Morphology and Barrier Mechanism of Biaxially Oriented Poly(ethylene terephthalate)/Poly(ethylene 2,6-naphthalate) Blends

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ABSTRACT: To improve the barrier properties of poly(ethylene terephthalate) (PET), PET/poly(ethylene 2,6-naphthalate) (PEN) blends with different concentrations of PEN were prepared and were then processed into biaxially oriented PET/PEN films. The air permeability of bioriented films of pure PET, pure PEN, and PET/PEN blends were tested by the differential pressure method. The morphology of the blends was studied by scanning electron microscopy (SEM) observation of the impact fracture surfaces of extruded PET/PEN samples, and the morphology of the films was also investigated by SEM. The results of the study indicated that PEN could effectively improve the barrier properties of PET, and the barrier properties of the PET/PEN blends improved with increasing PEN concentration. When the PEN concentration was equal to or less than 30%, as in this study, the PET/PEN blends were phase-separated; that is, PET formed the continuous phase, whereas PEN formed a dispersed phase of particles, and the interface was firmly integrated because of transesterification. After the PET/PEN blends were bioriented, the PET matrix contained a PEN microstructure consisting of parallel and extended, separate layers. This multilayer microstructure was characterized by microcontinuity, which resulted in improved barrier properties because air permeation was delayed as the air had to detour around the PEN layer structure. At a constant PEN concentration, the more extended the PEN layers were, the better the barrier properties were of the PET/PEN blends. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 1309–1316, 2006

Key words: blends; drawing; gas permeation; morphology

INTRODUCTION

Polymeric materials are increasingly used in packaging as substitutes for glass, wood, or metal, and the market demand for such polymer materials is growing. Poly(ethylene terephthalate) (PET) has now become the most widely used polymer packaging material because of its good processing properties, excellent mechanical properties, and low cost. However, although PET packaging materials are increasingly widely applied, its poor barrier properties, especially its poor air-barrier properties, have hampered its application to many fields.[1]

Substantial research and development efforts have been directed to improving the barrier properties of PET packaging materials through, for example, multilayer coextrusion blow molding, the deposition of barrier layers on packaging containers, and the development of new high-barrier polyesters. Although these methods can improve the barrier properties of PET packaging materials, they have not yet found wide applications because of a substantial increase of investment in equipment, complicated manufacturing processes, a substantial increase of material cost, and decreasing transparency or mechanical properties of packaging materials.[2,3]

Poly(ethylene 2,6-naphthalate) (PEN) is an interesting new high-barrier thermoplastic polymer synthesized by the polycondensation of 2,6-naphthalene dicarboxylic acid or dimethyl-2,6-naphthalenedicarboxylate with ethylene glycol. PEN is superior to PET in all properties, and in particular, it is a high-barrier material with excellent air-barrier properties. However, the application of PEN in packaging is limited because of its high cost. Thus, it has become a focus of research and development in packaging recently to find alternative ways to use the good barrier properties of PEN at lower costs. One suggested method is to produce special blends of PET and PEN with high-barrier properties for packaging applications.[4–6]

In this study, PET/PEN blends were prepared with a one-step method of melting and blending and were then processed into biaxially oriented PET/PEN films. The barrier properties and morphology of the PET/

PEN blends were studied by the testing of the air permeability of the films, by scanning electron microscopy (SEM) observations of the impact fracture surfaces of extruded samples, and by SEM observations of the tearing fracture surfaces of the films. Furthermore, the barrier mechanism of the PET/PEN blends was clarified.

EXPERIMENTAL

Polymers

The polymers were PET with an intrinsic viscosity of 0.81 dL/g (produced by Taekwang New Tec Co., Ltd., Korea) and PEN with an intrinsic viscosity of 0.61 dL/g (DuPont Co., Teijin, China).

Melting and blending of PET/PEN

PET and PEN were dried at 120°C for 12 h, and then PET, PEN, and other additives (discussed later) were proportioned and dry-mixed. The mixture was melted and blended in a TE-34 double-screw extruder (Keya Co. Ltd., Nanjing, China) at a melting temperature of 220–280°C. The extruded blends were granulated and dried for further analysis and processing.

