Transesterification Reaction Kinetics of Poly(ethylene terephthalate/Poly(ethylene 2,6-naphthalate) Blends

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ABSTRACT: The transesterification reaction of poly(ethylene terephthalate)/poly(ethylene 2,6-naphthalate) blends during melt-mixing was studied as a function of blending temperature, blending time, blend composition, processing equipment, and different grades of poly(ethylene terephthalate) and poly(ethylene 2,6-naphthalate). Results show that the major factors controlling the reaction are the temperature and time of blending. Efficiency of mixing also plays an important role in transesterification. The reaction kinetics can be modeled using a second-order direct ester–ester interchange reaction. The rate constant (k) was found to have a minimum value at an intermediate PEN content and the activation energy of the rate constant was calculated to be 140 kJ/mol. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 2422–2436, 2001

Key words: transesterification; PET/PEN blend; ester–ester interchange reaction

INTRODUCTION

Poly(ethylene 2,6-naphthalate) (PEN) is a polyester with a chemical structure similar to that of poly(ethylene terephthalate) (PET). The difference between PEN and PET is that, instead of the benzene ring in PET, PEN has a naphthalene ring,[1,2] which makes the PEN chain stiffer than the PET chain, resulting in the higher heat resistance, mechanical properties, and barrier properties of PEN. Because of its high price, PEN is commercially used only in special applications such as magnetic recording tape and electronic applications. Needs for clear polymers with properties intermediate to those of PET and PEN are currently arising from both the refill and hot-fill segments of the PET bottle business.[3–9] Blends of PET and PEN combine the superior properties of PEN with the economy of PET and have properties intermediate to those of PET and PEN.

Both PET and PEN are polyesters. When melt mixing PET and PEN, a transesterification reaction will occur.[10] This reaction is not unique for PET and PEN blends; however, it is common for the polyester family. Although there have been many studies of this transesterification between polyesters,[11–26] there is not complete agreement as to the mechanism of the reaction.

Kimura and Porter[11] studied the transesterification reaction in poly(ethylene terephthalate)/polycarbonate (PET/PC) blends and pointed out that the blends converted first to block copolymers. As the reaction time increased, nearly completely random copolymers were formed. Devaux et al.[12–15] also demonstrated this in their experiments.

Kotliar[16] reported that blends of two different polycondensation polymers, such as polyesters and polyamides, can react if their chain links are broken as a consequence of high temperature such as occurs in melt processing. Kotliar[16] re-

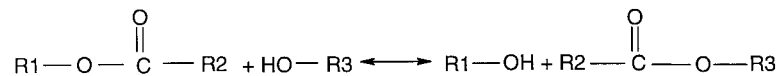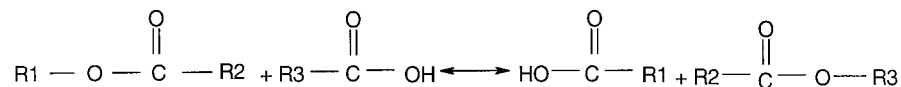viewed interchange reactions involving the condensation polymers, polyesters, and polyamides. He discussed the statistics of three different exchange reactions, in which the chains are terminated by hydroxyl or carboxyl groups and suggested three possible mechanisms:
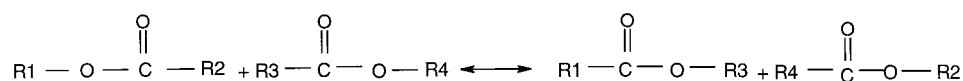
1. Intermolecular alcoholysis

2. Intermolecular acidolysis

3. Transesterification

The term transesterification reaction, however, is generally used to describe all of the preceding reactions. R represents part of the polymer chain.

As many authors have pointed out,[17–20] the transesterification reactions of polyester blends depend strongly on their initial compatibility and on their blending conditions. These include temperature, duration of mixing, preparation method, viscosity match, and the presence of catalysts and inhibitors. The methods generally used in transesterification reaction studies of polymer blends are: infrared spectroscopy (IR)[21–23]; nuclear magnetic resonance (NMR)[12–15,24–32]; thermal analysis such as DSC, DTA, and DMA[33–35]; and chromatography.[17] The most commonly used technique for studying the transesterification reaction is NMR.[24–29] The work of Devaux and Godard et al.[12–15,24,30] on PC/poly(butylene terephthalate) (PBT) and PC/PET blends shows that the reaction can be assumed to be a second-order reversible direct ester–ester interchange reaction. These results show that the rate constant (k) for PC/PET blends can be expressed as follows:

$$k(1/\text{min}) = 3.8 \times 10^{20} \times [\text{Ti}]^{1.85} \times e^{(-31,100/RT)}$$

where Ti is the titanium catalyst used for manufacturing polyesters. The activation energy for the reaction was calculated to be 130.0 kJ/mol for PC/PET blends and 130.9 kJ/mol for PC/PBT blends.

Stewart et al.[7] studied (by means of NMR and DSC) the reactive processing of PEN/PET blends with high PEN contents, melt-mixed through a single-screw extruder. Their results showed that the transesterification reaction of PEN/PET blends is a strong function of both blending temperature and blending time. The level of the transesterification reaction was found to have approximately a linear relationship to blending time. The activation energy for the rate constant was determined to be 110 kJ/mol. This value is very similar to those reported for other polyester blends.[15,30,31,36–40] Minor effects on the reaction were reported to be caused by the composition of the blends and the catalyst systems. Thus they suggested that the transesterification reaction mechanism of PET/PEN blends might be different from that of PC/polyester blends.[36–41]

McGee and Jones[6] studied the effect of different PEN materials on the reaction, by using both PEN homopolymers and PEN and PET copolymers. (PEN-T is a PEN copolymer composed primarily of PEN with a small percentage of terephthalate units.) A higher level of randomness was observed for blends of PET with PEN-T copolymer than that for blends made from PET and PEN homopolymer, which was the result of the inherent initial randomness level in the PEN-T copolymer. The rate of reaction was almost the same with both systems.

Ihm et al.[42] observed results similar to those of Steward et al.[7] The degree of randomness is sig-

nificantly influenced by temperature and time, but is negligibly influenced by blend composition. Based on the sequence length, calculated from homo and hetero segments, they concluded that the transesterification reaction first produces a block copolymer and then proceeds to form a random copolymer. They also concluded that transesterification might take place with no preference between PEN and PET.

