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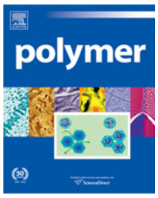

Fast in situ copolymerization of PET/PEN blends by ultrasonically-aided extrusion

Kaan Gunes [a], Avraam I. Isayev [a,*], Xiaopeng Li [b], Chrys Wesdemiotis [b]

[a] *Institute of Polymer Engineering, The University of Akron, Akron, OH 44325-0301, USA*
[b] *Department of Chemistry, The University of Akron, Akron, OH 44325-3601, USA*

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ABSTRACT

An ultrasonically-aided extrusion process was developed for fast in situ compatibilization of immiscible polymer blends. PET, PEN, and their 50/50 blend were ultrasonically extruded at various amplitudes. PET underwent homopolymerization and degradation, respectively, at ultrasonic amplitudes of 7.5 and 10 μm, while PEN underwent degradation at amplitudes of 5, 7.5, and 10 μm. MALDI-TOF mass spectrometry revealed greater amounts of hydroxyl and carboxyl terminated oligomers in ultrasonically treated PET and PEN, indicating their greater reactivity. Ultrasonic treatment at short residence time led to the enhancement of transesterification reaction in the PEN/PET blend, as shown by ^{1}H NMR and MALDI-TOF, indicating greater randomization with ultrasonic treatment. The latter was also observed through a shift in T_g that closely follows Gibbs–DiMarzio relation and an increase in viscosity of blend with treatment at an amplitude of 10 μm. No crystallinity was observed in the blend due to the already high level of transesterification introduced by extrusion without treatment. Accordingly, crystallinity, mechanical properties, oxygen permeability, and optical clarity of the blend were not influenced by ultrasonic treatment.

1. Introduction

PET/PEN blends offer advantages over PET in their mechanical, thermal and barrier properties. These blends are immiscible [1], but may undergo interchange reactions, which create a copolymer that acts as a compatibilizer. A certain level of copolymerization is necessary to prevent phase separation in these blends. As the interaction of light with phase boundaries retards optical clarity, miscibility is important to achieve desirable properties in PET/PEN blends [2].

Three types of interchange reactions can occur in polyesters having chains terminated by hydroxyl or carboxyl groups. These reactions include alcoholysis, acidolysis, and ester exchange that are referred to as transesterification in this study [3]. Rate determining parameters are temperature, time, catalyst (including residual amounts from polymerization), and mixing processes. At the start of transesterification, larger blocks are formed as in block copolymers. At higher extents of transesterification, sequence lengths of PET and PEN decrease, leading to random copolymers.

In order to achieve optically clear PET/PEN blends, multiple passes through a single screw extruder are commonly required [4]. Twin screw extrusion can provide more uniform thermal distribution and good mixing and lead to better clarity after the first pass [5]. However, significant residence time is required to achieve the required level of transesterification. While the effect of crystallinity also should not be disregarded in determining optical clarity, miscibility in these blends is a prerequisite for transparency.

Ultrasonic treatment in the melt can induce copolymerization reactions in polymer blends. In PET/PEN blends, ultrasonic extrusion is expected to enhance transesterification reactions [6]. Ultrasonic oscillations lead to chemical reactions through the scission of polymeric chains and their recombination. Chemical structure and amplitude of ultrasonic oscillations dictate the effects of ultrasound on materials. In studies on ultrasonic extrusion, high power ultrasound was found to promote reactions at short residence times, leading to copolymerization in rubber–rubber and rubber–plastic blends [7], and in PA6/PP blends [8]. Homopolymerization of PA6 [8], and PET [9] was also observed with treatment at certain ultrasonic amplitudes. The present paper studies the effects of ultrasonic treatment during extrusion of PET, PEN, and 50/50 PET/PEN blends. It is aimed to explore the possibility of development of a rapid process for transesterification of this blend. In addition, mechanical, thermal, and rheological properties of components and blends are studied. Chemical structure, oxygen permeability, and optical transparency are also determined to analyze the nature of transformations occurring during ultrasonically-aided extrusion.

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* Corresponding author. Tel.: +1 330 972 6673; fax: +1 330 258 2339.
E-mail address: aisayev@uakron.edu (A.I. Isayev).

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2. Experimental methods

2.1. Materials

Polyethylene terephthalate (PET: Eastapak PET 7352, Eastman Chemical Company, intrinsic viscosity (I.V.) of 0.74 dl/g) and polyethylene naphthalate (PEN: VFR 40046, Shell Chemical Company, I.V. of 0.64 dl/g) were used in this study.

2.2. Preparation of PET/PEN blends

PET and PEN resins were dried at 120 °C in a vacuum oven for 24 h prior to use. PET was prepared in the ultrasonic single screw extruder as described previously in ref. [9]. PEN and PEN/PET blend were prepared in the extruder with a modified screw: the mixing element after the ultrasonic treatment zone in the extruder [9] was replaced with screw flights.

The barrel temperatures were 260 °C in the feeding zone and 285 °C in all other zones for the extrusion of PET and the blend. While the feeding zone temperature was the same for the extrusion of PEN, the temperature of other zones was set at 300 °C in order to ensure its complete melting. Pressure, temperature and ultrasonic power consumption were recorded by a data acquisition system (Dataq Instruments, DI-715-U).

The ultrasonic amplitude was varied in the range of 0–10 μm. In order to prevent overheating of the ultrasonic system, each horn was cooled with tap water at a flow rate of 0.3 cm^3/min. Streamlined reliefs on the sides of the barrel guided the polymer melt to flow through the 2.54 mm thick channel between the horns and the screw shaft.

Under flood feeding conditions, a screw speed of 10 rpm was used and yielded a mass flow rate of 1 kg/h for pure PEN. The same flow rate for PET and the blend was achieved at 13 rpm. The exiting melt was run into a water bath at room temperature, dried, and then converted to particles in a grinder (Weima, WSL180/180).

Impact bars ($127 \times 12.7 \times 3.2$ mm^3) and dumbbell shaped mini tensile bars ($63.5 \times 9.5 \times 1.5$ mm^3, ASTM D 638-03) were injection molded simultaneously using a Van Dorn 55 HP-2.8F injection molding machine. Molded impact bars were cut into two along the lengthwise direction to give samples of the size described in ASTM D 256-05. For PEN and the blends, the barrel temperature was set at 285 °C in all zones except the feeding zone, which was set at 260 °C. The mold was kept at 27 °C. Other molding parameters were: a clamping force of 55 tons, an injection speed of 15 cm/s, holding pressure of 4 MPa applied for 5 s, and a cooling time of 25 s.

A compression molding press (Carver 4122, Wabash, IN) was used to prepare films for permeability and light transmission studies, and discs for rheological testing. For measurements of oxygen permeability, films of 220–250 μm thickness and 13 cm diameter were molded at 290 °C for the pure materials and blends. Two aluminum plates of 3.18 mm thickness and two aluminum sheets of 0.254 mm thickness were used, with the mold placed between these sheets, to obtain smooth, transparent molded films. The aluminum sheets were coated uniformly with a high temperature mold release agent (Frekote HMT2, Henkel, Rocky Hill, CT) before use. Following a heating time of 5 min with no load, force was gradually applied to give a total force of 5 tons for 5 min, after which the plates were removed and cooled for 2 min by setting down over a steel surface and placing a steel plate over them. For rheological testing, four discs of 2 mm thickness and 25 mm diameter were molded simultaneously at 280 °C for PET, PET/PEN blends, and at 300 °C for PEN using steel mold and plates, which were also sprayed with high temperature mold release agent before use. Following preheating of pellets in the disc mold for 2 min, a force of 1 ton was applied for 50 s and released for 10 s for 3 consecutive times. After that, a force of 5 tons was applied for 2.5 min and released for 10 s for two consecutive times. The plates were removed from the press and allowed to cool for 8 min in air before removing discs from the mold.

