactions proceed rapidly during conventional melt processing using a single-screw extruder, and levels of transesterification ranging from less than 5 to approximately 45% were obtained by varying the time and temperature of the blending. The kinetics of transesterification for this blend are in general agreement with those for other polyester/polyester blends.

D.s.c. measurements support the conclusion that the interchange reactions produce copolymer which improves the miscibility of the system. The improved miscibility, in turn, results in improved clarity. Based on the present preliminary results it appears that approximately 10% transesterification is required to produce clear samples. However, in any scheme to produce materials from melt blends of PEN and PET, several other factors would also have to be dealt with. Other important considerations include identifying the point at which the critical properties of the blend are detrimentally affected by interchange, identifying the effects of processing and interchange reactions on molecular weight degradation and determining the effects of other processing variables. Furthermore, the present study dealt exclusively with melt processing in one single-screw compounding extruder. It is expected that behaviour of blends processed in other equipment would be at least qualitatively similar, but the effects of the specific type of processing equipment on the transesterification and properties of the blend would also have to be determined.

ACKNOWLEDGEMENTS

F. Shepherd and R. R. Light performed much of the previous work with these blends and supplied samples and advice. Their assistance was invaluable. Our estimates of reaction times were based on a residence time distribution study for the Brabender extruder conducted by C. M. Stipe. P. P. Shang and J. H. Dean assisted with the d.s.c. measurements. Finally, H. L. Rauch helped with the experimental design and performed a statistical analysis of the data.

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