In this study, in addition to blending temperature, blending time, and blend composition, different grades of PEN and PET were used to study the effects of material source on the reaction. The effects of processing conditions on the reaction were also studied.

EXPERIMENTAL

Materials

Four kinds of PET and three kinds of PEN were used for this study. PET A is a PET homopolymer prepared from dimethyl terephthalate (DMT) by Eastman Chemical Company (Kingsport, TN). It has an intrinsic viscosity (IV) of 0.72, which corresponds to a number-average molecular weight (M_n) of 24,300. PET B and PET C were also prepared from DMT by Eastman Chemical Company, with IVs of 0.80 (M_n 28,400) and 1.03 (M_n 41,200), respectively. These copolymers were modified with 3.5 mol % cyclohexane dimethanol (CHDM). PET D is a copolymer prepared from terephthalic acid (TPA) by Shell Chemical Company (Akron, OH). It is modified with low levels of isophthalic acid (IPA) and has an IV of 0.80 (M_n 28,400). Both PEN A and PEN B are homopolymers manufactured by Hoechst (Spartanburg, OH), with IVs of 0.57 (M_n 22,400) and 0.63 (M_n 27,200), respectively. PEN C is a PEN copolymer with 8 mol % terephthalate content, manufactured by Hoechst with an IV of 0.57. The corresponding equivalent copolymer M_n is 22,400, based on PET homopolymer. The IV determination of PET was done at 25°C in 60/40 (w/w) phenol/tetrachloroethane solution, whereas the IV of PEN was determined at 30°C in the same solution.

Extrusion

The effects of blending temperature, blending time, composition, material source, and processing equipment were studied. A summary of exper-

Table I   Experimental Parameters

Composition of PEN/PET (w/w)	PET	PEN	Extruder	Extruder Temperature, T (°C)
5/95	A	A	Single	300
20/80	A	A	Single	290
20/80	A	A	Single	300
20/80	A	A	Single	310
40/60	A	A	Single	300
60/40	A	A	Single	300
80/20	A	A	Single	300
20/80	B	A	Single	300
20/80	D	A	Single	300
5/95	D	B	Single	300
10/90	D	B	Single	300
20/80	D	B	Single	300
40/60	D	B	Single	300
50/50	D	B	Single	300
60/40	D	B	Single	300
20/80	C	B	Single	300
20/80	C	C	Single	300
50/50	D	C	Single	300
10/90	D	B	Twin	300
20/80	D	B	Twin	300

imental parameters is given in Table I. Prior to the extrusion, all materials were vacuum dried at 120°C for at least 20 h in a Forma Scientific (Marietta, OH) model 3237 vacuum oven. The temperature was then turned down to let the material cool under vacuum to avoid absorption of moisture during cooling. The dried resins were mixed using a model LS-1390 twin-shell blender (Patterson-Kelloy Co., East Stroudsburg, PA) before being fed into the extruders.

A lab-scale Brabender (Rochelle Park, NJ) single-screw extruder with a general purpose screw of diameter of 19 mm, a length-to-diameter (L/D) ratio of 22/1 and a compression ratio of 3/1 was used. For each processing temperature, a constant temperature profile was used to minimize the temperature fluctuation. The temperatures used were 290, 300, and 310°C as summarized in Table I. A nitrogen purge was used during extrusion to prevent oxidative degradation. The extrudate was run through a narrow die to give a ribbon approximately 1.25–2.0 in. wide and 26–41 mils thick. The extrudate was quenched to room temperature using a winder consisting of water-cooled rolls. Ribbons obtained from the Brabender were chopped into small pieces and subjected to multiple passes through the extruder. The chopped pieces were dried at the

same conditions as described previously, prior to extrusion. Samples after each pass were saved for analysis.

A Werner and Pfleiderer (Ramsey, NJ) (ZSK-30) self-wiping corotating twin-screw extruder was used to study the effects of processing equipment on the transesterification reaction. A uniform temperature profile was used to minimize the effect of temperature fluctuation. Screw speeds of 100 and 80 rpm were used and found to give equivalent results. A nitrogen purge was used during processing to prevent oxidative degradation. The extrudate passed through a cooling water bath and then through a pelletizer. Pellets obtained from the twin-screw extruder were collected and subjected to multiple passes through the twin-screw extruder. The pellets were vacuum dried at the same conditions as the PET and PEN resins, prior to extrusion. Samples were saved for analysis after each pass.

Simulated Static Mixing

PEN B and PET D were ground into fine powders. Powders with two different particle sizes were obtained, one with particle sizes of less than 40 mesh, the other with particle sizes of around 10 mesh. The powders were physically mixed at a weight ratio of 10/90 PEN/PET and vacuum dried at the same conditions as described previously. The dried mixture was introduced into the differential scanning calorimeter (DSC) pan and heated to 300°C at 320°C/min and held at 300°C for 2, 5, 8, and 10 min, respectively, before being quenched to room temperature. The samples prepared under each condition were saved and subjected to NMR study.

Melt Viscosity of Pure PET and PEN

A Rheometrics (Piscataway, NJ) Visco-Elastic Tester (RVE) was used to measure the melt viscosity of pure PET and PEN used in this experiment. All the PET and PEN samples were analyzed at 300°C. A nitrogen atmosphere was used when performing the experiment to prevent oxidative degradation at high temperatures.

Nuclear Magnetic Resonance (NMR)

Solution proton (^{1}H) NMR was used to study the extent and kinetics of the transesterification reaction. The specimens for the NMR experiments were dissolved in 30/70 (w/w) mixtures of deuterated trifluoroacetic acid (TFA) and chloroform (CDCl$_3$). Proton NMR was performed at 20°C on a Varian VXR-400 spectrometer (Varian Associates, Palo Alto, CA). The spectrometer was operated at a field strength of 399.95 MHz. Spectra were accumulated using 30,016 data points, 5999 Hz frequency window, 6-s relaxation delay, and 32 transients with double-precision acquisition. The proton 90° pulse width was 28 μs. The central peak of CDCl$_3$ was assigned a value of 7.24 ppm with respect to tetramethylsilane (TMS). The spectra were Fourier transformed and phased using the software with VXR-400 data processing system. The optimum apodization was accomplished by convolution function of the sum of Lorentzian and Gaussian functions with the software provided by Varian Associates.