2.3. Rheological studies

An Advanced Rheometric Expansion System (ARES, TA Instruments, New Castle, DE) was used in oscillatory shear mode with parallel plate geometry. Strain amplitude was fixed at 2% and frequency sweep experiment in an angular frequency, ω, in the range of 0.1–100 s^{-1} was performed at 280 °C for PET, PEN and their blends under nitrogen atmosphere. The reported complex viscosity results, $|\eta^*|$, had percentage error (standard deviation/average) of 5%.

2.4. Differential scanning calorimetry (DSC)

A differential scanning calorimeter (DSC-29210, TA instruments, New Castle, DE) was used to determine the thermal behavior of materials at a heating rate of 10 °C/min from room temperature to 300 °C under N_2 atmosphere at a N_2 gas flow rate of 50 ml/min. A sample of 5–8 mg was cramped in an aluminum hermetic pan was used in each case. The difference between weights of empty sample pan and reference pan was less than 0.2 mg.

The results of the second heating run were reported to erase thermal history experienced in processing. The crystallinity (X_c) was determined by subtracting the enthalpy of cold crystallization (ΔH_{cc}) from the enthalpy of fusion (ΔH_f), and dividing that by the enthalpy of fusion of the perfect crystals (140 J/g for PET [10], 103.4 J/g for PEN [11]).

2.5. Tensile testing

An Instron 5567 tensile tester with an extensometer having 7.62 mm gauge length was used to study the stress–strain behavior of injection molded mini tensile bars following ASTM D 638-03. A 30 kN load cell was used for testing at a constant crosshead speed of 5 mm/min. A minimum of 6 samples was used for each test.

2.6. Impact testing

Injection molded impact bars, which were cut into two equal pieces labeled dead end (DE) and gate end (GE) to conform to the size specifications of ASTM D 256-05, were tested with reverse notching using an Izod impact tester (Testing Machines Inc., Ronkonkoma, NY) with a 4536 g load. No statistically significant differences were found between results from the DE and GE samples. An average of 20 samples was reported for each condition.

2.7. ^{1}H NMR

^{1}H NMR spectroscopy of 50/50 PEN/PET blends was performed in a Varian VNMRS 500 MHz system (Palo Alto, CA). Parameters were: 90° pulse width of 8 μs, relaxation delay of 10 s, 32 scans, average time of 2.049 s, transform size of 32 k, line broadening at 0.11 Hz, spectral width of 14 to −2 ppm, a temperature of 26 °C, and spin of 20 Hz. Samples were dissolved in a 70/30 by weight mixture of deuterated chloroform and trifluoroacetic acid, and filtered through a 100 μm filter before transferring to NMR tubes (5 mm diameter and 203 mm (8″) length).

In ^{1}H NMR of PET, PEN and their blends, the ethylenes from PEN are seen at 4.88 ppm, while those from PET occur at 4.78 ppm. The presence of copolymer is detected from the ethylenic protons in the PEN/PET copolymer located at 4.83 ppm. The extent of transesterification, which is defined as the degree of randomness, was calculated following Stewart et al. [12]. Repeats were run, and the standard deviation in percent transesterification was 0.2%.

2.8. Mass spectrometry

MALDI-TOF MS experiments were carried out on a Bruker Ultraflex III TOF/TOF mass spectrometer (Bruker Daltonics, Inc., Billarica, MA), equipped with a Nd:YAG laser emitting at a wavelength of 355 nm. All spectra were measured in positive reflector mode. The instrument was calibrated prior to each measurement with an external PMMA standard. The preparation of the samples analyzed involved the following steps. Tetrahydrofuran (THF) solutions of the matrix, *t*-2-(3-(4-*t*-Butyl-phenyl)-2-methyl-2-propenylidene)malononitrile (DCTB, 20 mg/mL) and the cationizing agent, sodium–trifluoroacetic acid (NaTFA, 10 mg/mL) in THF were mixed in 10:1 ratio, and 0.5 μl of final mixture was deposited on microtiter plate wells (MTP 384-well ground steel plate). After the spots were dried, 0.5 μl of a solution of PET, PEN, or their blends in 1,1,1,3,3,3,-hexa-fluoro-iso-propanol (10 mg/ml) were deposited on top of the matrix and salt layer.

2.9. Oxygen permeability

Oxygen permeability of PET, PEN and their blends were determined on compression molded films by means of an oxygen permeation analyzer (Model 8000, Illinois Instruments, Johnsburg, IL) in accordance with ASTM D 3985-95. Circular films having a diameter of 10 cm were cut from compression moldings having thickness in the range of 215–250 μm and clamped in the testing chamber following the application of silicon vacuum grease around film circumference for sealing. Oxygen and nitrogen gas pressures were both set at 0.345 MPa. Purge level was set at 1 unit. Tests were run until equilibration of oxygen transmission rate (OTR), which took 20 h for PET films, 40 h for films of PET/PEN blends, and 60 h for PEN films.

2.10. Optical transmission

Optical transmission of molded films, varying in thickness from 215 to 250 μm, was measured in a UV-3600 UV–VIS–NIR Spectrophotometer (Shimadzu, Columbia, MD), and the average transmittance in the visible light range [13] was calculated by averaging the 750–450 nm range.

Beer–Lambert law was used to correct% transmittance for differences in sample thickness [13]. The recorded transmittance was first converted to absorbance (*A*) by using the following relation:

$$A = 2 - \log_{10}\%\mathrm{T} \qquad (1)$$

where ε is the molar absorbtivity, b is the thickness of sample, and c is the molar concentration of chromophore. According to Beer–Lambert law, the absorbance is given by:

$$A = \varepsilon \times b \times c \qquad (2)$$

As the absorbance is zero for a sample of zero length, the sample thickness, b, is directly proportional to absorbance. Values of ε and c are unknown but the same for the same material, and absorbance is affected by film thickness (b). Therefore, the absorbance was normalized with respect to the ratio of the recorded thickness to the average thickness of molded films, 230 μm. This normalization removed the dependence of absorbance on film thickness. Finally, absorbance was converted back to transmittance by using Eq. (1).

3. Results and discussion

3.1. Process characteristics

Fig. 1 shows ultrasonic power consumption and pressure before the ultrasonic treatment zone for PET, PEN and their blend. The reported power consumption was the average net power consumption of the two ultrasonic horns after the subtraction of zero power consumption, determined with the horn in air. While the ultrasonic power consumption increased with amplitude of ultrasonic treatment for all materials, it was higher for PEN and the blend than it was for PET.

Pressure during extrusion decreased with amplitude of ultrasonic treatment. The pressure for PEN was lower than that for PET and the blends. The lower pressure for PEN was due the higher processing temperature (300 °C), which was selected to ensure its complete melting, as compared to the processing temperature for PET and the blends (285 °C). While the higher processing temperature for PEN prevented pressure fluctuations during its processing, it also led to lower recorded pressure, even though untreated PEN has greater viscosity than PET and the blend.

Pressure was observed to decrease with amplitude of ultrasonic treatment. This was due to thixotropic and permanent changes with ultrasonic treatment, as well as possible slip of polymer melt along the surface of the horns [6]. The reduction in pressure was the least in 50/50 PET/PEN. This is correlated with viscosity measurement reported in the next section.

