Fibers from Poly(ethylene Terephthalate) and Poly(butylene Terephthalate) Blends I. Mechanical Behavior

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Synopsis

Fibers prepared from poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) blends show a sharp decrease in tensile strength and modulus when blends are on the verge of phase segregation. The modulus values differ for homopolymers for their differences in chain configuration and methylene groups and that of the blends are in proportion. The experimental strength values are higher than the predicted values according to Paul's model for incompatible polymers. At 90/10 PET/PBT blend, the modulus is high, which may be a relative factor to the smaller crystal size of the components.

INTRODUCTION

Blending provides a straightforward, versatile and relatively inexpensive method to develop new polymeric material with superior combination of useful properties. Several recent reviews have appeared on blends.[1-3]

Due to thermodynamic incompatibility of most polymers, heterogeneous polyblends are generally obtained with varied degrees of incompatibility. The final properties will be determined by those of pure polymers, geometrical arrangement of the phases, their morphology, the extent of their interpenetration, and the nature of interface.[4] One of the most important properties of polyblends is their mechanical behavior. A compatible polyblend exhibits mechanical properties proportional to the ratio of the components.[5] Schreiber and Ross[6] selected the tenacity of the spun fiber as an index of useful property development. In principle, property enhancement should depend on the ability of the constituent materials to remain in molecular contact when constraints are imposed on the complex structure. In crystallizable polyblends, the mechanical behavior is affected by properties of individual constituents, mode of dispersion, degree of crystallinity, morphology and compatibility in the amorphous state.[7,8]

Recent studies[9-11] indicate that significant improvement in properties of poly(ethylene terephthalate) (PET) fiber can be achieved by blending with poly(butylene terephthalate) (PBT). The cohesive energy density of these polymers are the same in the zones of aromatic segments and differ in the aliphatic portion because of the difference in length of methylene chains.[12] We have predicted theoretical compatibility of PET and PBT blends through

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different thermodynamic concepts.[13] Escala and Stein[14] have shown that these polymers are compatible in the amorphous state, however, they crystallize separately according to their own unit cell structure. Due to their peculiar characteristics, they are expected to give fibers having significantly different properties at different proportions and processing conditions. Li and Wong[15] have found that the extruded films prepared from blends of PET and PBT improve the toughness and tear strength. They have shown that the morphology, domain structure, and number of tie points in the crystalline polymer network have a significant impact on the orientation efficiency in the alloy film and its mechanical properties.

In a recent study,[16] we observed that the presence of 2% PBT in PET increases melt viscosity and decreases the activation energy due to entanglement. The melting behavior of the isothermally crystallized sample shows that the crystallization behavior in the blend is governed by the mobility of PBT.[17] In this first part of the series, we have investigated the mechanical properties of the fibers produced from blends of PET and PBT. Different models are applied on strength and modulus to determine the extent of compatibility.

EXPERIMENTAL

Commercial polymers were selected for this study. The characteristics of these polymers are given in Table I. The blend compositions and spinning temperature of the blend fibers from PET and PBT are given in Table II. The fibers were prepared in a laboratory scale melt-spinning unit having a static mixture with parts for mixing by its internal geometric design. The as-spun fibers were drawn in a laboratory scale stretching unit to 4.22X at 110°C. The drawn materials were given a thermal treatment at 70°C for 30 min. Heat-set samples were prepared by heat-setting under tension the drawn yarn in a silicone oil bath for 1 min at 190°C.

Tensile properties of the undrawn, drawn, and set fibers were measured at standard atmosphere with strain rate of 0.0167 s^{-1}. Stress, strain, and modulus are calculated for the present study from an average of 25 samples. Sonic velocity was measured on a Dynamic Pulse Propagation Meter at 5 KHz. Sonic modulus was calculated from the sonic velocity.

ANALYSIS OF MODULUS BY MODELS

Different authors[19-21] used different rules and models to follow the nature of interaction from modulus. The models to predict the modulus of heteroge-

TABLE I
Material Characteristics of the Chips

	PET	PBT
Source	Teijin Co. Ltd.,	GEC Co. Ltd.,
I.V.	0.67	1.04
M_n	1.88×10^4	2.00×10^4
Chips shape	Cubical	Cylindrical
No. of chips/g	27–30	50–54

TABLE II
Sample Composition and Spinning Temperature of the Blends

Sample	Wt. percentage of PET (%)	Wt. percentage of PBT (%)	Spinning temp. (°C)
100/0	100	0	265
98/2	98	02	265
96/4	96	04	265
94/6	94	06	265
92/8	92	08	265
90/10	90	10	265
85/15	85	15	265
80/20	80	20	265
60/40	60	40	265
40/60	40	60	265
20/80	20	80	265
10/90	10	90	262
06/94	06	94	260
02/94	02	98	260
00/100	0	100	250

neous system may be roughly divided into two categories. The first calculation is from an idealized picture of the actual structure. The second entails calculations based on an equivalent assembly of mechanical elements with properties identical to those of the individual constitutents. These elements are connected either in series or in parallel. Nielson[21] modified the general equation proposed by Helpin[22] and Tsai,[23] which includes both morphologies. He accommodated the complete range of morphology, invoking the concept of maximum packing fraction of the dispersoids and co-continuity of the phases.