Preparation of the bioriented films

Pure PET, pure PEN, and PET/PEN blends were carefully dried and were extruded at temperatures of 230–290°C by a single-screw extruder to form flat sheets 140 mm wide and 0.8 mm thick. From the sheets, 100 mm × 100 mm plates were cut. The plates were inserted into a biaxial film drawing machine (Toyoseiki Company, Japan) to prepare bioriented films. The biaxial draw ratio was 1:3.7 at a draw rate of 2500–3000 mm/min. Drawing was performed at 103–105 (PET/PEN = 90/10), 106–107 (PET/PEN = 80/20), and 108–109°C (PET/PEN = 70/30).

Performance test

Testing air permeability of the PET/PEN films

Air permeability was tested by the differential pressure method. When the air permeation reaches its steady state, air permeation q is proportional to pressure drop Δp between the two sides of the film tested and increases linearly with time t:

$$q = P \times \frac{\Delta p}{d} \times At \tag{1}$$

where A is the permeation area of the film and d is the film thickness. Air permeability P can then be calculated from

$$P = \frac{\Delta p}{\Delta t} \frac{V}{A} \frac{d}{P_0} \frac{T_0}{T} \frac{1}{(p_1 - p_2)} \tag{2}$$

where $\Delta p/\Delta t$ is the arithmetic average of the air pressure change per unit of time at the low-pressure side of the permeation chamber when the air permeation reaches its steady state, V is the volume of the low-pressure side of the permeation chamber, $p_1 - p_2$ is the pressure difference between the two sides of the sample, T is the test temperature, T_0 is the standard temperature, and p_0 is the standard pressure.

The sample thickness was measured before the sample was mounted in the permeation chamber, and the high-pressure side and low-pressure side were totally sealed. The low-pressure side was depressurized to below 5 Pa. When the air permeation reached its steady state, the pressure of the low-pressure side of the permeation chamber was recorded regularly, and $\Delta p/\Delta t$ was determined. The test temperature was recorded.
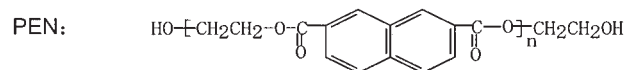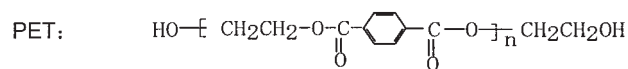
Observations of the morphologies of the fracture surfaces

A Hitachi S-4000 scanning electron microscope (Hitachi Company, Japan) was used. The impact fracture surfaces of extruded PET/PEN samples (plates) were produced via the cooling of the samples in liquid nitrogen for 5 min before impact testing. The tearing fracture surfaces of the bioriented films were similarly produced via the cooling of the samples in liquid nitrogen for 1 min before fracture. The fracture surfaces were surface-gilded with an SCD 030 Balzers Union FL9496 (Balzers, Lichtenste).

RESULTS AND DISCUSSION

Structure and performance of PET and PEN

The molecular structures of PET and PEN are as follows: Comp: See p 4 for an unnumbered structure

PET: $HO\text{---}[\text{CH}_2\text{CH}_2\text{---}O\text{---}\overset{\text{O}}{\underset{\text{||}}{C}}\text{---}\langle\bigcirc\rangle\text{---}\overset{\text{O}}{\underset{\text{||}}{C}}\text{---}O\text{---}]_n\,\text{CH}_2\text{CH}_2\text{OH}$

PEN: $HO\text{---}[\text{CH}_2\text{CH}_2\text{---}O\text{---}\overset{\text{O}}{\underset{\text{||}}{C}}\text{---}\langle\bigcirc\bigcirc\rangle\text{---}\overset{\text{O}}{\underset{\text{||}}{C}}\text{---}O]_n\text{CH}_2\text{CH}_2\text{OH}$