3.2. Rheology

Complex dynamic viscosity measurements were carried out. Fig. 2 illustrates the ultrasonic amplitude dependence of complex viscosity for untreated and ultrasonically treated PET, PEN and blends at frequencies of 1 rad/s (a) and 100 rad/s (b). From Fig. 2a and b, it was observed that viscosity of the untreated PEN is greater than viscosity of the untreated 50/50 PEN/PET blend. Viscosity of the blend is higher than the viscosity of untreated PET. The viscosity of PEN decreased at all amplitudes of ultrasonic treatment. Ultrasonic treatment at an amplitude of 7.5 μm led to increased viscosity of PET. The viscosity of 50/50 PET/PEN blends did not change with ultrasonic treatment up to an amplitude of 7.5 μm, above which it increased slightly. PET and the blends showed almost Newtonian behavior without and with ultrasonic treatment, as indicated by comparison of viscosities at frequencies of 1 and 100 rad/s. PEN became more shear thinning with treatment at ultrasonic amplitudes of 7.5 and 10 μm, indicating extensive structural changes.

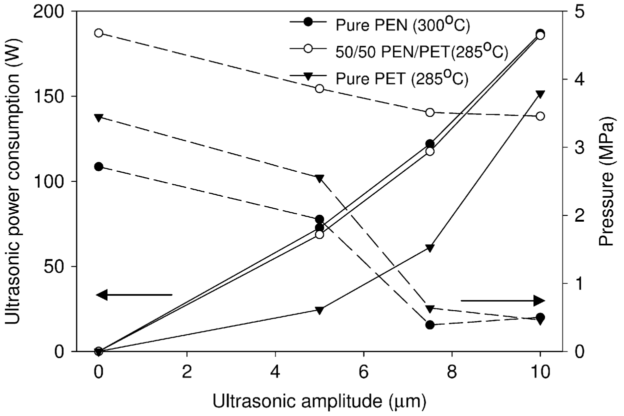


Fig. 1. Ultrasonic power consumption and extrusion pressure for PEN, PET and their 50/50 blend.

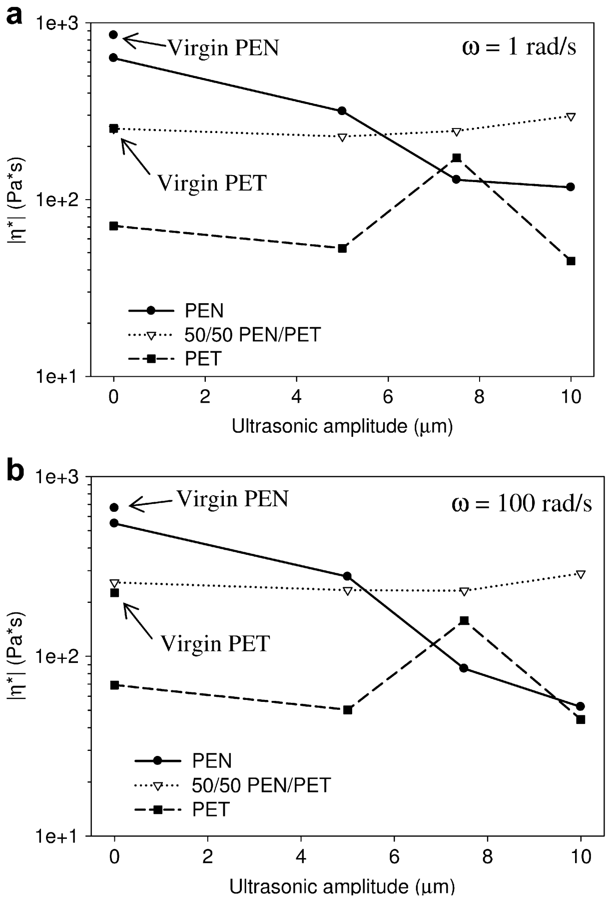


Fig. 2. Complex viscosity at 280 °C vs. ultrasonic amplitude for PET, PEN and their blend at angular frequencies of (a) 1 rad/s, and (b) 100 rad/s, with and without treatment.

For both PET and PEN, there is some degradation associated with passing through the extruder, as observed by comparing viscosities of virgin (as-received) and untreated PET and PEN in Fig. 2a and b. Comparison of untreated samples shows that PET, PEN and their blend show the highest, lowest, and intermediate viscosities, respectively. In contrast to the homopolymerization of PET with ultrasonic treatment at an amplitude of 7.5 μm, as observed from the increase in its viscosity, only degradation of PEN is observed with treatment, as observed from the reduction in its viscosity. Moreover, PEN exhibits shear thinning with ultrasonic treatment at amplitudes of 7.5 and 10 μm. In case of the blends, there is considerably less change in viscosity with ultrasonic treatment; however, an increase in the viscosity of the blend was recorded with treatment at an amplitude of 10 μm. This effect of increase in viscosity due to copolymerization was also shown to lead to increase in viscosity in other extruded blends, including polycarbonate (PC)/polyarylate [14], and PET/PC [15].

3.3. ^{1}H NMR spectroscopy

^{1}H NMR spectroscopy was performed on untreated and ultrasonically treated PET/PEN blends to determine the extent of copolymerization. A simplified representation of the expected product of PET/PEN ester exchange reactions is shown in Scheme 1. It should be noted that the copolymer formed is not necessarily in separate blocks as depicted in Scheme 1, but rather that the majority of these blocks are expected to be randomly distributed, as shown by ^{1}H NMR.

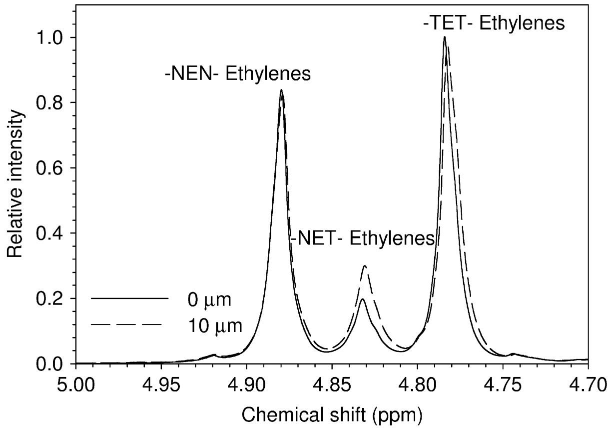


Fig. 3. ^{1}H NMR relative intensity in 5–4.70 ppm range for 50/50 PEN/PET blend without and with ultrasonic treatment at an amplitude of 10 μm, based on normalized intensity of –NEN- ethylenes peak of untreated blend.

Fig. 3 shows the ^{1}H NMR spectra of PET/PEN blends without and with treatment at an ultrasonic amplitude of 10 μm. In this figure the ethylenes from PEN (NEN) and PET (TET) are seen at 4.88 ppm and 4.78 ppm, respectively. The presence of copolymer is detected from the ethylenic protons in the PEN/PET copolymer located at 4.83 ppm (NET). Degree of randomness (% transesterification of PET/PEN) was calculated following procedure described by Stewart et al. [12].