The modulus can be represented by rule of mixtures, which gives the upper bound and lower bound in the modulus for a multiphase system. For a two-phase system, the equations are as follows:

$$\text{Upper bound:} \quad E_b = \phi_1 E_1 + \phi_2 E_2 \tag{1}$$

$$\text{or} \quad E_b = w_1 E_1 + w_2 E_2$$

$$\text{Lower bound:} \quad E_b = \left[\frac{\phi_1}{E_1} + \frac{\phi_2}{E_2} \right]^{-1} \tag{2}$$

where E_b, E_1, and E_2 are the modulus of the blend, first and second component, respectively. ϕ is the volume fraction and w is the weight fraction.

The above models are without any strength of interaction between the two components. When the strength of interaction is considered, then the equation has the following form:[24]

$$E_b = w_1 E_1 + w_2 E_2 + \beta_{12} w_1 w_2 \tag{3}$$

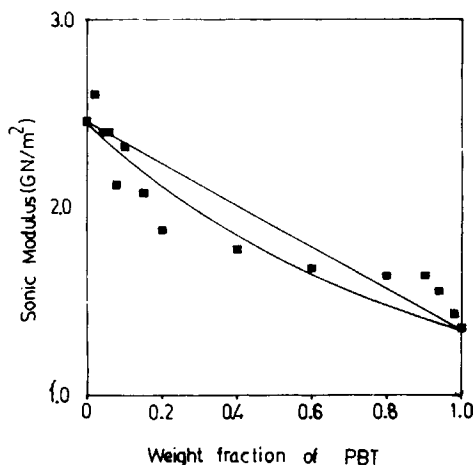where β_{12} expresses the magnitude of the deviation from nonlinearity. A

Fig. 1.   Sonic modulus of undrawn fibers. Continuous lines show the theoretical value.

positive β_{12} represents a nonlinear synergism and an indication of compat'bility.

ANALYSIS OF STRENGTH BY MODELS

Prediction of the nature of interaction from strength is given by Nolley and Paul.[33] The total tensile strength σ_b of a binary blend is given by:

$$\sigma_b = \sigma_{11}\phi_1^2 + \sigma_{22}\phi_2^2 + 2\sigma_{12}\phi_1\phi_2 \qquad (4)$$

where σ_{11} and σ_{22} refers to the adhesive strengths of the pure components to themselves, ϕ is the volume fraction and σ_{12} is the adhesive strength between polymer 1 and 2.

In the limit of very poor adhesion, tensile strength of the blend is equal to

$$\sigma_b = \sigma_{11}\phi_1^2 + \sigma_{22}\phi_2^2 \qquad (5)$$

RESULTS AND DISCUSSION

Figures 1 to 8 shows the effect of blend composition on stress and modulus of undrawn, drawn and set yarn. There are large variations of these properties with composition. There are two competing morphological factors which are expected to affect the tensile behavior of the blends,[18] namely (1) deterioration of properties as a result of incompatibility and consequent two-phase structure and (2) improvement of properties by the formation of more intercrystalline structure. In other words, differences in interaction between blend components, the mechanical behavior, can differ from the additivity rule.

The modulus values of drawn and heat-set fibers are nearly 6–7 times higher than that of drawn and heat-set PBT fiber and it only two times greater than the as-spun fiber. The elastic modulus parallel to the chain axis is closely related to the molecular conformation in the crystal lattice.[36] The
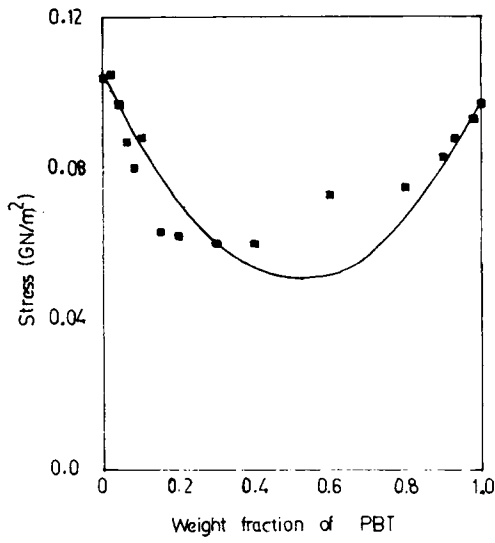
Fig. 2.   Breaking stress of undrawn yarns. The continuous line shows the theoretical predictions by Paul.[33]
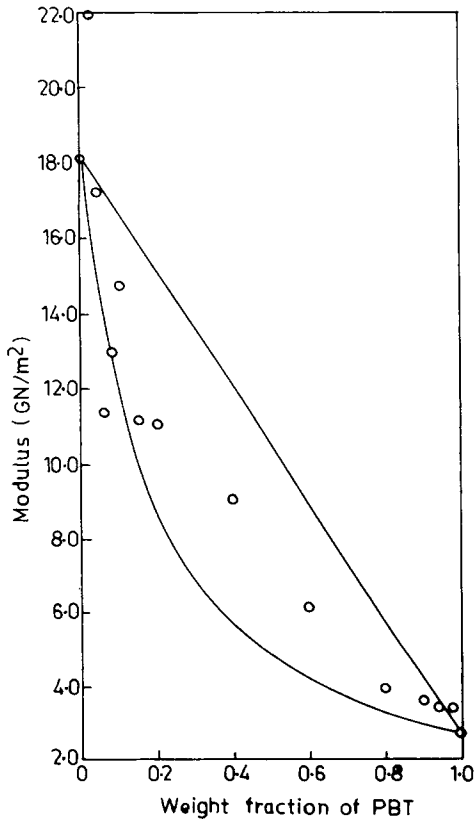