The two ends of both the PET and PEN macromolecule are ethoxyl-linked by an ester group; each repeating unit is linked together by ester groups into symmetric linear macromolecules with functional groups regularly arranged on both sides of C—C bonds. Both PET and PEN are thermoplastic polymers that can be easily oriented to form fibers or films, and both PET and PEN show a high crystallinity of up to 40–50%.
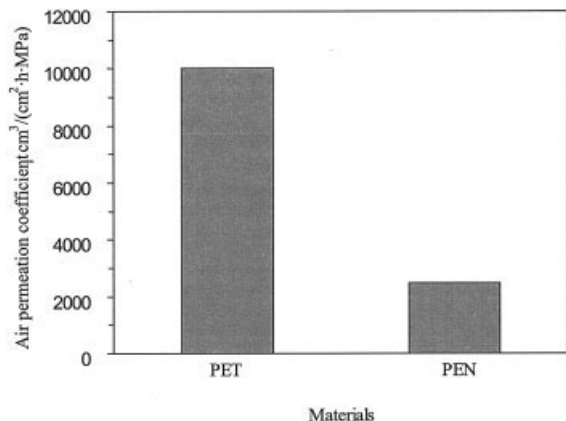
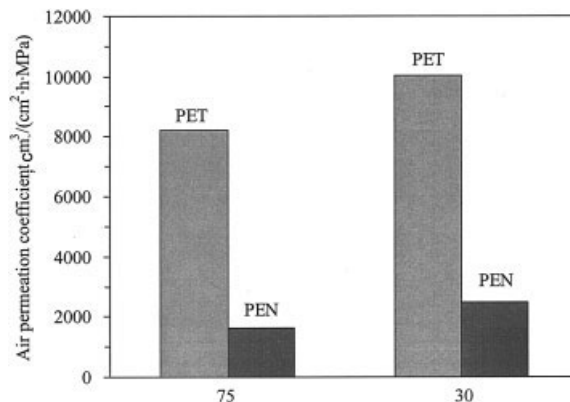**Figure 1** Comparison of the air permeability of BOPET and BOPEN films.

Figure 2 Influence of the film thickness on the air permeability of BOPET and BOPEN.

The yield stress, strength, modulus, and hardness improve with increasing crystallinity.[7–10]

As the naphthalene ring is bigger than the benzene ring, PEN is superior to PET in the regularity of crystallization, barrier properties, mechanical properties, and heat resistance. As for mechanical properties, the elastic modulus and strength of PEN are relatively stable even under high temperatures and high humidity. The melting point of PEN is 265°C, 16 K higher than that of PET; the glass-transition temperature of PEN is 130°C, 50 K higher than that of PET; and the heat distortion temperature of PEN is 100°C, 30 K higher than that of PEN. Thus, PEN has good heat stability. Furthermore, PEN containers will not deform when used for canning hot materials or when heated for sterilization; packaging made from PEN shows low shrinkage and stable dimensions. After PEN has been in humid air under 130°C for 500 h, its elongation to break only decreases by 10%; after PEN has been in dry air under 180°C for 10 h, its elongation to break can still retain 50% of the original. Moreover, PEN has good corrosion stability, low absorption of chemicals and odor, and good hydrolysis resistance against hot water and steam. Therefore, PEN is an excellent packaging material.

Barrier properties of the PET/PEN blends

Comparison of the barrier properties of PET and PEN

Figure 1 presents a comparison of the air permeability of bioriented poly(ethylene terephthalate) (BOPET) film and bioriented poly(ethylene 2,6-naphthalate) (BOPEN) film produced according to the Preparation of the Bioriented Films section in the case of identical film thickness. Figure 2 shows a comparison of the air permeability between BOPET film and BOPEN film with different thicknesses. As illustrated in the figures, when PET and PEN films of the same thickness were

tested under the same conditions, the air permeation of the PEN film was much lower than that of the PET film, and the latter could be over 5 times as high as the former. Besides, there was a tendency for the air permeation of both PET and PEN films to decrease with increasing film thickness. In conclusion, PEN is a polymer with excellent barrier properties.

Influence of the PEN concentration on the barrier properties of the PET/PEN blends

PET/PEN blends have good barrier properties because of their PEN component, and the PEN concentration is related closely to the improvement of their barrier properties. As PEN is much more expensive than PET, it is necessary to determine the appropriate PEN concentration for realizing good barrier properties at lower costs.