RESULTS

Data Analysis

The —CH$_2$O— region of the NMR spectrum was used to determine the distribution and relative intensities of sequences representing the ethylene moiety between two naphthalene groups (NEN), between two terephthalate units (TET), and between one naphthalate and one terephthalate unit (NET). The peak at approximately 4.9 ppm was assigned to be PEN homopolymer (NEN),[7] the peak at 4.8 ppm was assigned to be PET homopolymer (TET), and the peak in between was assigned to be PEN/PET copolymer (NET). These three peaks can be used quantitatively to determine the compositions of the blends and the extents of the transesterification reactions. The area under each peak was measured and a standard method developed by Amoco Chemical[26] as well as Yamadera and Murano[24] was used to calculate the degree of transesterification or the degree of randomness present after various processing histories. According to this method, three NMR peaks from high to low frequency represent the NEN, NET, and TET ethylene residues, respectively. Mole fractions of naphthalate units (P_n) and terephthalate units (P_t) are obtained from the intensities or areas of these three peaks. Total area of the peaks (A) is calculated from the area of each peak ($A_{NEN} + A_{NET} + A_{TET}$). The mole fraction ($P$) of each ethylene glycol residue is then calculated as a fraction of the total area, by dividing each area by the total area to obtain P_{NEN}, P_{NET}, and P_{TET}.

The mole fractions of naphthalate (P_n) and terephthalate (P_t) units can be obtained as

$$P_n = (P_{NET}/2) + P_{NEN}$$

$$P_t = (P_{NET}/2) + P_{TET}$$

The percentage mole fraction of naphthalate units (mol % NDC) of the total naphthalate and terephthalate units is therefore ($P_n \times 100$).

If the units along the PEN/PET copolymer chain could be examined from one end to the other, the probability of finding an N unit next to a T unit would be $P_{tn} = (P_{NET}/2P_t)$. Similarly, the probability of a T unit next to an N unit is $P_{nt} = (P_{NET}/2P_n)$. The degree of randomness (B) is defined as

$$B = P_{nt} + P_{tn} = (P_{NET}/2P_t) + (P_{NET}/2P_n).$$

From probability theory $P_t = 1 - P_n$; therefore,

$$B = P_{NET}/[2P_n(1 - P_n)]$$

If one defines

$$(NET)_{obs} = P_{NET}$$

$$(NET)_{cal} = 2P_n(1 - P_n)$$

then the percentage transesterification is defined as:

$$\%B = [(NET)_{obs}/(NET)_{cal}] \times 100$$

This is identical to the percentage degree of transesterification defined by Amoco Chemical.[26] Accordingly, if $B = 1$, the N and T units take a totally random distribution, that is, the copolymer formed is a random copolymer and the probability of finding a copolymer unit is described by Bernoulli statistics. If $B < 1$, the N and T units tend to cluster in blocks of each units, that is, the sequence length is long and the copolymer formed is a block copolymer. If $B = 0$, the system is a mixture of homopolymers. If $B > 1$, the sequence length becomes shorter and the copolymer generated tends to form an alternating copolymer. Finally, if $B = 2$, an alternating copolymer is formed. The number-average sequence lengths (L) of N and T units in the polymer are given by

$$L_n(N) = (2P_n/P_{NET}) = 1/P_{nt}$$

$$L_t(T) = (2P_t/P_{NET}) = 1/P_{tn}$$

According to Devaux and Godard et al.,[12–15,24,30] in terms of a direct ester–ester interchange, the overall reaction mechanism can be written as

$$–NEN– + –TET– \leftrightarrow –NET– + –TEN–$$

If the initial mole fractions of NEN and TET units are a and b, and the mole fraction x of the copolymer NET peak at time t is $x = (NET)_t$, assuming a second-order reversible reaction (i.e., first-order to either unit) we can write[12–15]

$$\frac{dx}{dt} = k(a - x)(b - x) - k'x^2 \qquad (1)$$

Using the same method of Devaux and Godard et al.[12–15,24,30] at equilibrium, $x_e = ab$, $k = k'$. With these assumptions, eq. (1) can be written as

$$\frac{dx}{dt} = k(x_e - x) \qquad (2)$$

Now defining the transesterification ratio (r) as $r = x/a$ and integrating eq. (2), the following equation can be obtained:

$$\ln\left(\frac{b}{b - r}\right) = kt \qquad (3)$$

Thus, a plot of $\ln[b/(b - r)]$ versus reaction time (t) gives a straight line, the slope of which is the rate constant (k).

Equation (3) assumes that complete mixing has been achieved since the start of the reaction. This is not always true, especially during the initial extrusion. For example, during the first pass through an extruder, the two components are usually not completely mixed and the resultant extrudates are usually not uniform, which causes a retardation in the reaction. This retardation results in the observation of the degree of randomness occurring after a certain induction time. This retarded reaction or reaction after a certain induction time period can be modeled by the modification of eq. (3) by introducing a parameter describing the retardation effect (t_0). The modified equation can be described as

Table II   Degree of Randomness for PET A/PEN A Blends Extruded through Brabender at 300°C

Pass Number	Composition: PEN/PET, w/w (mol % NDC)				
	5/95 (3.2)	20/80 (13.6)	40/60 (31.2)	60/40 (56.3)	80/20 (78.2)
1	—	0.45	0.77	1.03	9.1
2	0.52	6.1	6.2	15.3	17.2
3	11.3	11.5	10.6	21.1	29.6
4	33.8	16.7	16.6	29.4	33.5
5	—	25.1	—	—	—

$$\ln\left(\frac{b}{b-r}\right) = kt + t_0 \qquad (4)$$

This equation gives a better data fit for the reaction of the blends through the extruder. In addition, it solves the problem of the induced reaction time or retarded reaction. However, to maintain consistency and to enable comparison of our data with literature values, eq. (3) was used in the analysis.

DISCUSSION

The degree of transesterification (degree of randomness) was calculated from NMR measurements. The calculated transesterification levels for samples are presented in Tables II–IV. Clearly, the transesterification reaction proceeds very fast in PEN/PET blends, in that all the blends tested show the occurrence of the reaction. The change of blending time was achieved by reprocessing the extrudates by multiple passes through the extruder. The transesterification levels range from less than 5% for blends extruded just once through the single-screw extruder to more than 70% for blends run through the twin-screw extruder for three passes.

