Structure and Properties of Naphthalene-Containing Polyesters. 4. New Insight into the Relationship of Transesterification and Miscibility

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ABSTRACT: It is generally agreed in the literature that transesterification leads to or enhances miscibility; that is, transesterification is a necessary condition for miscibility in the polyester blends. We present here, for the first time, indirect and direct experimental evidence to prove that this statement is not completely correct. The experiments have been designed on the basis of three considerations: (1) to avoid sample artifacts, we prepared binary blend systems by coprecipitating the blend from the solution; (2) blends were melt pressed at different times in vacuum; (3) both solution and solid state NMR were simultaneously used to study the same sample sets. For many liquid crystal polyester and crystal polyester blends, 45 min melt-press times show neither transesterification nor miscibility. Based on the solid state NMR results, the PEN-d_{10}/PET blend becomes miscible after melt press time greater than 0.5 min. Based on solution NMR results, there is no transesterification for the blends that were melt pressed for 30 s and 2 min. The transesterification kinetic rate constant of 0.028 37 min^{-1} and a 1.5 min retardation time are obtained. During this 1.5 min retardation time the blend system becomes miscible. After that time the polyester blend undergoes transesterification following conventional kintics. This is the strong and direct evidence to prove that transesterification is not a necessary condition for miscibility.

Introduction

During the last several decades, polymer blends have become of prime commercial importance. Many commercially useful blends are based on polyesters. It is well-known that polyester blends undergo transesterification reactions during melt processing. The result of this exchange reaction is the formation of block/random copolyesters from the original binary pair. Understanding the relationship between transesterification and miscibility is important on both theoretical and practical grounds.

The majority of studies in the literature have qualitatively monitored miscibility through phase changes, as measured by DSC, DMTA, WAXD, or microscopy.[1−5] Indeed, these indirect measurements cannot provide quantitative information with regard to the transesterification in polyester blends. Other studies have employed direct measurements, such as IR and solution NMR to identify the transesterification. It is surprising that few studies have correlated phase changes with the extent of transesterification.[11−13] Details of the transesterification 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 midchain ester exchange).[1−13] Whatever the mechanism of transesterification, it is generally agreed in the literature that transesterification leads to or enhances miscibility; that is, transesterification is a necessary condition for miscibility in the polyester blends.

The results of the present study show that this conclusion is not completely correct. We have tried to answer the following question: is the formation of a single phase a consequence of transesterification or, vice versa. The experiments have been designed based on the following considerations. The extruder, which is frequently used to prepare polymer blends, is a “black box”; the process chemistry is often complex. To avoid the complexity, we prepared our binary blend systems by coprecipitating the blend from a solution of common solvent. By this method there is good mixing and no transesterification occurs for our starting blends. We tried to determine whether transesterification or miscibility occurs first. The initial state of the mixture is very important in this study. For most systems reported in the literature, both events have already finished; therefore, it is difficult to answer which occurs first. We have used both solution and solid state NMR to simultaneously study the same sample sets. These methods were used because high-resolution solution NMR spectroscopy is an efficient method to detect the chain structure and the sequence distribution for samples with different transesterification contents, while solid state NMR[14,15] is a sensitive method to detect the miscibility, morphology, and molecular motion of the blend before and after transesterification.

Experimental Section

Details on the synthesis of the poly(ethylene naphthalene-2,6-dicarboxylate) (PEN), deuterated PEN, the copolyesters of poly(ethylene terephthalate) and poly(4-hydoxybenzoate) (PET-*co*-PHB), and the copolyesters of PEN and PHB have been reported.[1] The catalyst system is $Mn(OAc)_2/Sb_2O_3$. Polycarbonate (PC) is the product of Polysciences Inc. The blends were obtained by dissolving both polymers in $CHCl_3/(CF_3)_2CHOH$ (4/1, v/v) and coprecipitating in ethanol. The precipitate was dried in vacuo at 40 °C. The amorphous films for transesterification studies were obtained from the precipitate powder by melt-pressing in vacuo for various times at 280 °C. Since the thickness of the samples is only about 0.1 mm, only 5 s is necessary for the samples to reach the temperature of the upper and lower hot plates.

