DOUBLE BUBBLE TUBULAR FILM EXTRUSION OF POLYBUTYLENE TEREPHTHALATE-POLYETHYLENE TEREPHTHALATE BLENDS

Kwangjin Song* and James L. White
Institute of Polymer Engineering
The Univ. of Akron, Akron, OH 44325-0301

Abstract

A technology has been developed to produce biaxially oriented films of blends of polybutylene terephthalate (PBT) and polyethylene terephthalate (PET) using double bubble tubular film extrusion. The mechanical instabilities and the mechanisms associated with their sources of occurrence are described. The films have been structurally characterized by wide angle X-ray diffraction and optical techniques. The structure of the film is related to processing conditions.

Introduction

The double bubble tubular film process has been used commercially for a half century with various thermoplastic polymers (1,2). It is, however, not possible to apply the process to every thermoplastic with equal ease. The first stage is generally possible, but the second stage requires the film to have a strain hardening character. There has generally been difficulty in applying double bubble tubular film extrusion either to vitrifying polymers or to polymers which rapidly crystallize as there is no natural 'strain hardening' characteristic of the material in the second bubble. Patents by Baird et al. (3) and Benning et al. (4) describe a continuous crosslinking of polyethylene after the first stage. Another approach involving polymer blending was described in a patent by White and Nie (5). It is our purpose in this paper to develop a processing technique to produce biaxially oriented PBT films in double bubble extrusion process. PBT is unstable in the process (6). We seek to overcome this problem by suppressing its crystallizability.

Experimental

Materials

The polymers used in this study were PBT Ultradaur KR4036-Q692 of BASF Corporation and PET Tenite 7352 of Eastman Chemical Co. The PBT has an intrinsic viscosity of 1.24 dℓ/mg and the PET 0.8 dℓ/mg. The pellets were dried overnight at 110°C in a laboratory vacuum oven before being fed into the extruder.

* Yale University, 9 Hillhouse Ave, New Haven, CT 06520

Blend Preparation

A series of PBT/PET blends were prepared by melt blending using a 25 mm Werner & Pfleiderer co-rotating twin screw extruder (ZSK-30). The blend ratios of PBT/PET by weight were 95/5, 90/10, 80/20, 70/30 and 50/50. The screw speed was set at 100 rpm and the barrel temperatures 285°C. The pellets were mechanically mixed before processing.

Film Formation

Tubular films were prepared with a Killion tubular film extrusion apparatus equipped with an annular die. Pure PBT was extruded at temperatures of 260°C and PBT/PET blends at 280°C. The extrusion rate was fixed at 1,500 cm^3/hr. In the first stage, the amount and temperature of cooling air were carefully controlled for processability experiments. In the second stage, the first bubble with blow-up ratio (FBR) x draw-down ratio (FDR) = 1.25 x 25 was inflated again by air at the deformation temperature of 90°C. Selected films were annealed at 200°C for 10 min.

Film Characterization

X-ray Diffraction. WAXS diffraction patterns were taken using Rigaku and GE X-ray generators. The X-ray beam was monochromatized with a nickel foil filter to obtain CuKα radiation. All specimens had thickness of 1.2 mm. The overlap of PBT and PET crystalline peaks was a major difficulty in quantifying orientation in the blend films. The overlapped peaks were separated to correct diffracted intensity (7). White and Spruiell biaxial orientation factors were then computed (8):

$$f_{1,j}^{B} = 2\overline{\cos^2 \phi_{1,j}} + \overline{\cos^2 \phi_{2,j}} - 1 \qquad (1)$$

$$f_{2,j}^{B} = 2\overline{\cos^2 \phi_{2,j}} + \overline{\cos^2 \phi_{1,j}} - 1 \qquad (2)$$

where $\phi_{i,j}$ is the angle between film direction i (1: MD, 2:TD) and crystallographic axis j.

Optical Property. Refractive indices and birefringences of the films were obtained using a Bellingham Stanley Abbe 60/HR refractometer with a polarizing eyepiece. A monochromatic sodium lamp of wavelength 589.6 nm was used as a light source and diiodomethane sulfur ($n_D = 1.75$) as an immersion liquid.

Results

Instabilities of Tubular Film Extrusion

Single Bubble. We observed two kinds of instabilities; a bubble instability, an axisymmetric periodic fluctuation of bubble diameter and second a helical type instability (Fig.1). Instabilities of first bubbles occurred at all processing conditions below FDR = 20. The bubble instability occurred at low FBR while the helical instability appeared at high FBR. At PET contents $\leq$ 10 wt%, severe instabilities were observed. Bubble stability increased with increasing PET content. First bubbles with PET levels $\geq$ 30 wt% revealed wide stable regions.