Tables II–IV show that the transesterification reaction proceeds with increased blending time. The compositions of the blends, therefore, change as copolymers continue to form. It is thus inappropriate to use the term PEN or PET composition to describe the blend composition. The dimethyl-2,6-naphthalene dicarboxylate (NDC) content, which is the percentage fraction of naphthalate unit of the total terephthalate and naphthalate units, however, does not change with the reaction. The NDC content is a more appropriate and accurate term to use for the blend composition; however, for the sake of simplicity, we will still use PEN composition to describe the blend composition in some cases. Tables II and III give the blend composition in terms of both wt % blended as well as mol % measured with NMR.

Blending Time

Different blending times were achieved by processing the blends through the extruder for multiple passes, with samples retained after each extrusion. The averaged residence times at the 300°C processing temperature were obtained from our previous study.[43] The degree of randomness or transesterification levels were plotted versus the blending times for two blend systems ex-

Table III   Degree of Randomness for PET D/PEN B Blends Extruded through Brabender at 300°C

Pass Number	Composition: PEN/PET, w/w (mol % NDC)				
	5/95 (3.6)	10/90 (7.6)	20/80 (17.7)	40/60 (33.3)	60/40 (53.9)
1	10.6	5.74	2.85	2.31	2.81
2	15.3	12.9	6.7	7.98	9.63
3	27.1	20.0	11.5	11.4	14.8
4	28.9	28.9	15.6	16.4	20.5
5	—	40.5	21.1	—	—

Table IV   Degree of Randomness for Blends Extruded through a Twin-Screw Extruder or Single-Screw Extruder as Well as with Different PEN and PET Sources

| Pass Number	Twin-Screw Extruder		Single-Screw Extruder			
	90% PET D/ 10% PEN B	80% PET D/ 20% PEN B	80% PET C/ 20% PEN B	80% PET C/ 20% PEN C	80% PET B/ 20% PEN A	80% PET D/ 20% PEN A
1	30.7	23.9	—	—	8.9	2.5
2	68.4	47.5	7.7	18.5	11.9	7.3
3	—	74.5	10.3	20.9	13.2	8.8
4	—	—	17.1	25.6	31.2	15.8
5	—	—	19.8	28.6	—	—

truded at 300°C, as shown in Figures 1 and 2. It is clear from these figures that the transesterification levels are, to a first approximation, linear functions of blending times. This is also expected from our theory. Earlier we discussed that the reaction mechanism can be modeled by a second-order ester exchange reaction. According to this model, the extent of the reaction will level off after some time and the changes of the extent of the reaction with the reaction time will follow an exponential function. Using the Taylor series expansion, the extent of the reaction changes approximately linearly with the reaction time for the initial part of the reaction. Figures 1 and 2 also show that, although there is a difference for lower and higher NDC content blends, in terms of the reaction, the difference is not very substantial.

Transesterification kinetics were modeled as second-order equilibrium reactions and the rate constants (k) were determined for the blends as described in the data analysis section. A plot of $\ln[b/(b - r)]$ versus blending time for the PEN A with PET A blend system is shown in Figure 3. A linear relationship was obtained for different blend compositions, indicating that the assumed mechanism is valid. The rate constants can be obtained from the slopes of the straight lines shown in Figure 3. Values for k, thus calculated, are tabulated in Table V. The range of k values obtained here are in agreement with those obtained by Stewart et al.[7] for their PEN/PET blend system and are also in agreement with the values obtained by other authors for other polyester blend systems.[15,30,36–39]

Blending Temperature

Temperature is an important factor for the transesterification reaction.[5–9,14,15,41,42] Figure 4 shows degree of randomness or transesterification levels plotted against blending times for 20%
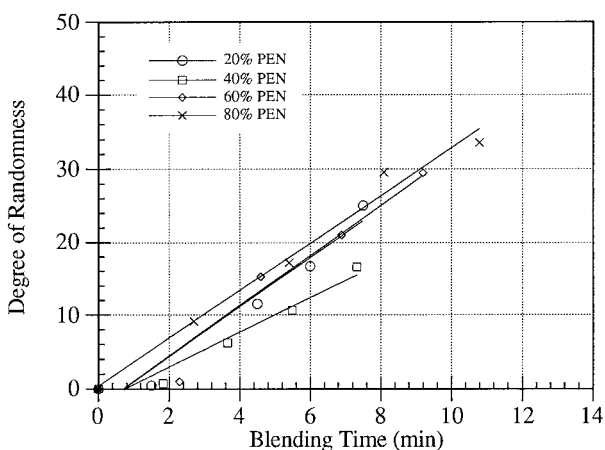
Figure 1   Degree of randomness versus blending time at 300°C for PET A/PEN A blends.
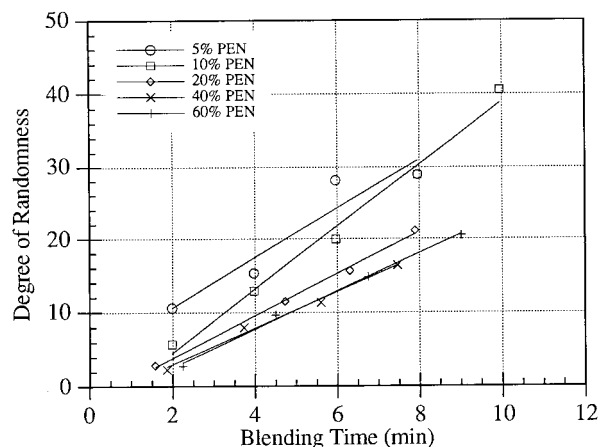
Figure 2   Degree of randomness versus blending time at 300°C for PET D/PEN B blends.
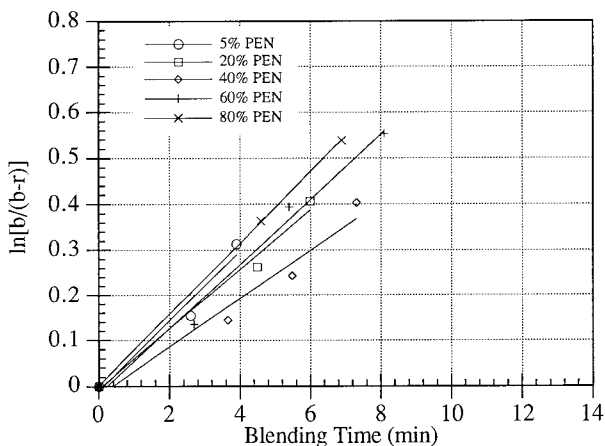
Figure 3 $\ln[b/(b-r)]$ versus blending time at 300°C for PET A/PEN A blends.

Figure 4 Degree of randomness versus blending time for PET A/PEN A (80/20) blends at different blending temperatures.