The solid state ^{13}C NMR spectra were performed at room temperature on a Chemagnetics CMX 200 NMR spectrometer, operating at 50.38 MHz for ^{13}C. Samples were spun in a Chemagnetics 7.5 mm Pencil MAS probe at spinning speeds of 4.5 kHz. The solution ^{13}C NMR spectra were performed on Varian Gemini 200, XL 400, and Unity 600 NMR spectrometers in a mixture of deuterated chloroform and trifluoroacetic acid(4/1, v/v). To run the CP/MAS^{13}C NMR with no decoupling

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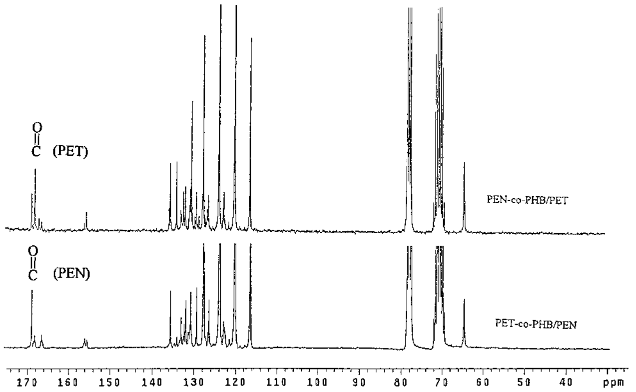

Figure 1. ^{13}C NMR spectra of 50/50 blends of PET-*co*-PHB-(40:60)/PEN and PEN-*co*-PHB(50:50)/PET after 45 min melt-pressing in a vacuum.

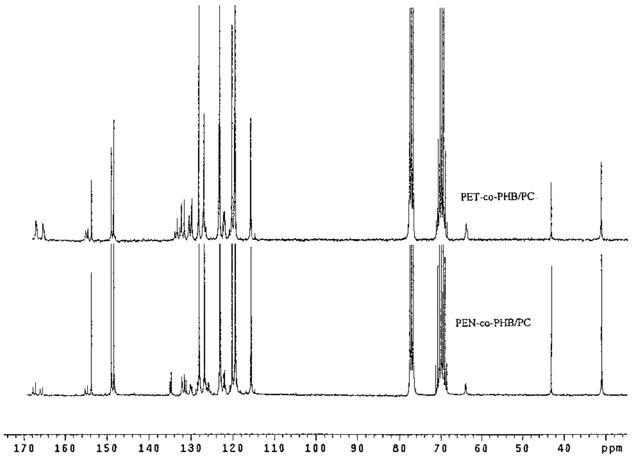

Figure 2. ^{13}C NMR spectra of 50/50 blends of PET-*co*-PHB-(40:60)/PC and PEN-*co*-PHB(50:50)/PC after 45 min melt-pressing in a vacuum.

conditions, the proton 90° pulse length was 4 μs, corresponding to a spin-locking field strength of 62.5 kHz. Due to the low sensitivity of the method, 10 000 transients were accumulated to obtain a satisfactory signal-to-noise ratio. The contact time was 3 ms, and the recycle time of the pulse was 4 s. Spinning sidebands were suppressed by using TOSS.[9] Chemical shifts were referenced to TMS in solution and via the carbonyl carbon line of glycine (176.03 ppm) in solid.

Results and Discussion

Indirect Evidence: No Miscibility, No Transesterification. Figure 1 shows the ^{13}C NMR spectra of 50/50 blends of poly(ethylene naphthalene-2,6-dicarboxylate) (PEN), a (40:60) copolymer of poly(ethylene terephthalate) and poly(4-hydoxybenzoate) (PET-*co*-PHB), and a 50/50 blend of PET and PEN-*co*-PHB(50:50) after 45 min of melt-pressing in vacuo. No hybrid sequence signal due to transesterification between blends was detected, although transesterification has been reported for copolyesters PET-*co*-PHB,[16] PEN-*co*-PHB,[17] and PEN-*co*-PET.[18] Recent results[19] indicate the two blends studied here are immiscible.