Figure 3 shows a comparison of the air permeability of PET/PEN films with different PEN concentrations. The air permeation of PET/PEN films decreased with increasing PEN concentration; that is, the barrier prop-
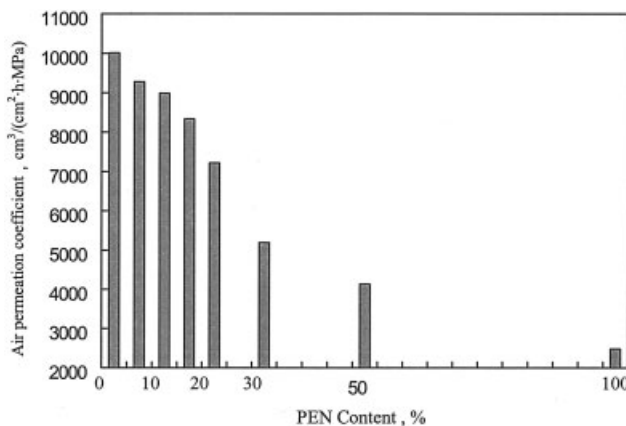

Figure 3 Influence of the PEN concentration on the air permeability of BOPET/BOPEN films.
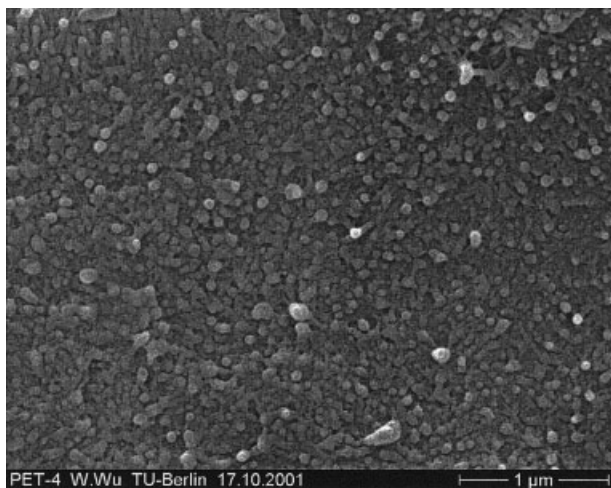
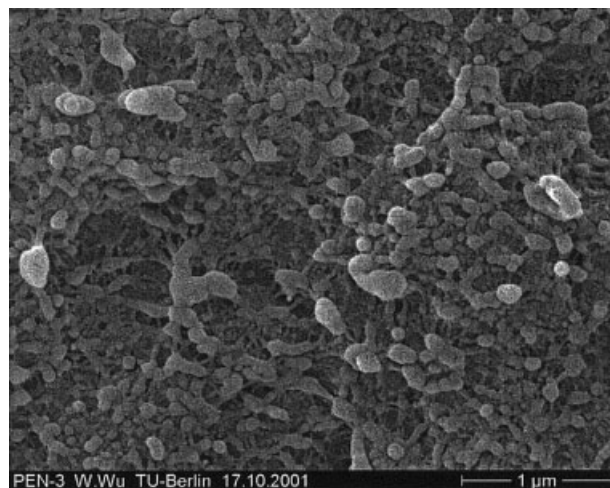**Figure 4** SEM photograph of the fracture surface of an extruded sample of pure PET.

Figure 5 SEM photograph of the fracture surface of an extruded sample of pure PEN.

erties of the films improved considerably with increasing PEN concentration. Because such PET/PEN films with different PEN concentrations were prepared under the same conditions, it could be concluded that their barrier properties improved mainly because of the increase in the PEN concentration.

Morphology of the PET/PEN blends

The barrier mechanism of PET/PEN blends is related closely to the morphologies of the blends. The fracture surfaces of extruded PET/PEN samples and BOPET/BOPEN films were investigated and are now analyzed.

Morphology of the impact fracture surfaces of the extruded PET/PEN samples

Figures 4 and 5 present SEM photographs of extruded pure PET and pure PEN samples, respectively. The fracture surface of pure PET had a fine-grained, spherulitic structure. The fracture surface of pure PEN was similar, but the PEN particles were bigger and more inhomogeneous.

Figures 6–8 present SEM photographs of fracture surfaces of extruded PET/PEN samples with PEN concentrations of 10, 20, and 30%, respectively.