The areas under the ethylene peaks were measured for untreated and ultrasonically treated blends. The mole fraction of ethylene glycols from PET (P_{tet}), copolymer (P_{net}), and PEN (P_{nen}), shown in Table 1, were determined for different ultrasonic amplitudes by dividing the area under the respective peaks by the total area. As equal amounts of ethylene glycols from PET and PEN were taken to be present in the copolymer, mole fractions of terephthalate (P_{t}) and naphthalate (P_{n}) units were obtained as

$$P_{\mathrm{t}} = \frac{P_{\mathrm{net}}}{2} + P_{\mathrm{tet}} \tag{3}$$

$$P_{\mathrm{n}} = \frac{P_{\mathrm{net}}}{2} + P_{\mathrm{nen}} \tag{4}$$

The probability of finding an N unit next to a T unit (P_{tn}) in a PEN/PET copolymer chains is

$$P_{\mathrm{tn}} = \frac{P_{\mathrm{net}}}{2P_{\mathrm{t}}} \tag{5}$$

Similarly, the probability of finding a T unit next to an N unit in a PEN/PET copolymer chains (P_{nt}) is

$$P_{\mathrm{nt}} = \frac{P_{\mathrm{net}}}{2P_{\mathrm{n}}} \tag{6}$$

Table 1
Mole fraction of ethylene glycols from PET (P_{tet}), PEN (P_{nen}) and copolymer (P_{net}), mole fractions of terephthalate (P_{t}) and naphthalate (P_{n}) units, degree of randomness (B), and average sequence lengths of PET, $L(T)$, and PEN, $L(N)$, of PET/PEN blends without and with ultrasonic treatment at different amplitudes.

Amplitude	P_{tet}	P_{nen}	P_{net}	P_{t}	P_{n}	B	$L(T)$	$L(N)$
0 μm	0.473	0.402	0.125	0.535	0.465	25.1%	8.66	7.45
5 μm	0.503	0.368	0.129	0.568	0.432	26.2%	8.83	6.71
7.5 μm	0.485	0.373	0.142	0.556	0.444	28.7%	7.84	6.26
10 μm	0.457	0.380	0.163	0.539	0.461	32.8%	6.60	5.65

The degree of randomness (B) is defined as:

$$B = P_{\mathrm{nt}+}P_{\mathrm{tn}} = \frac{P_{\mathrm{net}}}{2P_{\mathrm{t}}} + \frac{P_{\mathrm{net}}}{2P_n} \tag{7}$$

From the probability theory

$$P_{\mathrm{t}} = 1 - P_n \tag{8}$$

Therefore,

$$B = \frac{P_{\mathrm{net}}}{2P_n(1-P_n)} \tag{9}$$

The experimentally and statistically calculated ethylene glycol moieties from PET/PEN copolymer is defined as

$$(\mathrm{Net})_{\mathrm{exp}} = P_{\mathrm{net}} \tag{10}$$

$$(\mathrm{Net})_{\mathrm{cal}} = 2P_n(1-P_n) \tag{11}$$

Hence, the degree of randomness (B) is given by:

$$B = \frac{(\mathrm{Net})_{\mathrm{exp}}}{(\mathrm{Net})_{\mathrm{cal}}} \tag{12}$$

The value of B describes the extent of copolymerization and its nature, as follows:

1. When $B = 1$, N and T units are distributed randomly within the copolymer, and a random copolymer following Bernoulli statistics is formed.
2. When $B<1$, N and T units are in blocks of different lengths, and block copolymers are formed.
3. When $B = 0$, no copolymers are present.
4. When $B > 1$, sequence lengths decrease, leading to formation of alternating copolymers.
5. When $B = 2$, a copolymer of alternating N and T units is formed.

The number average sequence lengths of N and T units are given as [16]:

$$L(N) = 2P_{\mathrm{n}}/P_{\mathrm{net}} = 1/P_{\mathrm{nt}} \tag{13}$$

$$L(T) = 2P_{\mathrm{t}}/P_{\mathrm{net}} = 1/P_{\mathrm{tn}} \tag{14}$$

As seen from Table 1, the extent of transesterification in 50/50 PET/PEN following extrusion without treatment was 25.1%. This high value was due to the long mean residence time (4.8 min) in the extruder, and presence of mixing sections in the screw. However, ultrasonic treatment at an amplitude of 10 μm for a mean residence time of 7 s raised the extent of transesterification to 32.8%, indicating fast copolymerization.

The average sequence length of PET ($L(T)$) was higher than that of PEN ($L(N)$) in the copolymer, as can be observed from Table 1. This was expected as the PET used in this study had a higher MW than PEN, as indicated by their intrinsic viscosities. The average sequence length of PEN blocks in the copolymer decreased monotonously with ultrasonic amplitude. The average sequence length of PET block in the copolymer was not affected with treatment at an amplitude of 5 μm, but decreased faster than for PEN at amplitudes of 7.5 and 10 μm. This could indicate that with treatment at 5 μm, chain scission of PEN phase occurred more readily and these shorter chains copolymerized with longer PET blocks. As PEN is more viscous, its rate of diffusion is expected to be less than that of PET. It is therefore likely that PET blocks reacted in greater frequency than the PEN blocks with sonication at amplitudes of 7.5 and 10 μm, leading to larger decrease in average segment length of PET block than of the PEN block, as seen from Table 1.

3.4. Mass spectrometry

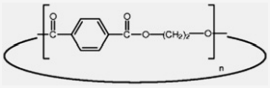
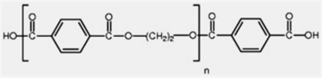
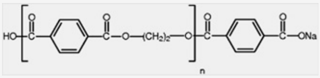
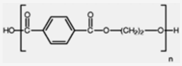
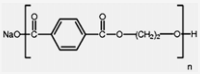
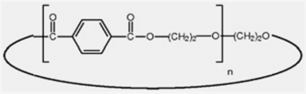
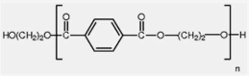
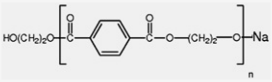
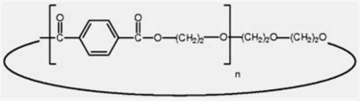
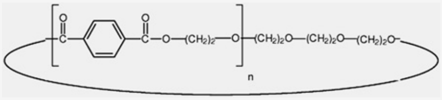
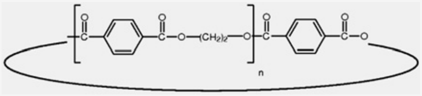
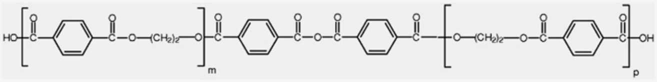
MALDI-TOF mass spectra of PET were interpreted on the basis of structures listed in literature [17–19]. Table 2 shows the chemical structures of the probable PET species and the legend for assignment of peaks in mass spectra. Assignments of mass spectral peaks are shown in Fig. 4 for untreated and ultrasonically treated PET (a), PEN (b) and 50/50 PET/PEN blends (c). In these spectra, labels A–K, with subscripts indicating the number of repeat units, refer to Table 2.

The changes in relative areas of peaks assigned to PET and PEN species after ultrasonic treatment at an amplitude of 10 μm is summarized in Table 3. Species A, corresponding to cyclic PET or PEN without end groups, served as the reference for comparison. Therefore, any possible changes in its area with ultrasonic treatment were not identified, and all A areas were set equal to 1.00. Significant increase in the amount of species B, C, C′, D, F, and G was observed with ultrasonic treatment of PET at an amplitude of 10 μm with respect to A. Because the changes observed after treatment at an amplitude of 7.5 μm were not as significant, the corresponding mass spectra are not shown or discussed in this study. The increase in areas of the peaks assigned to species B, C, C′, and F with ultrasonic treatment indicates formation of a greater amount of PET species with hydroxyl and carboxyl end groups. This could be due to a higher chain scission efficiency with ultrasound at an amplitude of 10 μm. The increased concentration of these highly abundant end groups would promote interchange reactions, such as transesterification [20]. This explains why the intensity of copolymer peaks is higher in 50/50 PET/PEN blends treated at the amplitude of 10 μm. There was also an increase in the amounts cyclic species D and G with ultrasonic treatment due to interchange reactions, indicating recombination of PET species following chain scission.