Double Bubble. Double bubbles exhibited only helical instability. Double bubble films of pure PBT could be produced only under uniaxial stretching conditions. Strikingly, blending PBT with PET drastically modified the stability of PBT second bubble. Bubble stability increased with increasing PET content. At PET levels of 20% or greater, the blend polymers were processed into a stable biaxial double bubble with wide operating windows.

WAXS Diffraction Photographs

First Bubble. At FDR $\leq$ 40, first bubbles with PET levels $\leq$ 5 wt% generally exhibited concentric Debye rings of crystalline reflections (Fig.2). With increasing PET content, the reflections became diffuse amorphous halos. The first bubbles produced at FDR $\geq$ 60, however, contained weak (010) Debye arcs on the equator.

Double Bubble. Double bubble films produced at second drawdown ratio, SDR = 4 generally showed diffuse Debye arcs. In the uniaxial double bubbles, the (010) arcs through the film of both PBT and PET phases and the edge direction (100) arcs were seen on the equator. End patterns revealed the (010) arcs on the meridian. Crystalline arcs weakened with the addition of PET. With biaxial blow-up, Debye arcs became faint. Annealed double bubble films exhibited distinct crystal character of the individual phases. The PBT α-phase was still dominant at PET contents $\leq$ 30 wt%. The crystalline arcs of a component continued intensifying with an increase of its content in the blends. The (100) arcs through the '13' plane intensified with rising SBR. An annealed 50/50 double bubble had diffuse edge direction PBT (001)α arcs.

WAXS Pole Figures

Unannealed Bubble. First bubble blend films exhibited largely isotropic pole figures suggesting little or no crystalline orientation. Double bubble blend films were generally similar to pure PBT films (Fig.3). The (010) pole figures contained reflection overlap. An increase in PET content and SBR distributed the (010) poles in the ND-TD plane. A 50/50 blend film comprised rather weak (010) Bragg maxima. With increasing SBR, the PBT (100)α normals concentrated in the ND and the poles of off-meridional reflections, concentrated in the MD, spread in the plane of the film. The PET ($\bar{1}$05) poles intensified with increasing PET content.

Annealed Bubble. Annealed double bubble films showed well defined and highly symmetric pole figures. In the uniaxial double bubbles, the poles of the PBT component weakened and distributed with the addition of PET while those of the PET component intensified. The PBT ($\bar{1}$04)α pole figures contained intense bimodal maxima in the MD with tilt toward the ND. The biaxial double bubbles exhibited the same tendency. Annealing substantially narrowed the distributions of pole densities. The poles of the (010) and PET ($\bar{1}$05) planes tended to spread in the MD-TD plane with increasing SBR while the (100) poles narrowly concentrated in the ND. This indicates that the c-axes of both components were oriented in the plane of the film.

Refractive Indices

First Bubble. The principal refractive indices underwent a minimum with PET composition (Fig.4). Increasing FDR increased n_{MD} and decreased both n_{TD} and n_{ND}. The n_{TD} arose with increasing FBR, but both n_{MD} and n_{ND} decreased. The blend films with PET levels of 30 wt% had the lowest refractive indices. Birefringences developed differently; they decreased with increasing PET content.

Double Bubble. The second deformation substantially increased both n_{MD} and n_{TD} and further decreased n_{ND} (Fig.5). The n_{MD} and n_{TD} decreased while the n_{ND} arose with increasing PET content. The individual blends with different composition responded similarly to deformation. An increase of SDR at SBR = 1 rapidly increased n_{MD} and decreased n_{TD} and n_{ND}. The double bubble films at SDR = 2 went through in-plane isotropy with SBR and then the n_{TD} continuously increased with further blow-up. Double bubble with PET contents $\leq$ 30 wt% possessed similar levels of birefringences. The birefringences however decreased with further increasing PET content above 30 wt%.

Annealed Double Bubble. Annealing further increased n_{MD} and n_{TD} and decreased n_{ND}. Blend films with PET levels $\leq$ 10 wt% were similar to pure PBT film having quite high n_{ND} at SDR $\leq$ 3. Annealed double bubbles at PET levels of 30 wt% had slightly higher birefringences with $\Delta n_{13} = 0.1829$ at SDR x SBR = 4 x 1 and $\Delta n_{23} = 0.1792$ at 2 x 3.