Figure 2 shows ^{13}C NMR spectra of 50/50 blends of polycarbonate (PC) and PEN-*co*-PHB(40:60), and a 50/50 blend of PC and PET-*co*-PHB(40:60), after 45 min of melt-pressing in vacuo. No hybrid sequence signal due to transesterification between these two blends was detected, although transesterification has been reported for the blends PET/PC, PEN/PC, and PET-*co*-PEN/PC.[20] These results show that the necessary condition for transesterification to take place is that the nonidentical ester groups from the homopolyesters are close to each. Similar results were obtained from studies of a blend of the ternary copolyester PEN-*co*-PET-*co*-PHB(35:35:30) with the binary copolyester PET-*co*-PHB(30:70).[21] The first one, when quenched from 280 °C in ice water, is isotropic, while the second one is liquid crystalline. The DMA results indicate that after a 45 min melt press, there are two phases. This is a consequence of the rule that isotropic and liquid crystalline polymers are not miscible. The existence of two phases also indicates that no transesterification has been detected. The sensitivity of the NMR method to detect the small amount of transesterification will be discussed in the following section. Therefore, the conclusion can be made that some miscibility is necessary for transesterification to occur.

Direct Evidence: Miscibility Occurs before Transesterification. The above three experiments provide the indirect evidence that transesterification is not a necessary condition for miscibility in the polyester blends. To provide direct evidence, several model blend systems were prepared. To get good mixing and no transesterification, all binary blend systems in our lab were made by coprecipitating the blend from a solution of the common solvent, $CHCl_3/(CF_3)_2CHOH$(4/1, v/v), in ethanol. The blends were then pressed in the melt state, 280 °C, at different times.

Preparing a set of samples with short melt press times is one of the key steps to answer the question. For long melt process time, both transesterification and the miscibility occur, making it difficult to determine which event occurs first. The first sets of sample were prepared with melt press times of 0.5, 2, and 10 min.

Simultaneous study of transesterification and miscibility for the same sample sets is another key step. In the present study, the same blend samples were divided into two parts. One was dissolved in deuterated solvent to measure solution NMR spectra, which will provide information about transesterification as a function of melt pressing time. The other part was used to measure solid state NMR spectra, which will provide information about miscibility of the blend systems. The first blend system we studied was PET/PEN, which has recently attracted significant industrial interest.[22−24]

The chemical shifts and the values of $^{H}T_{1\rho}$, proton spin−lattice relaxation times in the rotating frame, are almost the same for the polymer pairs, PEN and PET.[19] Therefore it is not possible to get information on the miscibility of the system by using normal solid-state NMR methods, which are based on the chemical shift difference and/or the proton relaxation time difference of the component polymers. Recently, we utilized delayed decoupling and no decoupling ^{13}C CP/MAS NMR for blends that contain protonated polymer A and deuterated polymer B.[19,25,26] These methods allow one to obtain miscibility information at the molecular level even if the values of chemical shift and/or proton relaxation times of the two components are the same.

Figure 3 shows the no decoupling ^{13}C CP/MAS NMR of a PEN-d_{10}/PET(50/50) blend after different melt pressing times at 280 °C. Under this condition, it is known that the high-resolution cross polarization resonance lines from protonated carbon atoms are not observed.[19,25,26] Magic angle spinning by itself, however, is sufficient to produce the high-resolution cross polarization resonance line from quaternary carbon atoms

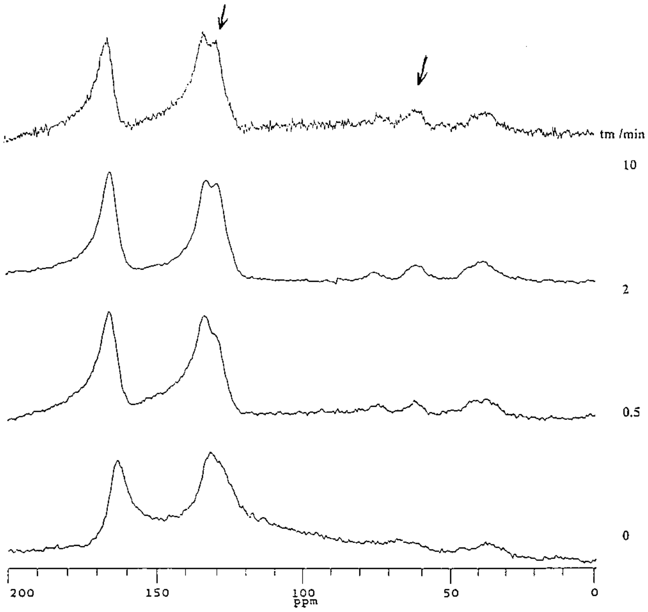

Figure 3. No decoupling ^{13}C CP/MAS NMR spectra of blends PEN-d_{10}/PET(50/50) after different melt pressing times at 280 °C. Arrows indicate the resonances due to the intermolecular cross polarization between the deuterated PEN and the protons in the protonated PEN.