MALDI-TOF mass spectra of PEN were assigned to the chemical structures listed in Table 2, with the naphthalene unit replacing the benzene ring [17–19]. The mass spectra of PEN without and with ultrasonic treatment in the m/z range of 2850–3150 are shown in Fig. 4b. Again, labels X_{n} refer to Table 2, with X representing the chemical structure present and the subscripted n representing the number of repeat units. Inspection of Table 3 reveals significant increases in the amounts of species B, C, D, and G, but a reduction in the amount of species E, after ultrasonic treatment of PEN at an amplitude of 10 μm; again, these changes are with respect to cyclic PEN without end groups (A). The increases observed for species B and C indicate a greater yield of hydroxyl and carboxyl terminated PEN species at the amplitude of 10 μm, as also observed for treated PET, consistent with increased reactivity under ultrasonic conditions. There is also an increase in the amounts of cyclic species D and G with ultrasonic treatment due to interchange reactions, involving recombination of PEN species following chain scission. The reduction of species E is attributed to the degradation of PEN with ultrasonic treatment.

The mass spectrum of the 50/50 PET/PEN blend was more complicated due to presence of cyclic and linear copolymers with different end groups. Only the cyclic PET/PEN copolymers were considered due to their higher abundance. Cyclic PET/PEN copolymers are expected to have the structure depicted in Scheme 1, where x and y are the number of PEN and PET repeat units in the copolymer with a total of n repeat units. Although the structure of copolymers is depicted here as being in separate blocks, the majority of them are expected to be random. Molecular weight of PET repeat unit is 192.17 g/mol, while that of PEN is 242.23 g/mol. Molecular weight of sodium (Na) is 22.99 g/mol. Based on these values, the molecular weights of possible copolymers of PET/PEN blends containing Na^{+} was calculated.

Table 2
Probable PET and PEN species in the MALDI mass spectra of PET and PEN; n indicates the number of repeat units.

Species	Chemical structure[a]	PET[b]	PEN[b]
A		(n)0	(n)0
B		(n−1) −26	(n−1) −26
B′		(n−1) −4	(n−1) −4
C		(n) +18	(n) +18
C′		(n) +40	(n) +40
D		(n) +44	(n) +44
E		(n) +62	(n) +62
F		(n) +84	(n) +84
G		(n) +88	(n) +88
H		(n) +132	–
I		(n) +148	(n) +198
J		(n−1) +122	–

[a] Listed chemical structures are for PET species. In PEN polymers contain the 2,6-naphthalene unit is in place of the 1,4-benzene ring of PET. The probable end groups for PEN and PET were similar.

[b] Number of repeat units (in parenthesis), followed by mass of probable end groups.

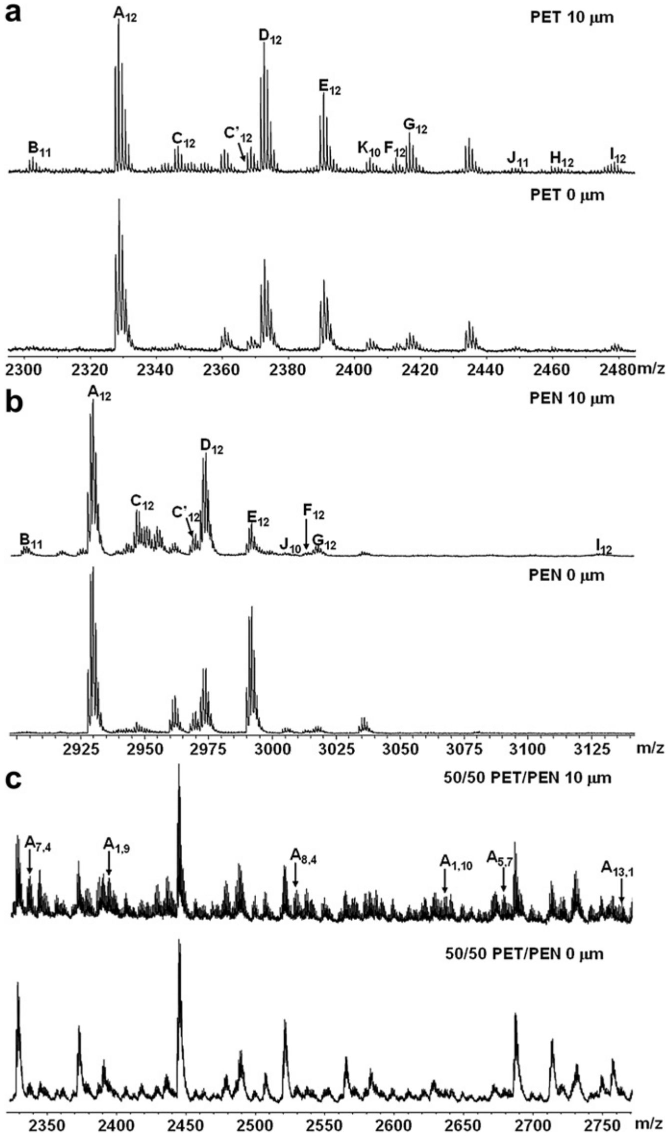


Fig. 4. Mass spectra of untreated and ultrasonically treated PET, PEN, and 50/50 PET/PEN blend. (a) PET in *m*/*z* range of 2280–2470. (b) PEN in *m*/*z* range of 2850–3150. (c) 50/50 PET/PEN blend with copolymers in the *m*/*z* range of 2320–2800.

The molecular weights of cyclic copolymer species used for assignment of spectra peaks are listed in Table 4. Copolymer species were identified in comparison to both the untreated and ultrasonically treated spectra of PET and PEN. The copolymer species in the *m*/*z* range of 2320–2800 are marked in Fig. 4c, where $A_{x,y}$ is the cyclic copolymer with *x* and *y* repeat units of PEN and PET, respectively. Due to the large number of isomers possible, the copolymers sequences were not identified in this study. However, reductions in the average block lengths of PET and PEN in the 50/50 PET/PEN blend with ultrasonic treatment were determined by ^{1}H NMR. The mass spectra indicate increases in the amounts of copolymer species, with respect to PEN and PET oligomers, after ultrasonic treatment. A quantitative analysis of the relative areas of copolymers with ultrasonic treatment could not be done due to the complicated nature of the spectrum.

Table 3
Relative areas with respect to those of cyclic structure (*A*) of observed peaks for PET and PEN species that exhibited significant changes with ultrasonic treatment.

Species	PET		PEN	
	0 μm	10 μm	0 μm	10 μm
A	1.00	1.00	1.00	1.00
B	0.00	0.13	0.00	0.08
C	0.04	0.25	0.19	0.79
C′	0.05	0.22	0.17	0.16
D	0.66	0.92	0.62	0.82
E	0.53	0.54	0.84	0.22
F	0.02	0.09	0.00	0.00
G	0.13	0.26	0.00	0.11

3.5. Thermal analysis

The DSC traces of PET, PEN and 50/50 PET/PEN blend are shown in Fig. 5 without treatment (a) and with ultrasonic treatment at an amplitude of 10 μm (b).

The glass transition (T_g), cold crystallization (T_{cc}) and melting temperatures (T_m), and crystallinity (X_c) of PET and PEN are reported in Table 5. It should be noted that the untreated and ultrasonically treated 50/50 PEN/PET blends showed no crystallization exotherms or melting endotherms.