Discussion

Mechanisms of Bubble Instabilities

Single Bubble. Under all processing conditions, an increase in FDR caused first bubbles to be stabilizing while increasing FBR destabilized bubbles. Stability increased with increasing PET content. It appears that this would involve variations in molecular rigidity as well as strain hardening characteristics of materials. PET is more rigid than PBT. Bubble instability occurring at low FBR = 1 would be associated with the viscosity, i.e., a self-supporting characteristic, of a polymer melt. Helical instability would involve nonuniform deformation along the hoop direction (HD). Increasing FBR causes an increase in gauge nonuniformity and a decrease in chain orientation in the flow direction, which as a result cause a local variation of axial rigidity of the material in the radial direction. At higher FDR and FBR, a helical motion of bubble may occur due to the anisotropic HD deformation coupled with aerodynamics.

Double Bubble. In the second stage, bubble deformation takes place in a rubbery solid-state. This cold-drawing increased the viscosity of materials, which results in narrowing the operating windows. The absence of the bubble instability in the second stage could be attributed to the higher viscosity. Instability decreased substantially with increasing PET content. Clearly this is related to the low crystalline character of first bubbles. The first bubbles at PET levels above 10 wt% were transparent and exhibited strain induced crystallization in the second stage. This variation in crystallizability of PBT substantially modified the stability of second bubble. The stability of PBT/PET blend systems would result from their melt miscibility.

Crystalline Character as Functions of Deformation and Composition

First bubble blend films generally possessed poorly ordered structure due to the suppression of PBT crystallization under mild processing conditions. Higher stress in the second stage developed crystalline textures, though still quite imperfect. The individual films with different composition behaved essentially in the same manner with deformation as the homopolymer films. Presumably the similarity in chemical structures of the PBT and PET species could provide a similar local deformation environment to that of the pure polymer. The individual components decreased in crystal perfection with increasing content of the other component. This could involve dilution effects and melt miscibility. The PBT crystalline phase may act as a nucleating site for the crystallization of PET whereas the large proportion of the PBT amorphous phase could behave as a highly viscous

polymeric diluent leading to the retardation of PET crystallization. The prevalence of PBT crystals at PET contents ≤ 30 wt% can be attributed to its still rapid crystallization. Stein et al. (9) reported that WAXS measurements did not detect PET crystals in PBT/PET blends with PET contents up to 20 wt%. The blends having a high content of one component exhibited principally the crystals of that component. This generally agrees with our results for the unannealed films. Annealing, however, introduced variations. The annealed films with PET levels ≥ 10 wt% exhibited distinct PET crystals suggesting the existence of poorly ordered PET textures in the unannealed precursors.

Crystalline Orientation

First bubble blend films exhibited little crystalline orientation. The values of $f_{1,c}^B$ (the MD orientation factor of the c-axes) and $f_{2,c}^B$ (the TD orientation factor) were found to be near zero. Substantial orientation developed in double bubble blend films (Fig.6). Interestingly, the orientation of the PBT phase generally decreased with rising PET content. It seems that this could involve decreasing amount and perfection of PBT crystallites with increasing PET content. Deformation also caused changes. For a given SBR, $f_{1,c}^B$ increased while $f_{2,c}^B$ decreased with increasing SDR. The phenyl ring on the chain backbone increasingly oriented with SDR ($f_{1,a}^B$, $f_{2,a}^B$). Biaxial blow-up increased $f_{2,c}^B$ at the expense of $f_{1,c}^B$. The phenyl rings further oriented with increasing SBR. The phenyl rings would align themselves parallel to the film surface during deformation due to their bulky and planar geometry. This parallelism could be expedited by the strong tendency toward molecular packing and the marked van der Waals interaction between the chemical moieties (10). In annealed blend films, the orientation of the PBT component reduced while that of the PET component increased with increasing PET content.