PEN composition blends, prepared at blending temperatures of 290, 300, and 310°C. The degree of randomness changes approximately linearly with blending time for all extrusion temperatures. The slopes and positions of these lines are different, as shown in Figure 4. As extrusion temperature increases, the transesterification reaction greatly increases in both the extent and the rate. Figure 5 shows plots of $\ln[b/(b-r)]$ versus the residence time for three different temperatures. Again, three lines were obtained, with 310°C at the top, 290°C at the bottom, and 300°C intermediate. The slopes of the straight lines give the rate constant k. The calculated k values are listed in Table VI. It is seen that k increases rapidly with temperature. It increases from 0.05 1/min at 290°C to 0.14 1/min at 310°C.
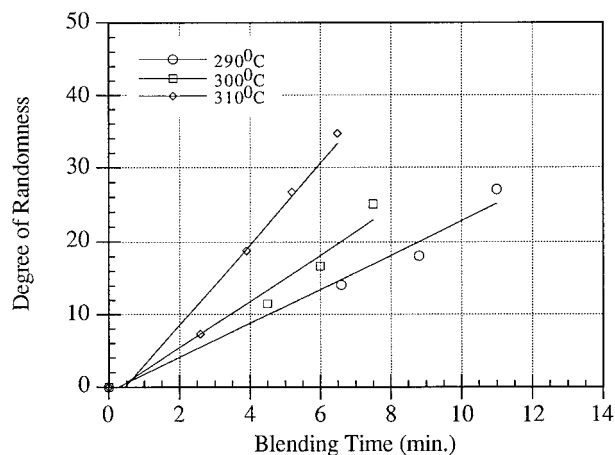
The Arrhenius equation was used to describe the temperature effects on the rate constant (k). The equation can be written as[44]

$$k = Ae^{-(E_a/RT)} \quad (5)$$

where E_a = activation energy for rate constant k

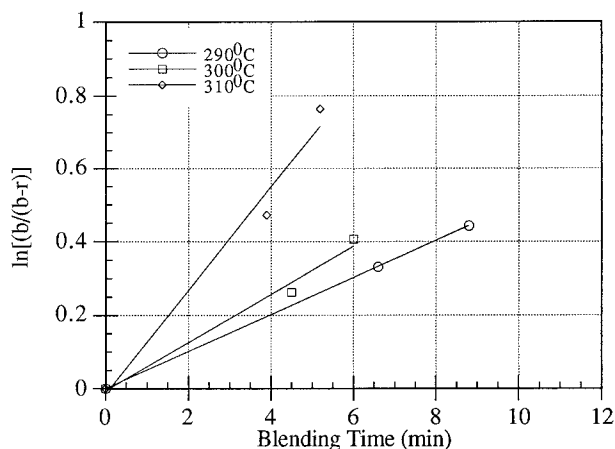**Table V   Rate Constant (k) for PET A/PEN A Blends Extruded through Brabender at 300°C**

NDC (mol %)	k (min^{-1})
3.2	0.08
13.6	0.07
31.2	0.05
56.3	0.08
78.2	0.11

A = frequency factor
R = gas constant
T = temperature (K)

The activation energy E_a can be obtained from the slope of the straight line drawn by plotting $\ln(k)$ versus $1/T$. The E_a value calculated using this method was 140.4 kJ/mol. This is in the same range as Stewart et al.'s[7] value of 110 kJ/mol calculated for their PEN/PET blend system and is also in agreement with values reported by other authors for other polyester blend systems.[15,36–39] The value is typical of ester interchange reactions[45–51] and thus provides a proof for our assumed transesterification mechanism.

Figure 5 $\ln[b/(b-r)]$ versus blending time for PET A/PEN A (80/20) blends at different blending temperatures.

Table VI   Rate Constant (k) for PET A/PEN A Blends at Different Blending Temperatures

Temperature (°C)	k (min^{-1})	Activation Energy (kJ/mol)
290	0.050	
300	0.066	140.4
310	0.141	

Blend Composition

Different groups have obtained different results as to the effect of blend composition[10] on the transesterification reaction. Previous investigations of PEN/PET blends[7,42] generally revealed that the composition has little effect on transesterification of the blends. Based on this, Ihm et al.[42] suggested that transesterification takes place with no preference between PET and PEN. Results from our laboratory show approximately linear relationships between transesterification levels and blending times for all blend compositions. Similar results were obtained by Stewart et al.[7] and Ihm et al.[42] There seem to be minor differences among different compositions, although lower and higher NDC composition blends show higher transesterification levels than those of the intermediate ones. The differences can be elucidated more clearly by a kinetics study in terms of the rate constant k.

The rate constants (k) calculated for different blend compositions are shown in Table V. Values of k for different compositions are within the same range, but there are differences among the compositions. Figure 6 plots k as a function of NDC content for blends of PET A and PEN A. Values of k first decrease with NDC content, go through a minimum at NDC mol % of around 32, and then increase with further increase in NDC content. This behavior can be explained by the utilization of reaction kinetics according to collision theory.[44] In the formation of intermediate active centers (intermediate active complexes), in which (k) contains two terms, entropy and enthalpy have been assumed and can be written as follows:

$$k = \frac{k_B T}{h} \gamma_A \gamma_B e^{(\Delta S/R)} e^{-(\Delta H/RT)} \tag{6}$$

where k_B = Boltzmann's constant, 1.380×10^{-16} erg/K

h = Plank's constant, 6.024×10^{-27} erg
γ_A, γ_B = activity coefficient
R = gas constant
ΔS = entropy term
ΔH = enthalpy term (related to the activation energy)

Comparing eq. (6) with the Arrhenius equation shows that

$$A = \frac{k_B T}{h} \gamma_A \gamma_B e^{(\Delta S/R)} \tag{7}$$

If we neglect the activity coefficient term, then ΔS can be calculated from the frequency factor A as[44]

$$\Delta S = 2.303R \, \log\left(\frac{Ah}{RT}\right) \tag{8}$$

A can be calculated from the intercept of the straight line of $\ln(k)$ versus $1/T$. In the case of the 20/80 PEN A/PET A blend, A was calculated to be 4.91×10^{11}. So ΔS was calculated to be -26.5 J/mol K from eq. (8). The large negative value of ΔS is consistent with the assumed ester–ester interchange reaction.[45–51]