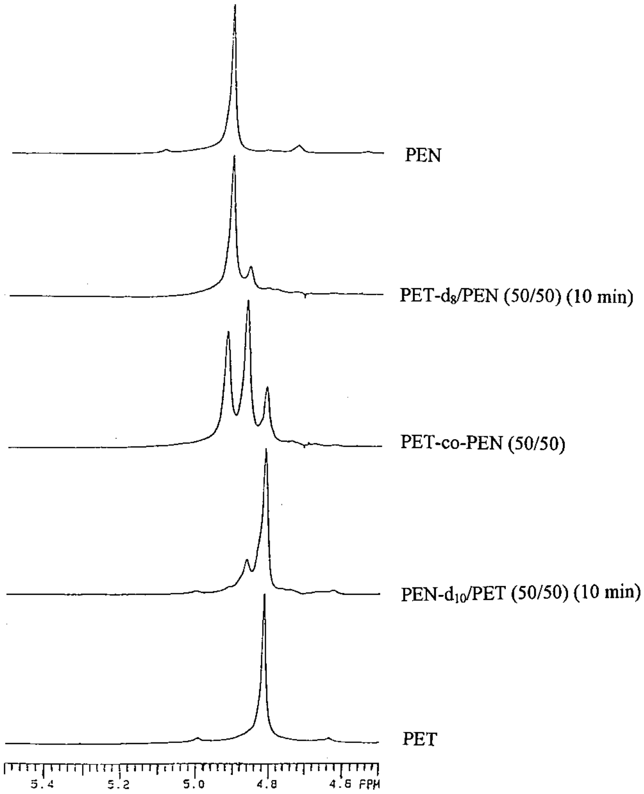

Figure 4. 400 MHz ^1H NMR spectra of (a) PET, (b) PET-d_8/PEN(50/50) after 10 min melt-pressing in a vacuum, (c) PET-*co*-PEN, (d) PEN-d_{10}/PET(50/50) after 10 min melt-pressing, and (e) PEN. The resonances at 4.80 and 4.90 ppm are from the CH_2 groups of triad TET and NEN, respectively, while the resonance at 4.85 ppm is from the CH_2 group of hybrid triads NET.

in protonated polymer and from deuterated carbon atoms in the miscible blend with protonated polymer. For the blend without melt pressing, the resonance lines of CD_2 and deuterated aromatic carbon atoms completely disappear. This shows that the resonances of deuterated PEN were not activated by the protons of PET, which proves that PEN and PET are phase-separated. When the melt pressing time was longer than 0.5 min, the resonance lines of CD_2 and deuterated aromatic resonance from PEN reappeared, which is proof of miscibility. The new resonance lines come from the contribution of the intermolecular cross polarization between the deuterated PEN and the protons in the protonated PET and the intermolecular cross polarization can only occur if the average proton−carbon distances in two different molecules are 6 Å or less. The intensity of these two lines became higher when the melt-pressing time was increased. These results indicate that after melt-press times longer than 0.5 min, the blend system becomes miscible. The interesting question is whether the miscibility is solely induced by thermodynamics or is a consequence of transesterification, as the literature has suggested.

To answer this question, the same set of the blend samples were dissolved in deuterated solvent for obtaining the solution NMR spectra. The sequence structure of PET/PEN copolyesters can be analyzed from the resonance signals that represent three types of ethylene units: TET, ethylene unit between two terephthalate groups, NEN, ethylene unit between two naphthalate groups, and TEN, ethylene unit between terephthalate and naphthalate groups. Unlike most polyester blends, the ^{13}C NMR spectra cannot distinguish the triad TEN from the triads NEN and TET. However, the ^1H NMR spectra can: the ^1H chemical shifts appear at 4.85, 4.90 and 4.80 ppm for the TET, TEN, and NEN triads. Figure 4 shows the 400 MHz ^1H NMR spectra of the model system, which confirm the triad assignment. The pulse field gradient 2D HMQC spectra show the small ^{13}C chemical shift difference between the four triads.[27] (Although the intensity of the triads TEN and NET are the same, the ^{13}C chemical shifts are slightly different.)