There have been studies of orientation in the individual phases of polymer blends. Wang and Porter (11) found that the orientation of polystyrene (PS) chains in a miscible PS/poly(2,6-dimethyl-1,4-phenylene oxide)(PPO) blend decreased with increasing PPO concentration. This was attributed to the interaction between PS and PPO chains. Endo et al. (12) found in studying tubular films of polyethylene (PE)/bisphenol-A polycarbonate (PC) blends that the orientation factors f_{1j}^B and f_{2j}^B of PE were reduced by introducing PC. They claimed that the mechanism of this behavior is that, as melt cools in the film line, the stresses redistribute themselves to concentrate on the vitrifying phase whose viscosity increase outruns that in the PE. Shimomura et al. (13)

noted that in tubular films of incompatible PE/PP blends, molecular orientation in the individual phases was lower than in the homopolymer films. This decrease of orientation was attributed to the reduced stretching stresses that were caused by the reduction in melt viscosity of the blends. Liang et al. (14) reported that in PP/nylon 6 blends, the presence of PP retarded orientation development in nylon 6 due to stress concentration on the PP phase.

In this study, we observed that in miscible crystalline-crystalline PBT/PET blends, the orientation in one phase decreased with increasing presence of the other over the composition range investigated. Our results are generally consistent with those of Shimomura et al. (13). It would seem that deformation mechanisms of PBT/PET blends largely involve changes in crystallizability of the components with composition. The suppression of PBT crystallization in the blends may cause stress reduction and redistribution during deformation. The PET phase, which is stiffer than the PBT phase, generally crystallized slowly owing to its slow crystallization characteristics and the dilution effect. The individual phases became less perfected with increasing content of the other. It is believed that in PBT/PET blends, the retardation of orientation in the individual phases can be attributed to the reduced crystallizability of the component polymers resulting from the presence of the other.

Overall Molecular Orientation

The overall orientation of polymer chains ($\Delta n_{13}, \Delta n_{23}$) decreased with increasing PET content. This tendency was more pronounced at lower levels of deformation. As discussed earlier, the mechanism of this behavior would involve changes in crystallizability of the individual polymers in the blends. The stress may concentrate on the PBT phase during the initial stage of deformation owing to its long flexible molecular segments. At lower levels of deformation, the PBT chains could orient more readily resulting in higher orientation in the films with lower PET contents. The PET phase may experience strain hardening at relatively higher deformation. Annealing induced a substantial increase in birefringence. The extents of this increment arose with decreasing MD stretch and increasing PET content. This would involve more amorphous fractions that were oriented in the unannealed precursors. Fixed annealing develops the contractible forces, which cause further molecular packing and stretching. It seems that the films with more amorphous phases oriented undergo larger internal rearrangement of microstructures upon annealing. Li and Wang (15) noted that uniaxial PBT/PET blend films underwent a maximum birefringence with composition. They argued that the maximum birefringence was due to the physical and/or chemical interconnection between the constituent chains.