Figures 6–8 indicate that the fracture surfaces of the PET/PEN blends had particles of two different size distributions and morphologies; of course, the bigger particles were PEN particles, whereas the smaller particles were PET spherulites. Therefore, it was concluded that the PET/PEN blends were phase-separated; that is, PET formed the continuous phase and PEN formed the dispersed phase in these blends.

Figures 6–8 also show that PEN particles were firmly integrated into the PET matrix. As is well known, transesterification can easily occur when PET and PEN are blended. The product of transesterification can be considered an excellent compatibilizer because it contains both PET and PEN chain segments. The amount of transesterification depends on the reaction conditions (e.g., temperature and time) and the PEN concentration. Under the same blending process conditions, the amount of transesterification grows with increasing PEN concentration. Therefore, when the PEN concentration reaches 30%, enough transesterification has occurred to effectively improve the compatibility of PET/PEN blends. This in turn results in less obvious phase separation as well as an indistinct interface between PET and PEN and smaller PEN particles.

Figure 6 SEM photograph of the fracture surface of an extruded sample of a PET/PEN blend (90/10).

Figure 7 SEM photograph of the fracture surface of an extruded sample of a PET/PEN blend (80/20).
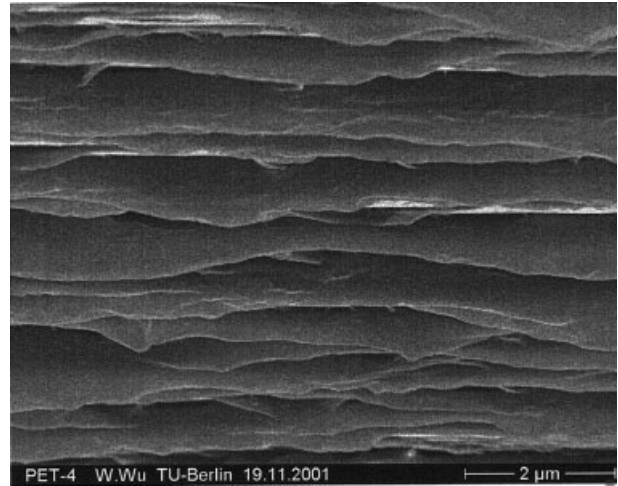

Figure 9 SEM photograph of the tearing fracture surface of a biaxially oriented film of pure PET.

Morphology of the tearing fracture surface of the biaxially oriented PET/PEN film

PET/PEN blends are often processed into films or containers to be used in barrier packaging applications. The PET/PEN blends discussed in the previous section were processed into BOPET/BOPEN films. The films were quickly torn and fractured after being frozen in liquid nitrogen, and the morphology of the tearing fracture surfaces was investigated with SEM.

Figures 9 and 10 present SEM micrographs of the tearing fracture surfaces of BOPET films and BOPEN films, respectively, whereas Figures 11–13 show SEM photographs of the tearing fracture surfaces of BOPET/BOPEN films with PEN concentrations of 10, 20, and 30%, respectively.

The tearing fracture surfaces of bioriented films of pure PET, pure PEN, and PEN/PEN blends possess layered structures. The cause of such layer structures is that when films are bioriented, the spherulitic structures observed in extruded samples are biaxially extended in the x and y axes, whereas their thickness in the direction of the z axis decreases. In the case of PET/PEN blends, PEN is distributed in the continuous PET phase in the form of particles before the blends are bioriented. Upon biorientation, the size of the PET particles increases along the x axis and y axis while decreasing along the z axis, and the size of the dispersed PEN particles also increases in the xy plane while decreasing along the z axis. As a result, PEN forms a dispersed phase with layers separated by the layered PET continuous phase. Thus, parallel and separated PEN layers are formed. Because the barrier properties of PEN are several times better than the barrier properties of PET, the laminate structure of
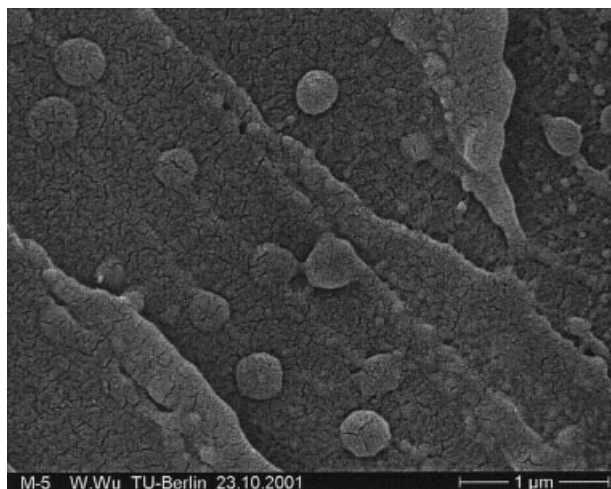