Figure 5 shows the 400 MHz ^1H solution NMR spectra of the same four PET/PEN blend samples with different melt press times. The results indicate that 10 min melt pressing leads to 25 mol % of PEN transesterification, while for the blend samples with 30 s and 2 min of melt-pressing, no TEN triad resonance due to transesterification has been detected. This is strong and direct evidence that transesterification is not a necessary condition for miscibility.

Transesterification Kinetics. The sensitivity of the solution NMR to detect the small amount TEN triad is critical in this paper. Therefore, the same sample sets were measured on 200, 400, and 600 MHz NMR spectrometers to probe the sensitivity of our experiment. If the sensitivity of the NMR spectra is not adequate, we may be unable to detect transesterification for the PEN/PET blend with 2 min melt pressing. To unambiguously address this concern, we prepared another set of samples that consist of six PEN/PET blend samples that were melt pressed at 280 °C for 0.5, 2, 10, 25, 40, and 80 min. The 600 MHz NMR spectra of the six samples have been recorded, and the transesterification kinetic data have been plotted. The linear regression line in the semilog plot has been extrapolated to 0 amount of transesterification. Details of the data analysis process follow.

Figure 6 shows the 600 MHz ^1H NMR spectra of the six PET/PEN blends samples. Based on the integral value of the three triads, resonating at 4.85, 4.90, and 4.80 ppm, sequence distribution data can be obtained.

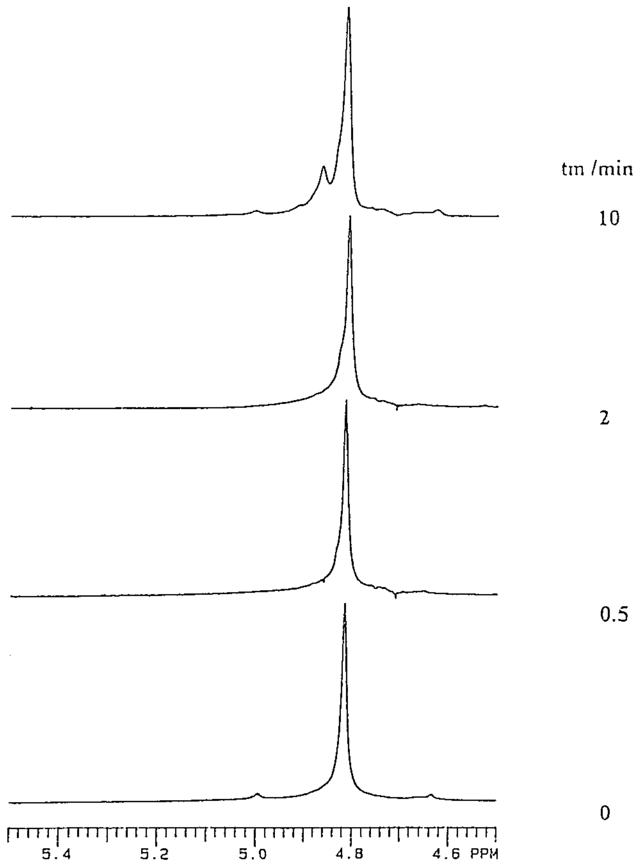

Figure 5. 400 MHz ^{1}H NMR spectra of blend PEN-d_{10}/PET-(50/50) after different melt pressing times at 280 °C. The resonance at 4.80 ppm is from the CH_2 group of triad TET, while the resonance at 4.85 ppm is from the CH_2 group of hybrid triads NET.

These data can be further converted to the transesterification kinetic data. The results are listed in Table 1. Before we discuss the quantitative transesterification results, the relevant theory in statistical analysis is briefly presented.

The probability of finding a terephthalate unit next to a naphthalate unit P_{NET} can be expressed as[28,29]

$$P_{NET} = I_{NET}/(2I_{NEN} + I_{NET}) \tag{1}$$

Similarly, the probability of finding a naphthalate unit next to a terephthalate unit P_{NET} can be expressed as

$$P_{TEN} = I_{TEN}/(I_{NET} + 2I_{TET}) \tag{2}$$

where I_{NEN}, I_{NET}, and I_{TET} are the integrated intensities of the resonance peaks at 4.90, 4.85, and 4.80, respectively. These integral values are listed in columns 2, 3, and 4 of Table 1.