References

1. W.T.Stephenson, U.S Patent 2,452,080 (1948)
2. K.G.Gerber, U.S Patent 2,862,234 (1958)
3. W.G.Baird, C.A.Lindstrom, A.L.Besse, and D.J. d'Entremont, U.S Patent 3,022,543 (1962)
4. C.J.Benning, R.Gregorian, and F.X.Werber, U.S.Patent 3,201,503 (1965)
5. J.L.White and T.Nie, U.S Patent 5,082,616 (1992)
6. K.J.Song, Ph.D Dissertation, The Univ. of Akron, 1998
7. C.R.Desper, R.S.Stein, *J.Appl.Phys.*, 37, 3390 (1964)
8. J.L.White, J.E.Spruiell, *Polym.Eng.Sci.,* 20,247 (1980)
9. R.S.Stein, F.B.Khambatta, F.P.Warner, T.Russel, A.Escala, and E.Balizer, *J.Polym.Sci.:Polym.Symp.*, 63, 313 (1978)
10. de P.Daubeny, C.W.Bunn, C.J.Brown, *Proc. R. Soc., London Ser.A*, 226, 531 (1954)
11. L.H.Wang and R.S.Porter, *J.Polym.Sci.:Polym.Phys.*, 21, 1815 (1983)
12. S.Endo, K.Min, J.L.White, and T.Kyu, *Polym.Eng.Sci.*, 63, 313 (1987)
13. Y.Shimomura, J.E.Spruiell, and J.L.White, *Polym.Eng.Rev.*, 2, 418 (1983)
14. B.R.Liang, J.L.White, J.E.Spruiell, and B.S.Goswami, *J.Appl.Polym.Sci.*, 28, 2011 (1983)
15. H.M.Li and A.H.Wong*, MMI Press Symp. Ser.*, Vol.2, 395, Harwood Academic, NY, 1982
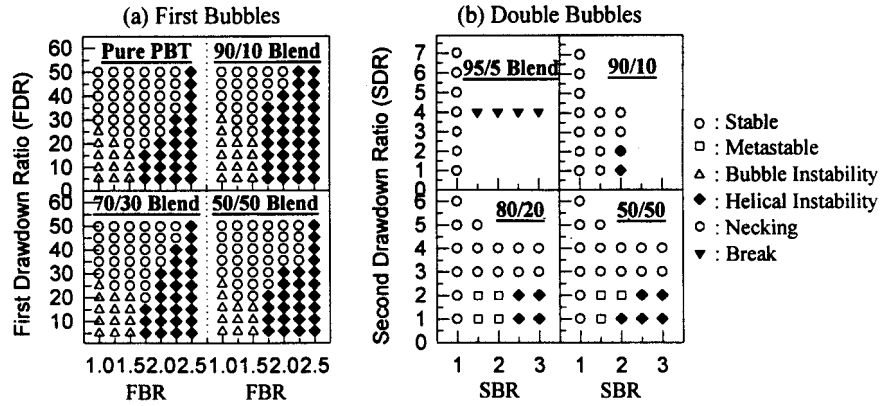
Figure 1 Stability of PBT/PET blend single and double bubble tubular films as functions of deformation and composition.
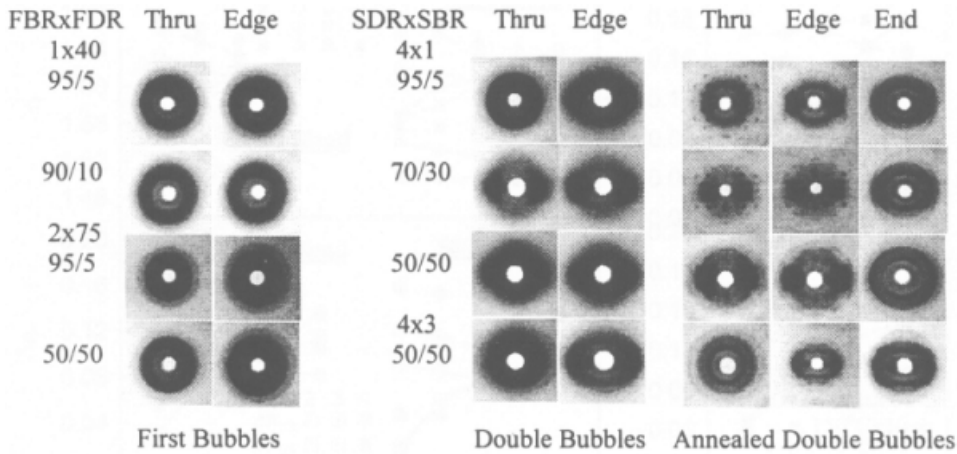

Figure 2 WAXS film photographs of PBT/PET blend single and double bubble tubular films produced under various processing conditions.
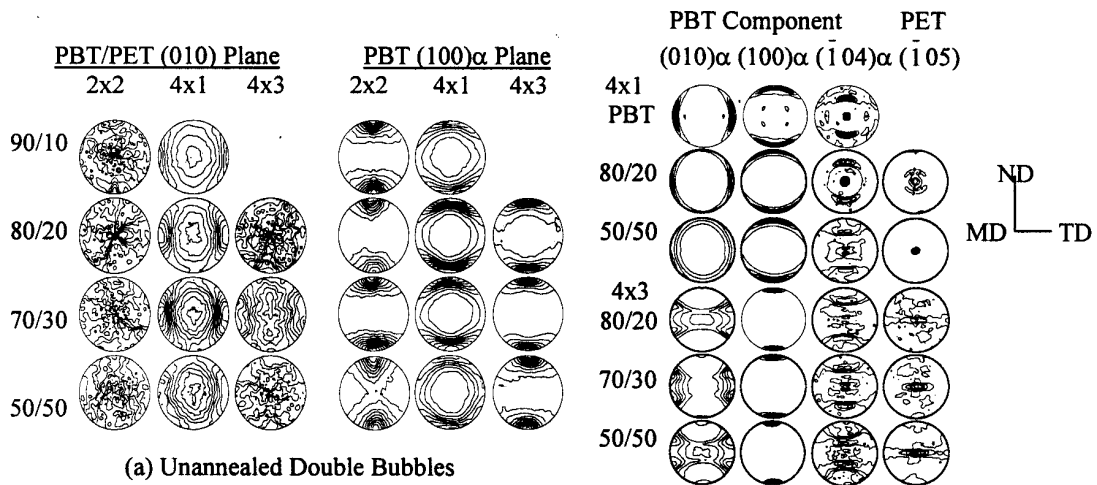