It is seen from Table 5 that the PET crystallinity in second heating run is much higher after extrusion. Moreover, crystallinity of extruded PEN treated at an amplitude of 10 μm is 20% in comparison with 4.5% for untreated (0 μm) PEN. These changes indicate reduction in MW of PET and PEN with treatment at the respective ultrasonic amplitudes. In contrast, the second heating run for the 50/50 PEN/PET blend does not show any crystallization or melting. Lower or no crystallinity is expected with transesterification in the blend [21–23] due to reduction in sequence length of PET and PEN blocks, as indicated by Table 1.

In completely miscible systems, a single $T_{g,}$ lying between those of the pure components, is observed. Fox suggested the following empirical relation for determining the miscibility of polymer blends [24]:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \tag{15}$$

where T_g is the glass transition temperature of the miscible blend, T_{g1} and T_{g2} are the glass transition temperatures of the components, and w_i are their weight fractions. Strictly speaking, the Fox equation cannot be applied to systems containing semicrystalline polymers, as the density of the amorphous and crystalline fractions are different. In the present study, this equation was used for comparative purposes.

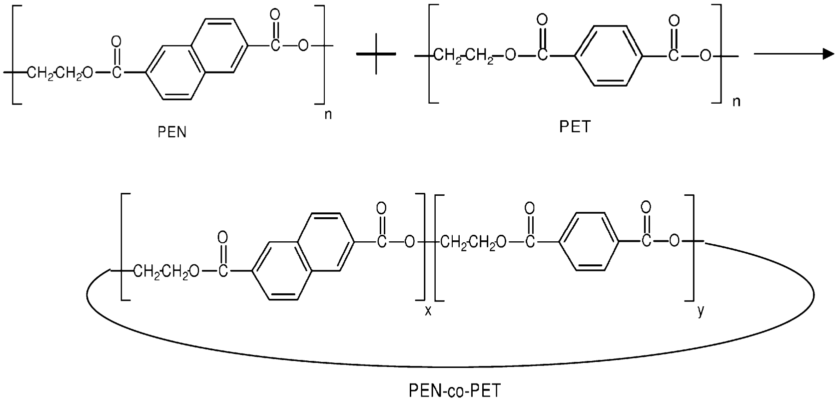
For random copolymers, the Gibbs–DiMarzio theory can be used to calculate variation of the glass transition temperature with composition [25,26]. The Gibb's–DiMarzio equation for calculation of T_g for random copolymer systems is provided by Shi and Jabarin in the following form [27]:

$$T_g = X_1 T_{g1} + X_2 T_{g2} \tag{16}$$

where T_g of the random copolymer system is shown to depend on the T_g's of the components (T_{g1} and T_{g2}) and their mole fractions (X_1 and X_2). In random copolymers, the T_g predicted by Eq. (16) is expected to lie closer to experimental observations than that predicted by the Fox equation (Eq. (15)) for miscible systems. Shi and Jabarin showed the presence of random copolymer due to transesterification of PET/PEN blends. The measured T_g was shown to be closer to T_g calculated by Eq. (16) [27].

The glass transition temperatures of 50/50 PET/PEN blends, experimentally determined by DSC second heating runs and theoretically calculated by Eqs. 15 and 16, are shown in Table 6.

Referring to Table 5, only a slight reduction in T_g of PET is observed with ultrasonic treatment at an amplitude of 10 μm, while



Scheme 1. Expected structure of copolymer of PEN and PET formed by transesterification, x and y refer to the number of PEN and PET segments, respectively. Although the copolymer is shown as cyclic and in separate PEN and PET blocks, it could also be random and have end groups.

there is a pronounced decrease in T_g for PEN at amplitudes of 7.5 and 10 μm, indicating its degradation. There is an increase in T_g of the 50/50 PET/PEN blend with ultrasonic treatment, as shown in Table 6. The experimentally determined values of T_g of the untreated and ultrasonically treated blends are compared with theoretical predictions of T_g from Fox equation (Eq. (15)) and Gibbs–DiMarzio equation (Eq. (16)) in Table 6.

Using the Fox equation (Eq. (15)) for miscible blends [24] based on the T_g's of virgin PEN and PET gives a value of 95.5 °C for 50/50 PEN/PET. Using T_g's of untreated (0 μm) PEN and PET, on the other hand, gives a value of 94.3 °C for the blend. The experimentally determined T_g of untreated blend was 95.1 °C and lied in between the two predicted values.

The Gibbs–DiMarzio equation (Eq. (16)) for random copolymers based on the T_g of PEN and PET at 0 μm gives a value of 97.2 °C for 50/50 PEN/PET blend. This value is closer to T_g of blend after ultrasonic treatment at different amplitudes. This signified greater randomization with ultrasonic treatment, as also suggested by ^{1}H NMR spectroscopy and MALDI-TOF mass spectrometry studies.

3.6. Mechanical properties

Virgin PET and PEN were injection molded into specimens for testing without any other processing for comparison of mechanical properties with materials that were extruded before injection molding.

The Young's modulus (Fig. 6a) of PEN shows the highest values, followed by 50/50 PEN/PET, and PET. The 95% confidence intervals were shown in these figures. The Young's modulus of PEN decreased with extrusion, and further decreased with increasing amplitude due to degradation of PEN with ultrasonic treatment. The Young's modulus of PET was not affected by extrusion without and with ultrasonic treatment at amplitudes of 5 and 7.5 μm. The Young's modulus of PET indicated a slight increase with treatment at an amplitude of 10 μm. 50/50 PET/PEN indicated an increase in the Young's modulus with treatment at an amplitude 7.5 μm.

Fig. 6b shows the strength of PET, PEN and 50/50 PET/PEN vs. amplitude of ultrasonic treatment. Untreated PEN shows the highest value of strength, followed by untreated 50/50 PEN/PET, and PET. Extrusion without treatment (0 μm) led to a decrease in the strength of PEN and an increase in that of PET. The strength of PEN was significantly reduced with ultrasonic treatment at an amplitude of 10 μm, due to degradation.

Impact strength of PEN, PET and 50/50 PET/PEN is shown in Fig. 7. The indicated values were averages of dead end (DE) and gate end (GE) impact bars, which were found to be statistically indifferent. Impact strength of both virgin PET and PEN decreased with extrusion without treatment. Among the untreated materials (0 μm) the 50/50 blend had the greatest impact strength, followed by PET and PEN. This could be due to reduced degradation of the blend during extrusion due to exchange reactions in the extruder. The impact strength of 50/50 blend indicated a slight increase with

Table 4
Molecular weights of Na+ containing cyclic oligomers of PEN (x), PET (y), and cyclic PEN/PET (x, y) copolymers with molecular weights up to 3000 g/mol.

x, y		Polyethylene naphthalate (PEN), x												
		0	1	2	3	4	5	6	7	8	9	10	11	12
Polyethylene naphthalate (PEN),y	0		265	507	749	991	1233	1475	1717	1959	2202	2444	2686	2928
	1	215	457	699	941	1183	1425	1667	1909	2151	2394	2636	2878	
	2	407	649	891	1133	1375	1617	1859	2101	2344	2586	2828		
	3	599	841	1083	1325	1567	1809	2051	2294	2536	2778			
	4	791	1033	1275	1517	1759	2001	2244	2486	2728	2970			
	5	983	1225	1467	1709	1951	2193	2436	2678	2920				
	6	1175	1417	1659	1901	2143	2386	2628	2870					
	7	1367	1609	1851	2093	2336	2578	2820						
	8	1559	1801	2043	2286	2528	2770							
	9	1751	1993	2235	2478	2720	2962							
	10	1943	2185	2428	2670	2912								
	11	2135	2378	2620	2862									
	12	2327	2570	2812										
	13	2520	2762											
	14	2712	2954											
	15	2904												