The number average sequence lengths of PET and PEN segments in the PET/PEN copolyester can be expressed as

$$L_{nPET} = 1/P_{NET} = (2I_{NEN} + I_{NET})/I_{NET} \tag{3}$$

$$L_{nPEN} = 1/P_{TEN} = (I_{NET} + 2I_{TET})/I_{TEN} \tag{4}$$

A parameter that characterizes the microstructure of copolyesters is the randomness degree, RD, which is defined as

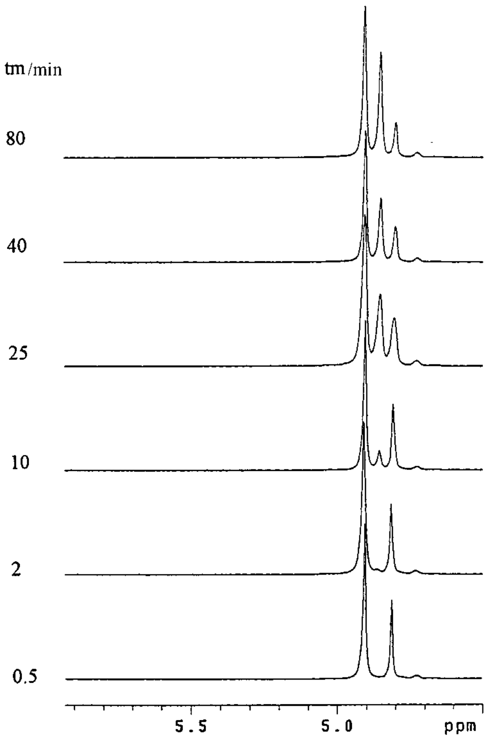

Figure 6. 600 MHz ^{1}H NMR spectra of ethylene region of 70/30 PET/PEN blends after 280 °C melt-pressing times of 0.5, 2, 10, 25, 40, and 80 min, recorded in $CDCl_3/(CF_3)CDOD$ (4/1, v/v).

$$RD = P_{NET} + P_{TEN} \tag{5}$$

RD is associated with the number average sequence length and the probabilities P_{NET} and P_{TEN} through the equations[24,30]

$$RD = 1/L_{nPET} + 1/L_{nPEN} \tag{6}$$

$$L_{nPET} = 1/(1 - X_T) \cdot RD \tag{7}$$

$$L_{nPEN} = 1/(1 - X_N) \cdot RD \tag{8}$$

where X_T and X_N are the monomer molar fractions. RD is independent of composition. Its value is 2 for an alternating copolymer, 1 for a random copolymer, and 0 for a mixture of homopolymers.

Assuming a second-order reversible reaction for the transesterification kinetics, we can write

$$dx/dt = k_2(a - x)(b - x) - k_{-2}x^2 \tag{9}$$

where x is the mole fraction of TEN at time t, and a and b are the initial mole fractions of PET and PEN.

Under equilibrium conditions, $X_e = ab$. Defining the transesterification ratio $r = x/a$ and integrating eq 9, a simple kinetic expression can be derived:[31]

$$\ln(b/(b - r)) = kt \tag{10}$$

This relation permits the determination of the transesterification rate, k, from measurements of the transesterification ratio.

The transesterification kinetic data are plotted in Figure 7. Linear regression analysis by using the linear least-squares method has been performed. The standard error of the kinetic constant is 0.002, and the coefficient of correlation between the uncertainty of

Table 1. Transesterification Kinetic Data for Melt-Pressing PEN/PET Blends at 280 °C

	peak intensity			mol fraction					
time *t*, min	I_{NEN}	I_{NET}	I_{TET}	P_{NEN}	P_{NET}	P_{TET}	RD[a]	ln(*b*/(*b* − *r*))[b]	fit[c]
0.5	10007		4289	0.700		0.300			−0.028
1.5[d,e]					0.000		0.000	0.000	0.000
2	12739	48	4563	0.734	0.003	0.264	0.007	0.007	0.015
10	5546	678	2534	0.633	0.077	0.314	0.184	0.204	0.242
25	7252	3268	2451	0.559	0.252	0.253	0.600	0.916	0.667
40	4142	2201	1270	0.544	0.289	0.235	0.688	1.166	1.093
80	5323	3822	1112	0.519	0.373	0.173	0.887	2.183	2.227
162[d]					0.416		0.990		4.605
243[d]					0.420		0.999		6.908
∞					0.420		1.000		∞

[a] Randomness. [b] $b = P_{\text{PEN}}$; $r = P_{\text{NET}}/2P_{\text{PET}}$. [c] Kinetic constant $k = 0.028\,37$ min^{-1}; frequency factor −0.042 11. [d] Extrapolation value. [e] Retardation time.