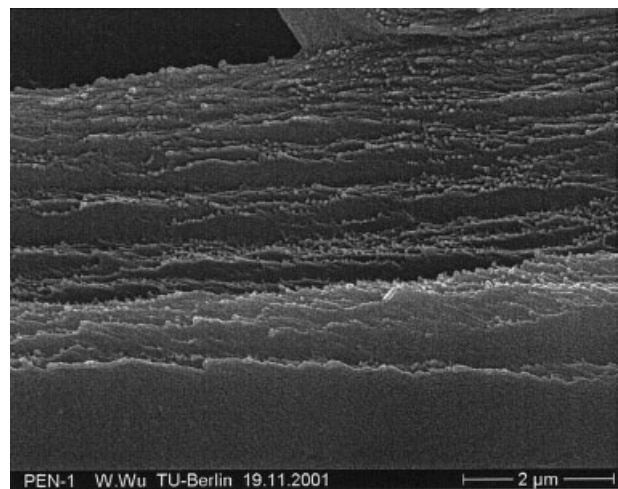**Figure 8** SEM photograph of the fracture surface of an extruded sample of a PET/PEN blend (70/30).

Figure 10 SEM photograph of the tearing fracture surface of a biaxially oriented film of pure PEN.

Figure 11 SEM photograph of the tearing fracture surface of a biaxially oriented film of a PET/PEN blend (90/10).

Figure 13 SEM photograph of the tearing fracture surface of a biaxially oriented film of a PET/PEN blend (70/30).

PEN in the PET matrix acts as an excellent barrier unit, preventing or delaying air permeation by the tortuosity of diffusion pathways, and thus improves the barrier properties of PET/PEN blends.

Obviously, to achieve a distribution of PEN in the form of parallel and extended layers, PEN must form a dispersed phase in PET/PEN blends consisting of particles of moderate size, the interphase must be firmly integrated, and the blends must be biaxially oriented. As illustrated in Figures 6–8, the number density of PEN particles was too low when the PEN concentration was 10%; thus, a PEN concentration of 20 or 30% may be practicable. As the blow-molding process of hollow bottles is actually a bioriented process, PEN can form microstructures consisting of parallel and separated layers when PET/PEN blends are used to produce hollow packaging containers (including drink bottles and beer bottles).
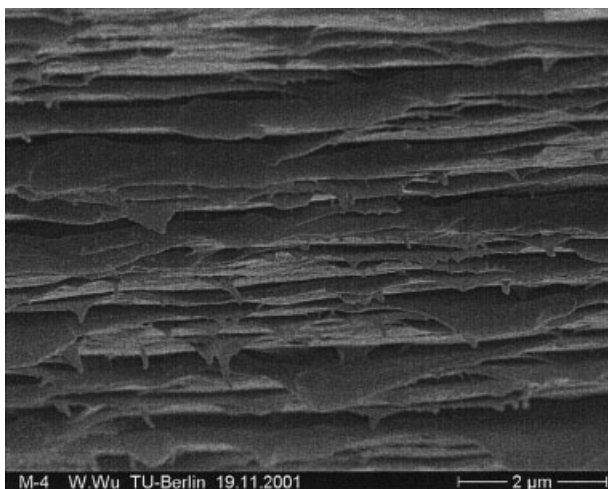