In eq. (6), ΔH is related to the activation energy (E_a), which remains almost the same for different compositions because the energy barrier is the same.[43] ΔS changes with composition and would assume a minimum value at the point at which the two components are at the equivalent composition.[52] In the case of the PET/PEN blend, this is around the NDC value of 32 mol % or 40 wt % PEN composition. The lower ΔS value at the
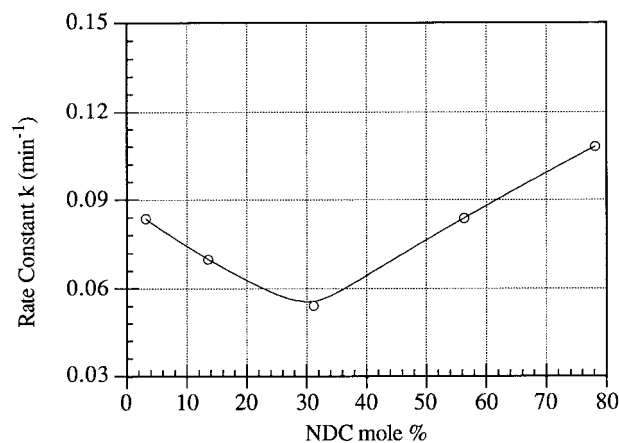
Figure 6   Rate constant (k) versus NDC content for PET A/PEN A blends processed at 300°C.

intermediate NDC content region causes the lowered k values at this region.

Mixing

Mixing always plays an important role in polymerization[43,53] because increased mixing provides more contact between reactant molecules, which is necessary for reactions to occur. Mixing is also a very complicated process, which is very difficult to simulate and quantitatively calculate. Here we qualitatively study the mixing effect by comparing two different cases, one of which deals with continuous mixing during processing and reaction, the other with premixed blends and involves no further mixing during the reaction. The former example was achieved by extrusion. During extrusion, the materials continue to mix while being transferred from the feeding zone to the die. The latter example was achieved by static heating in a calorimeter (DSC), in which the premixed samples were heated up to the reaction temperature and kept at that temperature for a certain period of time. These samples did not experience further mixing during the process of reaction. One point that needs to be emphasized here is that the reaction between PET and PEN in the melt state occurs at the interface of the two materials because of the high viscosity of the polymers. Thus, the area of the contact interface of the two reactant components determines the reaction. The diffusion of polymer molecules is so slow compared to the reaction rate that it can be neglected. As long as the interface is the same, or the mixing effect does not change much, the reaction is the controlling step. This explains the activation energy we achieved in the previous discussion. Usually, the activation energy of the viscosity change for polymers is around 40 kJ/mol,[54] which is much smaller than the activation energy of the ester interchange reaction, which in some ways is similar to solid-state polymerization.[55] Also, there exists a limit in the extruder as to the extent of the mixing,[56] which means that dispersed particle size can be reduced only to a certain value. That is the reason for the need of different extruders (twin-screw extruder) for blending to achieve good dispersive mixing. In the case of the single-screw extruder, discussed previously, the reaction occurs at the interface of the PET and PEN and it seems that the chosen processing conditions do not significantly affect the mixing effect for the same composition.

This means that the interface area for different temperatures does not change so much that it would cause substantial differences in the reaction. Simulated static mixing samples were made by premixing fine powders of pure PEN and PET. The mixture was introduced into a DSC pan and quickly heated to 300°C and kept at this temperature for different periods of time. Two kinds of powders with different particle sizes were used, one with particle sizes less than 40 mesh, the other with particle sizes around 10 mesh. More surface contact would be expected between the smaller-sized powders than between the larger ones, and the reactions therefore should be different.

For smaller-sized powders, the NMR spectra show a detectable occurrence of transesterification after 5 min at 300°C. For the larger-sized powders, the reaction could be detected only after 10 min of reaction time at 300°C. The NMR spectra for 5-min reaction time of smaller-sized powders and 10-min reaction time for larger-sized powders are shown in Figure 7. Previous discussions showed that the reaction for the same blend system with the same composition extruded through the Brabender single-screw extruder at the same processing temperature was detected immediately after the first pass (i.e., the reaction time is less than 2 min). The reason for this is mixing. In the extruder, the mixture was forced to mix continuously during the reaction process. The mixing effect in the extruder is better, compared to that in the DSC case, because the extruded reactant molecules are continuously forced to be in contact, thus causing more molecules to react. New molecules are brought to the interface continuously and the reacted molecules are removed from the interface, causing more molecules to come into contact and react. In the mixture of larger-sized powders, there are less surface contacts between the two reactant components, compared with the mixture of the smaller-sized powders, where more surface contacts are expected, resulting in more reaction. Ihm et al.[42] studied PEN/PET blends using DSC as the heating equipment and reported the observation of transesterification by NMR after 5 min. Their blends were made by solution/precipitation. Their premixed components were mixed at a molecular level compared to the macro- or microlevel of mixing in our DSC mixtures. This explains why they observed the reaction after 5 min, whereas for us the transesterification didn't occur until 10 min for the larger-sized particles. We concluded from the pre-
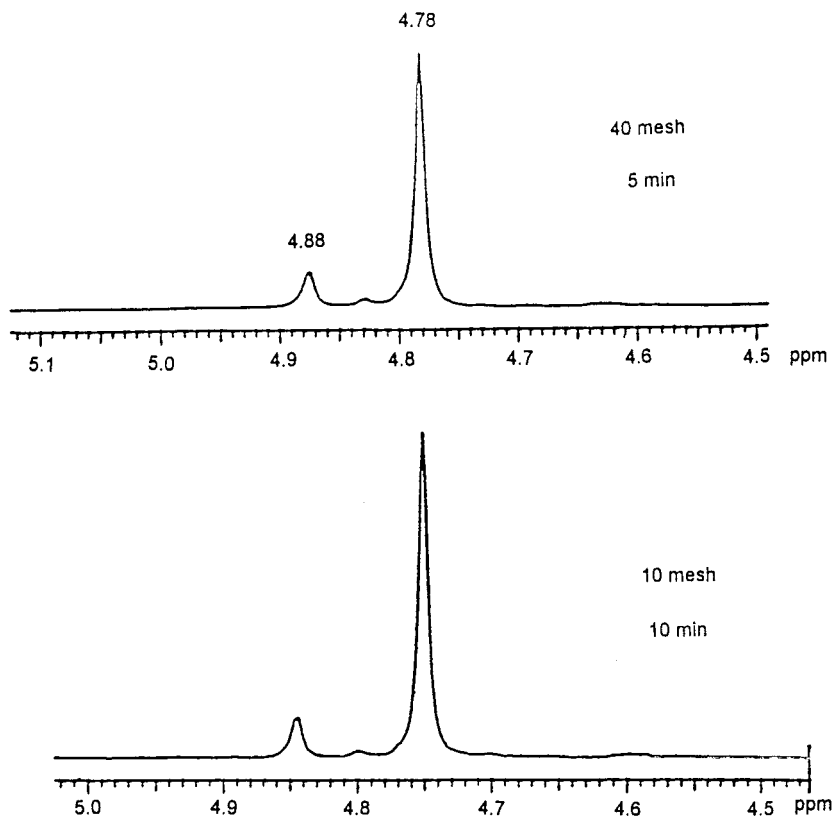
Figure 7 NMR spectra of PET D/PEN B blends prepared with a DSC at 300°C to simulate static mixing conditions.