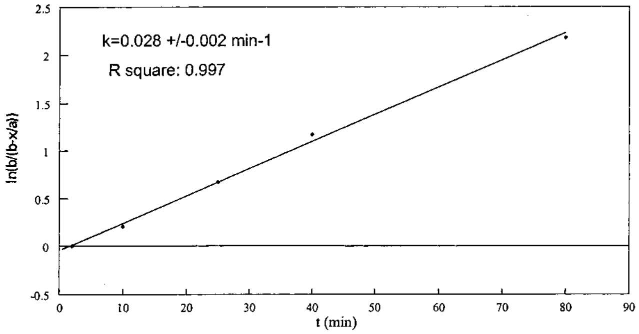

Figure 7. Transesterification kinetic plot of 70/30 PET/PEN PEN blends after 280 °C melt-pressing times of 0.5, 2, 10, 25, 40, and 80 min.

reaction content and uncertainty of reaction time is 0.998. The plot shows that theoretical expression (10) is closely followed and a transesterification kinetic rate constant of 0.028 37 min $^{-1}$ is obtained. This value is very close to the rate constant 0.029 75 min^{-1} obtained under typical processing conditions for the same polyester blend[6] and 2-fold larger than the same blend system annealed at 280 °C in the DSC cell (recalculated on the basis of the raw data from ref 28). This comparison indicates that our transesterification kinetics is close to the extrusion.

The most important result of this experiment is estimation of transesterification data at the initial stages of the reaction. For the deuterated PEN/PET blend, which was melt-pressed for 2 min at 280 °C, no hybrid triad TEN resonance signal was detected using 200 MHz NMR and even 400 MHz NMR spectrometers. For the protonated PEN/PET blend melt-pressed for 2 min at 280 °C, the 3% hybrid triad TEN resonance signal was detected using the 600 MHz NMR spectrometer. The reasons are 2-fold. First, the sensitivity of 600 MHz NMR spectrometer is higher than that of the 400 MHz NMR spectrometer. Second, the triad TEN intensity in the protonated PET/PEN blend is double the intensity of the triad in the deuterated blend.

Extrapolating the line to $r = 0$, we find the line does not pass through the origin. It intersects at $t = 1.5$ min. During this 1.5 min retardation time the two components of the blend system approach each other and the blend system becomes partially miscible. After that time the polyester blend undergoes transesterification following conventional kinetics. This direct experimental evidence indicates again that for the PEN/PET blend system, transesterification occurs after the nonidentical ester groups approach each other. That is, transesterification is not a necessary condition for miscibility.

An alternative interpretation is transesterification reactions proceeding at the interface of phase-separated blends, which would not be detected by the present techniques. The newly developed techniques matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF)[32−36] and gradient polymer elution chromatography (GPEC)[37−40] have been recently used to study transesterification of polyester copolymer and blends.[41−48] We plan to use the methods in combination with higher field (750 MHz) NMR to study PEN/PET blend samples with short melt-pressing times in the future.

Conclusion

Most literature supports the transesterification-leads-to-miscibility thesis, while a few authors[1,11−13] contend otherwise. Here we present some indirect and direct experimental evidence to prove that this commonly held view is not completely descriptive. We favor an evolution theory to explain the relationship between transesterification and miscibility. Both events are kinetic processes. The quantitative understanding of the two separate processes is a necessary condition to understand the competition between the two processes. Transesterification obeys the Arrhenius law, while phase separation and redissolution is a diffusion-controlled process; therefore, they have different temperature and time dependences. The necessary condition for transesterification is that both reactants are close to each other. It is difficult for transesterification to take place in a macrophase-separated blend system because of limited interface boundaries in the immiscible blend systems. Shearing and extruding will promote transesterification. Miscibility favors the transesterification and is not strictly a consequence of transesterification.

Miscibility describes a thermodynamic tendency of the blend to form a single phase. The miscible system is capable of mixing in any ratio without separation of two phases. Further work concerning the miscibility and the phase diagram of the PET/PEN blend systems with different composition is planned.

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