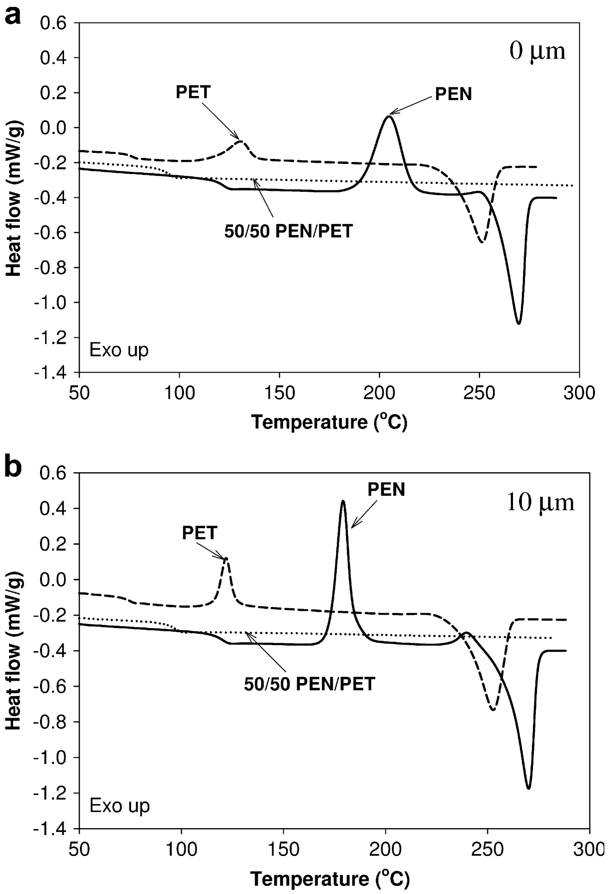


Fig. 5. Heat flow vs. temperature during DSC second heating for PEN, PET, and 50/50 PEN/PET without treatment (a), and with ultrasonic treatment at an ultrasonic amplitude of 10 μm (b).

treatment at amplitudes of 7.5 and 10 μm. On the other hand, impact strength of PEN dropped with treatment at 7.5 and 10 μm, while that of PET decreased only with treatment at an amplitude of 10 μm. PET also showed an increase in impact strength at an amplitude of 7.5 μm. Overall, it was concluded that the mechanical properties of the blend are retained or increased with ultrasonic treatment, indicating that copolymerization dominates over degradation.

3.7. Oxygen permeability

Oxygen permeability of PET, PEN and 50/50 PET/PEN blends were measured on compression molded films. The average thickness along with standard deviation for each prepared film is shown in Table 7. It should be noted that the sample of PEN treated at an amplitude of 10 μm was too brittle. Film for permeability testing of this material breaks down by removal from the mold. Therefore, it was not tested.

Table 5
Glass transition (T_g), cold crystallization (T_{cc}), and melting temperatures (T_m), and crystallinity (X_c) of PET and PEN.

DSC 2nd heating		T_g (°C)	T_{cc} (°C)	T_m (°C)	X_c (%)
PET	Virgin	77.3	165.1	249.7	0.4
	0 μm	76.5	130.5	251.4	20.9
	5 μm	76.4	129.8	251.4	22.3
	7.5 μm	77.0	132.5	252.2	21.6
	10 μm	75.4	121.9	252.7	26.4
PEN	Virgin	125.0	214.3	270.4	3.8
	0 μm	122.8	204.8	269.6	4.5
	5 μm	123.3	204.6	270.3	2.2
	7.5 μm	120.5	178.5	269.8	21.9
	10 μm	120.6	179.2	270.1	20.0

Table 6
Measured and calculated glass transition temperatures of untreated and ultrasonically treated 50/50 PET/PEN.

	Treatment	$T_{g\text{-exp}}$ (°C)	$T_{g\text{-FoxEq.}}$ (°C)	$T_{g\text{-Gibbs-DiMarzio}}$ (°C)
50/50 PET/PEN	Virgin	–	95.5	98.4
	0 μm	95.1	94.3	97.0
	5 μm	98.2	94.3	97.1
	7.5 μm	97.3	94.0	96.2
	10 μm	98.0	92.8	95.4

Table 8 shows O_2 permeability coefficient at different ultrasonic amplitudes for PET, PEN and 50/50 blend. No changes in the permeability coefficient were observed with ultrasonic treatment.

Gas permeability of polymer blends, P, depends on the permeabilities of pure components, and their miscibility. Robeson defined limits of gas permeability based on miscibility and immiscibility of a given system [28]. For miscible blends indicating presence of copolymers, its value is given by:

$$\ln P = \phi_1 \ln P_1 + \phi_2 \ln P_2 \tag{17}$$

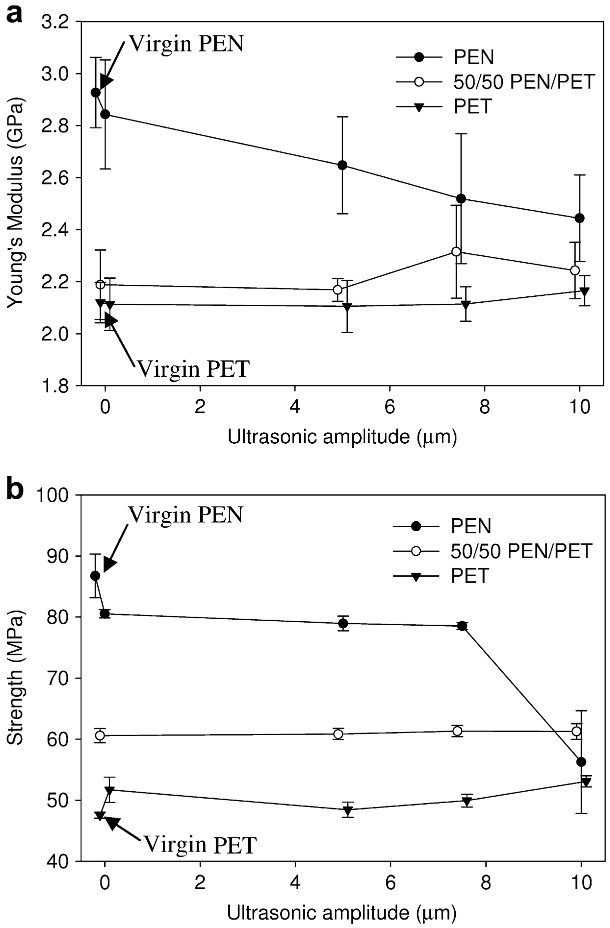


Fig. 6. Young's modulus (a) and strength (b) vs. ultrasonic amplitude for PEN, PET and their 50/50 blend (values shifted along abscissa for clarity).

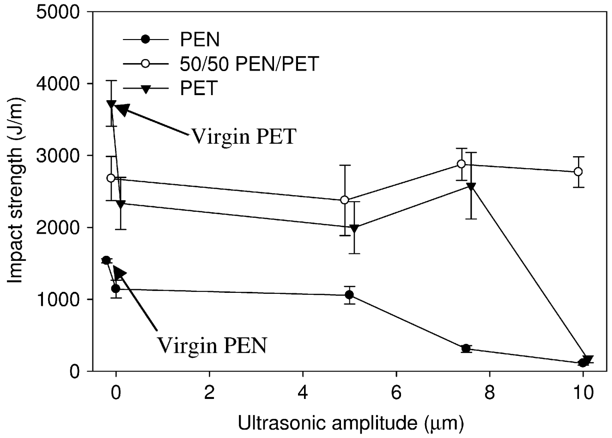


Fig. 7. Impact strength vs. ultrasonic amplitude for PEN, PET and their 50/50 blend (values shifted along abscissa for clarity).