Figure 12 SEM photograph of the tearing fracture surface of a biaxially oriented film of a PET/PEN blend (80/20).
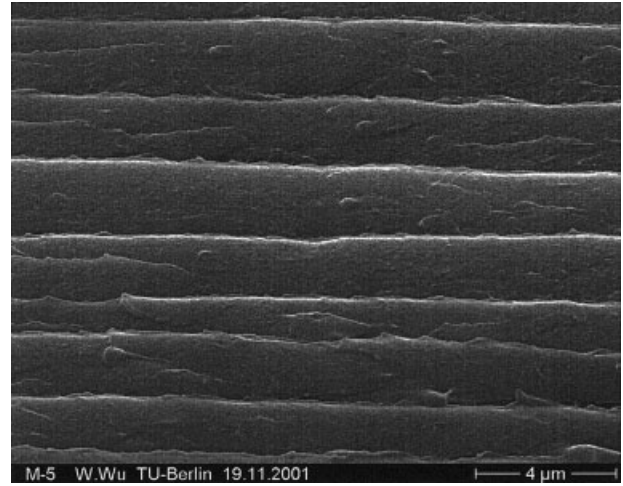
Barrier mechanism of the PET/PEN blends

The remarkable barrier properties of the BOPET/BOPEN blends are due to their specific morphology. This morphology allows us to obtain better barrier properties than expected by a simple addition of the barrier properties of each component. Usually, the morphology of blends with a homogeneous phase makes such superior expression of specific properties unavailable, and the morphology of blends with an inhomogeneous phase is the key to superior property expression.[11,12]

Blends with inhomogeneous phases (due to incompatibility) consist of a base component as a continuous phase and a barrier component as a dispersed phase.[13] For PET/PEN blends, air permeation depends on the particle shape of the barrier resin (PEN), on the adhesive bonding of the two phases, on the continuous phase (PET), and on other factors.

The permeability of phase-separated blends can be calculated by the use of the generalized Maxwell model for gas transport in heterogeneous media.[14–16] This model describes the dependence of the permeation properties in binary blends consisting of a dispersed component in a continuous matrix of a second component and can be expressed as

$$P_{\mathrm{Blend}} = P_c\left[\frac{P_d + A(P_c\Phi_c + P_d\Phi_d)}{AP_c + P_d\Phi_c + P_c\Phi_d}\right] \qquad (3)$$

where P_{blend} is the permeability of the blend, P_c is the permeability of the continuous phase, ϕ_c is the volume fraction of the continuous phase, P_d is the permeability of the dispersed phase, and ϕ_d is the volume fraction of the dispersed phase. A is a geometric factor accounting for the effect of the dispersion shape. The following special cases can be considered for the sys-
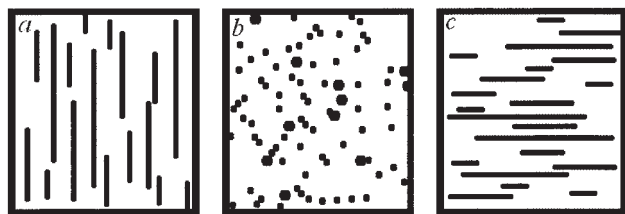
Figure 14 Schematic presentation of microparticulate dispersions for different values of A (gas permeation in the horizontal direction): (a) $A \to 0$, (b) $A = 2$, and (c) $A \to \infty$.

tem containing PET as the continuous phase and PEN as the dispersed phase, as indicated in Figure 14:[17,18]

1. $A = 0$ corresponds to planar laminate structures oriented perpendicularly to the gas flow direction, and eq. (3) reduces to the series rule

$$P_{\text{Blend}} = \frac{P_d P_c}{P_d \phi_c + P_c \phi_d} \tag{4}$$

2. $A = 2$ models the effect on the permeability of spherical (isometric) dispersed particles.
3. $A \to \infty$ corresponds to planar laminate structures oriented parallel to the gas flow direction, and eq. (3) reduces to the additivity rule