ceding discussion that better mixing gives faster and more complete transesterification because of the extensive contact of the reactant components.

Equipment Factor—Different Extruders

Different extruders were used for the equipment factor study (twin-screw extruder versus single-screw extruder). Because of the limited quantities of PEN raw materials, only two blend compositions were prepared using the twin-screw extruder. Figure 8 shows transesterification levels (degree of randomness) plotted against numbers of passes for blends with the same composition, passed through either the twin-screw extruder or the single-screw extruder. It is obvious that blends processed with the twin-screw extruder exhibit much higher transesterification levels than those processed with the single-screw extruder. Transesterification levels of up to 70% were observed for the 20% PEN composition blend, passed through the twin-screw extruder three times. At equivalent processing conditions, transesterification levels obtained for the same

composition with the single-screw extruder were less than 35%. Even if we consider the longer residence time in the twin-screw extruder, the transesterification level is still much higher for the twin-screw extruder than for the single-screw
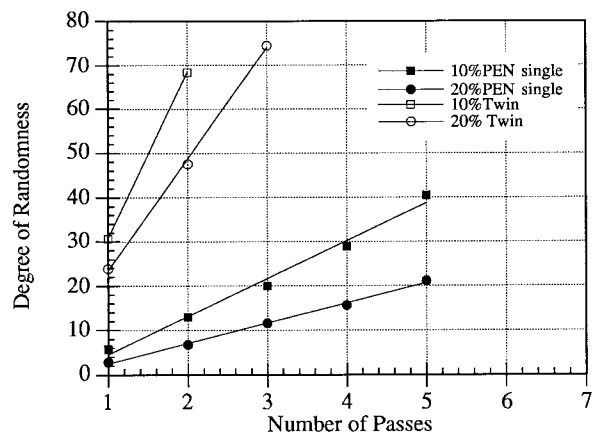

Figure 8 Degree of randomness versus number of passes for PET D/PEN B blends prepared at 300°C with different extruders.

extruder, one of the reasons for which is mixing. It is well known that a twin-screw extruder offers much better mixing effects than does a single-screw extruder.[56] The dispersed particle size that can be achieved by the single- and twin-screw extruder is different. There is a limit to the mixing or the dispersion that can be achieved in a single-screw extruder,[56] whereas a twin-screw extruder offers much better dispersive mixing.

Another possible reason for the higher levels of transesterification, obtained in the twin-screw extruder, might be the temperature control. The previous section already showed that transesterification is very temperature sensitive; thus, variations in temperature will cause great differences in the transesterification level. For both twin- and single-screw extruders, the temperature control is achieved by controlling the barrel temperature. This issue is very complicated because, within the extruder, temperatures vary along the radial cross-section direction. The shear-generated heat also alters the temperature and temperature distribution within an extruder. The temperature and temperature distribution are different for a twin-screw and single-screw extruder, even though uniform temperature profiles are set for both systems. The twin-screw extruder offers better heat transfer, resulting in more uniform temperature within the extruder. The higher transesterification levels resulting from twin-screw extrusion are the combined effects of mixing and temperature variations. Martin[56] used a specially designed mixing screw for the extrusion of PET and PEN blends and found an enhanced reaction with this screw, compared to the reaction obtained using a general-purpose screw. The enhanced mixing obtained also caused more shear-generated heat, which itself caused the temperature rise and therefore caused the enhanced transesterification. This enhanced reaction thus resulted from the combined effect of mixing and temperature variations (also possibly longer residence times).

Viscosity and Viscosity Match

The viscosities for the PET and PEN materials are different as shown in Figure 9. Wu[58] showed that the particle size (α) of a dispersed elastic phase in a viscoelastic matrix is a function of shear rate (G), the viscosity ratio (λ), the specific polar interaction (γ), and the viscosity of the matrix phase (η). The correlations can be described as follows:
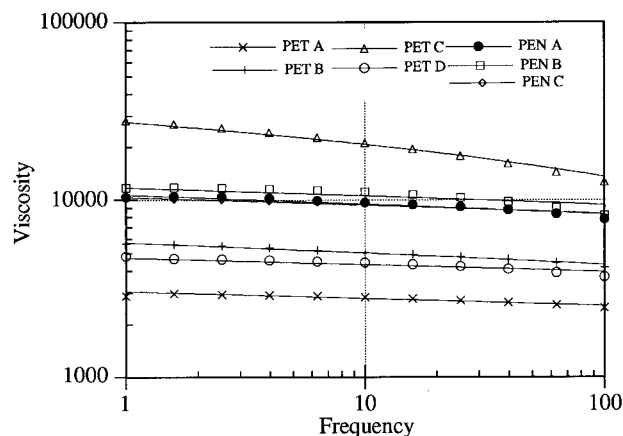
Figure 9 Melt viscosities of different PET and PEN materials measured at 300°C.

$$(G\eta\alpha)/\gamma = 4\lambda^{0.84} \quad \lambda > 1 \tag{9}$$

$$(G\eta\alpha)/\gamma = 4\lambda^{-0.84} \quad \lambda < 1 \tag{10}$$

Thus, different viscosities and viscosity ratios give different droplet sizes, which means different mixing effects (different contact surface area). Different viscosities and viscosity ratios will therefore affect the transesterification reaction. The shear rate exerted on the polymer in the extruder and the viscosity of the polymer both vary along the length of the extruder, as well as in the radial direction of the screw's cross section. Moreover, the viscosity of a polymer melt is a function of both the temperature and shear rate. This interdependence among the viscosities, shear rates, temperatures, and the complex strain fields in the extruder makes it difficult to estimate a single value of viscosity or shear rate for calculation purposes. A qualitative comparison is therefore presented instead.