Figure 3 WAXS pole figures of PBT/PET blend double bubble tubular films with different crystal lattice planes.
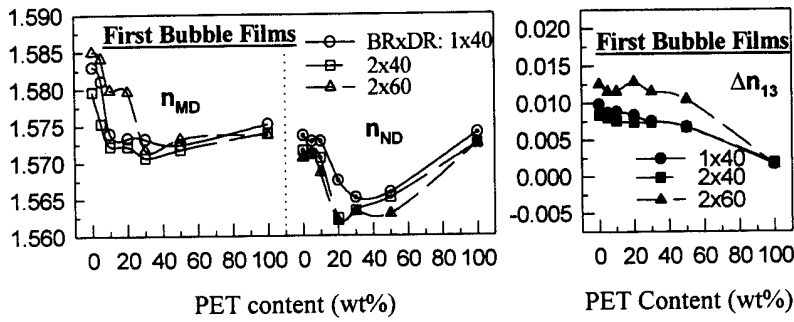
Figure 4 Refractive indices (n) and birefringences (Δn) of PBT/PET blend first bubble tubular films as a function of composition.
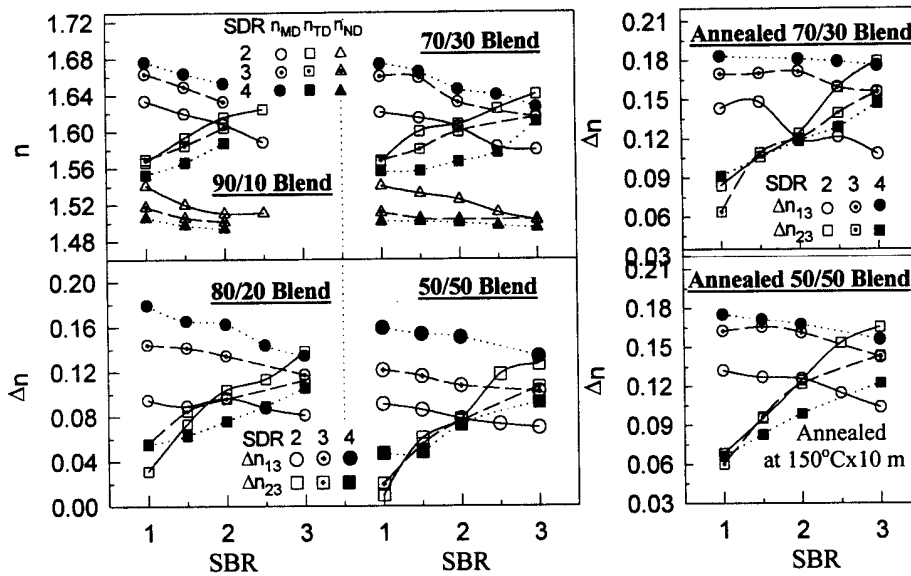

Figure 5 Refractive indices (n) and birefringences (Δn) of PBT/PET blend double bubble tubular films.
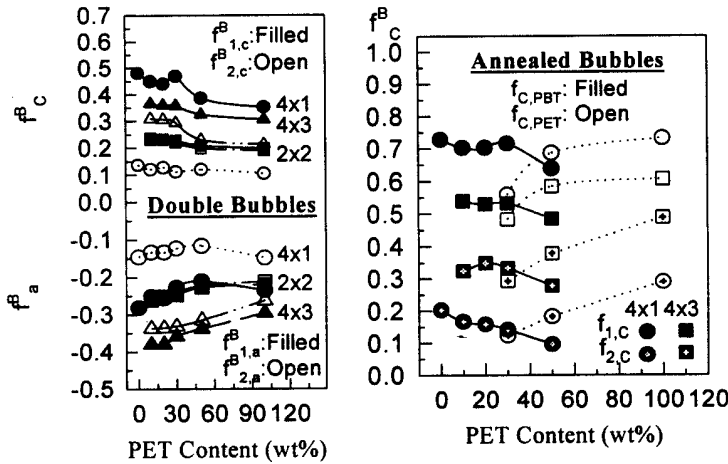

Figure 6 White-Spruiell biaxial orientation factors for PBT/PET blend double bubble tubular films.