$$P_{\text{Blend}} = P_c \phi_c + P_d \phi_d \tag{5}$$

Figure 15 shows the effect of the mixing ratio on the permeability, which implies a transition of the dispersed PEN from particulate to extended planar layers
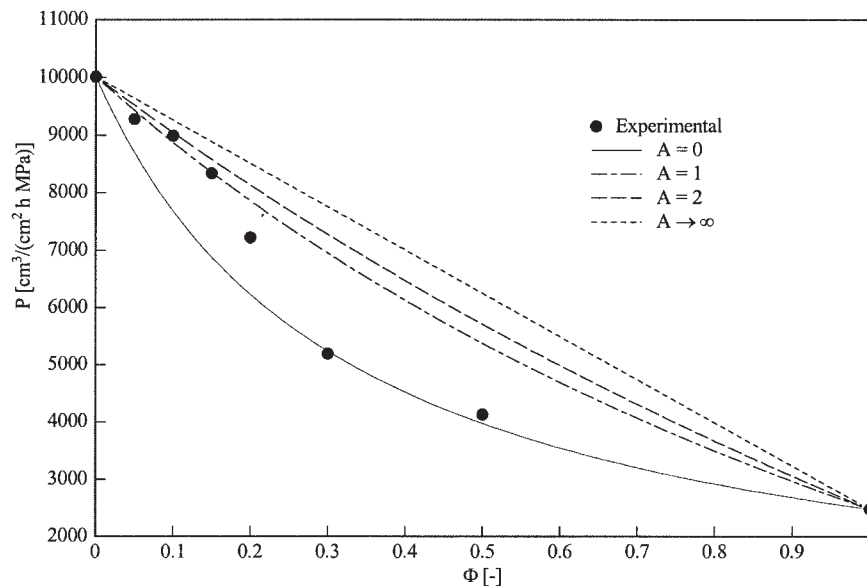
oriented perpendicularly to the permeation direction at volume fractions of 30% or larger.

According to this analysis of the morphology of PET/PEN blends, PEN forms the dispersed phase. In the case of extruded blends, PEN forms spherical particles ($A = 2$), whereas in the case of bioriented films, PEN forms extended planar layers with $A \to 0$. On the basis of this analysis, dispersed PEN particles have minor effects on the barrier properties of PET/PEN blends, whereas extended PEN layers oriented perpendicularly to the permeation direction can effectively improve the barrier properties of PET/PEN blends. The larger these multilayer microstructures are and the better they are oriented perpendicularly to the permeation direction, the better the barrier properties are of PET/PEN blends; when A tends to zero, the blends form true multilayer microstructures, and the best barrier properties are obtained. Consequently, a relatively small quantity of PEN can effectively improve the barrier properties of PET/PEN blends.[19–21]

To form such microstructures consisting of separated layers, PEN in PET/PEN blends must form particles of moderate size, the phase interface between PEN and PET must be firmly integrated, and the blends must be bioriented to form microstructures consisting of extended planar layers.

Based on these analyses, the barrier mechanism of PET/PEN blends is illustrated in Figure 16. In the case of extruded blends, PEN forms particles and air permeates along more or less straight routes. After PET/PEN blends are bioriented, PEN forms extended planar and separated layers, and air permeation is delayed as the air has to detour around the PEN layer
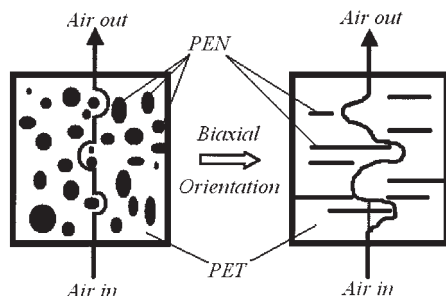

Figure 15 Permeability (P) of blends containing different volumetric fractions (Φ) of PEN: a comparison with the predictions of eq. (3).

Figure 16 Barrier mechanism of PET/PEN blends before (left) and after (right) biaxial deformation.

structures. Therefore, the barrier properties of BO-PET/BOPEN blends are effectively improved.

CONCLUSIONS

PEN is a perfect high-barrier polymer, and its air permeation is 4–5 times lower than that of PET. The barrier properties of PET/PEN blends are much better than the barrier properties of pure PET and improve with increasing PEN concentration.

When the PEN concentration is equal to or less than 30%, as in this study, PET/PEN blends are phase-separated; that is, PET forms the continuous phase, whereas PEN forms a dispersed phase of particles, and the interface is firmly integrated because of transesterification. After PET/PEN blends are bioriented, the PET matrix contains PEN microstructures consisting of parallel extended and separated layers.

The extended planar layers of PEN constitute multilayer microstructures characterized by microconti-

nuity, which results in improved barrier properties because air permeation is delayed as the air has to detour around the PEN layer structures. At a constant PEN concentration, the more extended the PEN layers are, the better the barrier properties of the PET/PEN blends can be.

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