Figure 9 shows the melt viscosities obtained for the different PET and PEN materials used in the experiments at the 300°C processing temperature. PEN A and PEN B were selected to react with PET D, the results of which are shown in Figure 10. There is not much difference in the transesterification levels after the same number of extrusion passes, which is expected because there is not much difference in the viscosities of PEN A and PEN B. The viscosity ratios between PET and two PENs are also similar. Both PENs are homopolymers having similar melting points and manufactured by the same company using the same method. Thus, no factor is expected to
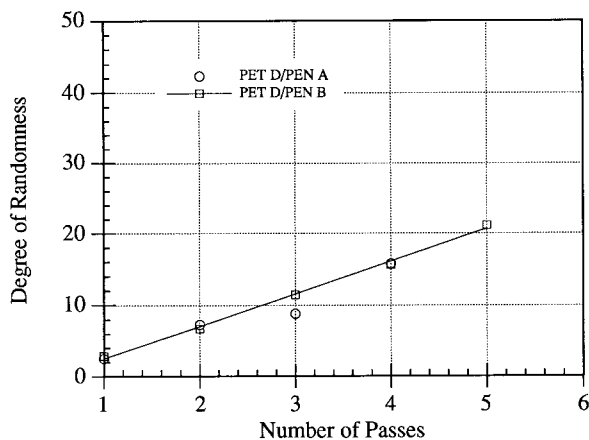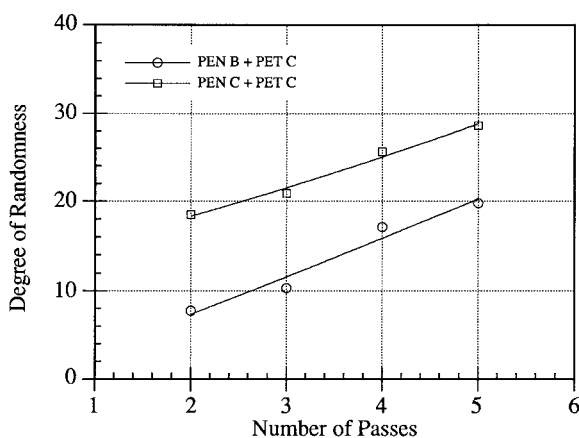
Figure 10 Degree of randomness versus number of passes at 300°C for blends of similar viscosity match.

cause substantial differences in the transesterification reaction between the two systems.

The study of the influences of matrix viscosity is very difficult to carry out because mixing can not be isolated from the viscosity effect. The higher the viscosity, the worse the mixing. Equations (9) and (10), however, do not include the mixing effect; thus, confusing results may be obtained if only eqs. (9) and (10) are applied.

PEN Source

Two different PENs were used for the study of PEN sources. PEN B homopolymer and PEN C copolymer, with 8 mol % terephthalate content, were blended with PET C copolymer. Figure 11 shows the transesterification level (degree of ran-
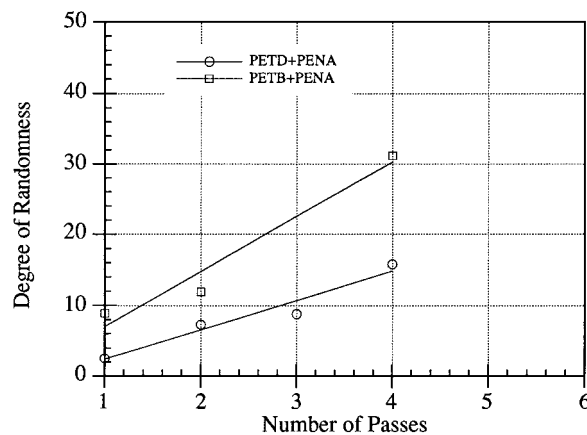
domness) plotted as a function of the number of passes through the single-screw extruder. It is obvious that blends with PEN copolymer show higher transesterification levels than do those with PEN homopolymer. Both PEN system blends exhibit linear relationships between transesterification levels and blending times. The two lines are almost parallel to each other, with the PEN copolymer blends in the upper position. This indicates similar reaction mechanisms and reaction rates have occurred between PET and PEN homopolymer and copolymer materials. The reason for the higher transesterification levels with the PEN copolymer blends is that there already exists an inherent initial randomness in the PEN copolymer, which causes the differences in the transesterification levels observed.[6]

PET Source

PEN A homopolymer was blended with two PET copolymers, made through different polymerization methods, and incorporated with different second monomers. Differences in blends prepared from PET B and PET D do not result from viscosity effects since these copolymers have similar molecular weights and melt viscosity values. As can be seen in Figure 12, changes in degree of randomness are linear with blending time for both blend systems. The transesterification reaction, however, is more favored in the system with PET B. After equivalent numbers of extruder passes, transesterification levels are higher for blends containing PET B than for those contain-

Figure 11 Degree of randomness versus number of passes at 300°C for 80% PET C blended with 20% PEN homopolymer (PEN B) or copolymer (PEN C).

Figure 12 Degree of randomness versus number of passes at 300°C for 20% PEN A blended with 80% PET copolymer B or D with equivalent melt viscosities, but from different manufacturing conditions.

ing PET D. Because melt viscosities and molecular weights of the PETs are almost the same, the differences must originate from the residual polymerization catalyst systems and the small amounts of the second monomers used to copolymerize the two PETs. It can be seen that different catalyst systems, different polymerization methods, or different copolymers of PET influence both the rate and extent of the transesterification reaction in PET/PEN blends.

CONCLUSIONS

From the preceding discussion, we can draw the following conclusions. The transesterification reaction between PET and PEN during melt processing is very complicated, and there are many factors affecting this reaction. The major effects can be attributed to blending temperature and blending time. The blend compositions and different PEN and PET materials used also affect the reaction. Moreover, the viscosity of the matrix material and the viscosity match are additional influencing factors; mixing is also very important for the reaction. The differences in the transesterification levels are related to differences in the contact surface areas. The reaction kinetics can be modeled with a second-order direct ester–ester exchange reaction. The rate constant (k) calculated from the NMR results has a minimum value at the intermediate NDC composition range, as has been explained in terms of collision theory. The activation energy of the reaction was calculated to be 140.4 kJ/mol, which is within the range of values obtained by other authors who assumed the same reaction mechanism in the study of polyester blends.

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