For immiscible blends, the upper bound model for P given by parallel combination of components, with the continuous phase having greater permeability:

$$P = \phi_1 P_1 + \phi_2 P_2 \tag{18}$$

The lower bound model for P given by series combination of components, with the continuous phase having lower permeability:

$$P = \frac{P_1 + P_2}{\phi_1 P_1 + \phi_2 P_2} \tag{19}$$

The oxygen permeabilities of untreated PET, PEN and 50/50 blend are plotted against theoretical predictions of the permeability of immiscible and miscible polymers in Fig. 8. The permeability coefficient for 50/50 PET/PEN blends lied closer to the miscible system.

3.8. Optical transmittance

Optical clarity of polymers is important in many applications. Especially in packaging industry, where PET and PEN are commonly used, optically good clarity is generally a requirement. As seen from Table 9, the average optical transparency of PET and 50/50 PET/PEN indicated little change with ultrasonic treatment. On the other hand, the transmittance of PEN was observed to decrease with amplitude of ultrasonic treatment. The reduction in transmittance of PEN could be due to ultrasonically created microcavities in PEN, which could not be totally removed during compression molding of films. The lack of significant change in transmittance of 50/50 PET/PEN blend with amplitude of ultrasonic treatment indicated that the increased transesterification due to ultrasonic treatment had no influence on its transparency.

Table 7
Thickness of films (μm) of PET, PEN and their blend without and with ultrasonic treatment at amplitudes of 7.5 and 10 μm.

	0 μm	7.5 μm	10 μm
PET	216 ± 8	231 ± 12	218 ± 7
50/50 PET/PEN	227 ± 11	231 ± 15	250 ± 4
PEN	223 ± 8	219 ± 10	231 ± 16

Table 8
Oxygen permeability coefficient (cm3/(m/24 h/0.1 MPa)) of PET, PEN and their blend without and with ultrasonic treatment at amplitudes.

Amplitude (μm)	PET	PEN	50/50 PET/PEN
0	148	44	88
7.5	156	42	91
10	151	–	92

The presence of random PET/PEN copolymer is not required to obtain optically clear blends; approximately 10% transesterification is sufficient to obtain totally clear blends. Above this critical level, additional transesterification is not expected to affect transparency [12]. The extent of transesterification of PET/PEN blends in this work is 25.0% without treatment, which is above the critical value required for optical clarity.

Multiple passes through a single screw extruder or shear intensive twin screw extrusion are commonly required in order to obtain optically clear blends [29]. In the present study of ultrasonic extrusion of PET/PEN blends, very low screw speed (13 rpm) was used. This led to an average residence time of 4.8 min in the extruder, as calculated from volume of melt in the extruder and the volumetric flow rate. Therefore, an already high level of transesterification was obtained after passing through the extruder once without treatment. The residence time in the ultrasonic treatment zone, in extruder was 7 s for a flow rate of 1 kg/h. The ultrasonic extrusion process can be scaled up to larger extruders. Comparable residence times and effects of ultrasonic treatment can therefore be obtained at higher flow rates. Hence, ultrasonic treatment could provide a level of transesterification to significantly affect optical properties when the extent of transesterification in blends is below the critical level required for clarity upon extrusion without treatment. This would translate to faster processing with extrusion at higher rpms, use of less shear intensive section and reduced number of passes through the extruder with sonication. Each additional processing operation causes degradation of polymer melt, which can adversely affect mechanical properties and cause yellowing of the sample [30]. Degradation was not observed with ultrasonic treatment of PET/PEN blends based on the rheological, thermal and mechanical properties reported in this study. Hence, it could be expected that in order to obtain blends with good clarity, less polymer degradation could be obtained in ultrasonic extrusion of PET/PEN blends than with multiple-step, high-shear processing or high temperature processing [5,29].

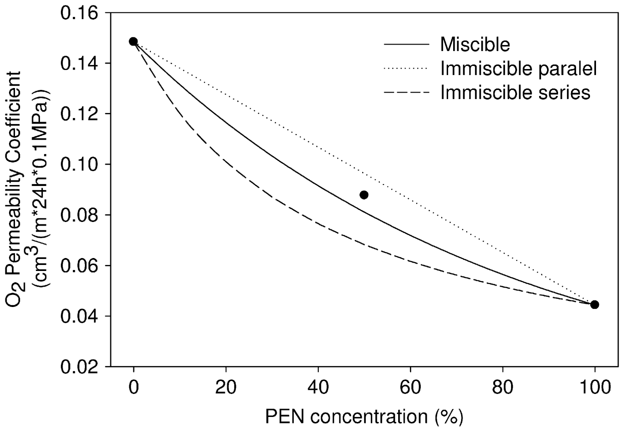


Fig. 8. Oxygen permeability of PET/PEN blend in comparison to theoretical predictions based on blend miscibility.

Table 9
Average transmittance (%) of PET, PEN and 50/50 PET/PEN films to visible light in the wavelength range of 750–450 nm.

Amplitude (μm)	PET	PEN	50/50 PET/PEN
0	88.7	90.2	90.0
7.5	90.0	87.2	89.1
10	88.2	85.3	89.7

4. Conclusions

PEN, PET and their 50/50 blend were prepared by ultrasonically assisted extrusion. The effects of ultrasonic amplitude on the 50/50 PET/PEN blend, the amount and structure of PET/PEN copolymers were studied.

Fast homopolymerization during extrusion of PET was found to occur at an ultrasonic amplitude of 7.5 μm. In contrast, degradation of PEN was observed with ultrasonic treatment. Viscosity of the blend was highest at an amplitude of 10 μm, indicating greater randomization. MALDI-TOF spectra of PET treated at an amplitude of 10 μm and of PEN treated at amplitudes of 7.5 and 10 μm showed increased amounts of hydroxyl and carboxyl terminated chain. This indicated greater reactivity of PET and PEN with ultrasonic treatment. Ultrasonic treatment at short residence time led to the enhancement of transesterification reaction in the PEN/PET blend, indicating that more copolymerization occurred during ultrasonic treatment.

Extruded PET/PEN blends were miscible, as indicated by their T_g. The extent of transesterification was increased by 31% in treated blend with respect to the blend without treatment. The block length of PET and PEN domains decreased with increasing amplitude of ultrasonic treatment. MALDI-TOF mass spectrometry of the blends indicated the formation of greater amount of copolymer species with ultrasonic treatment, which were mostly cyclic in the range of 2000–3000 Da.

While PET and PEN exhibited cold crystallization exotherms and melting endotherms upon second heating, these phase transitions were absent in 50/50 PET/PEN blends, both without and with ultrasonic treatment. This indicated that the degree of randomness in the PET/PEN copolymer formed by blending was too high to permit crystallization of PET and PEN blocks under the studied conditions. The glass transition temperatures of ultrasonically treated blends determined by DSC were higher and correlated with those obtained for the blend by the Gibbs–DiMarzio equation using T_g's of untreated and as-received PET and PEN. This also indicated increased chemical reactions and copolymer of greater degree of randomness with ultrasonic treatment.

The mechanical properties, oxygen permeability, and optical transmittance of 50/50 PET/PEN blend were not affected by ultrasonic treatment. The lack of changes in these properties indicated that the level of transesterification present in blends extruded without treatment was sufficient. It was concluded that ultrasonic extrusion is a fast process for in situ compatibilization of immiscible blends and could improve properties of blends if the extrusion process is carried out faster, allowing less time for interfacial reactions of components.

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