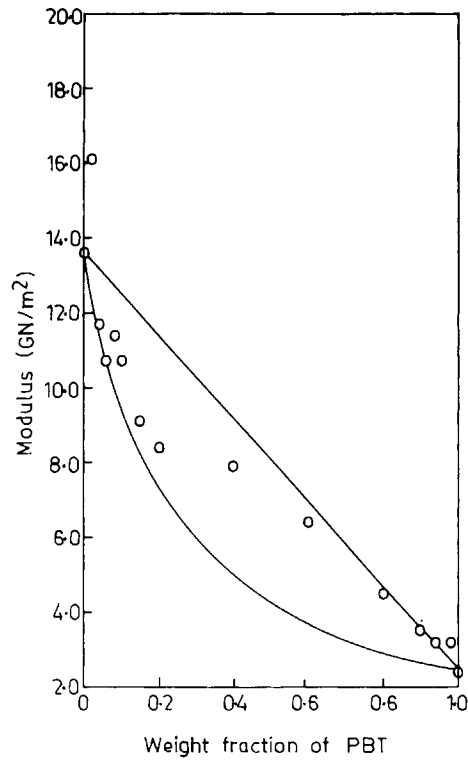Fig. 3.   Initial modulus of drawn fibers with calculated values (continuous lines).

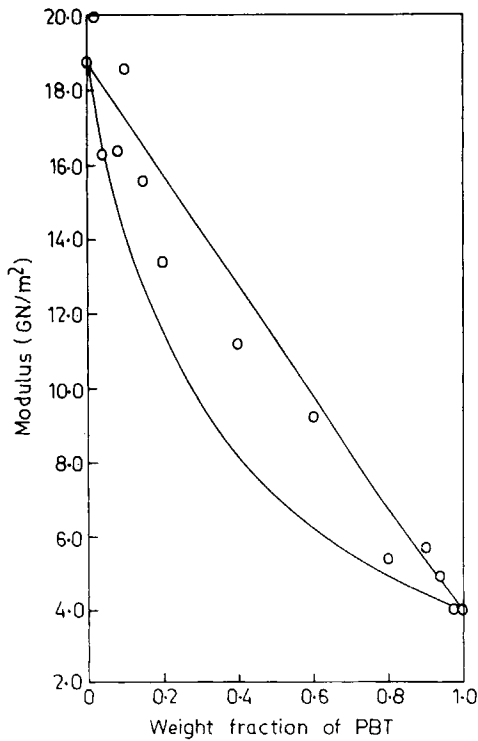Fig. 4. Initial modulus of set yarns with calculated values as continuous lines.

Fig. 5. Sonic modulus of drawn fibers with calculated values (continuous lines).
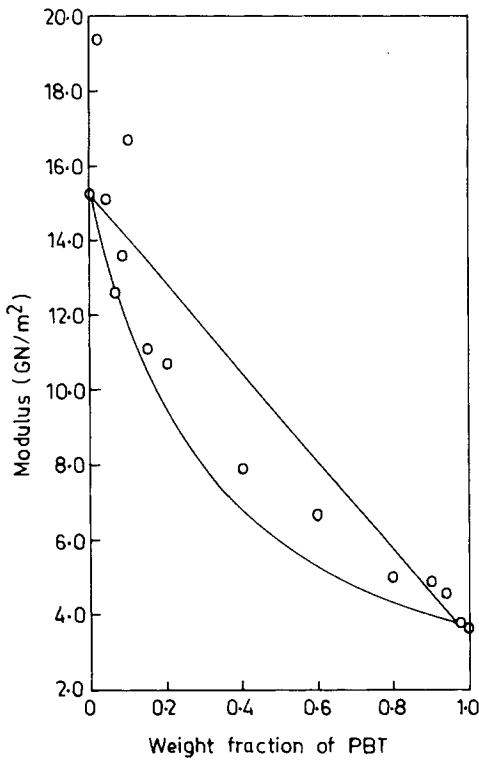
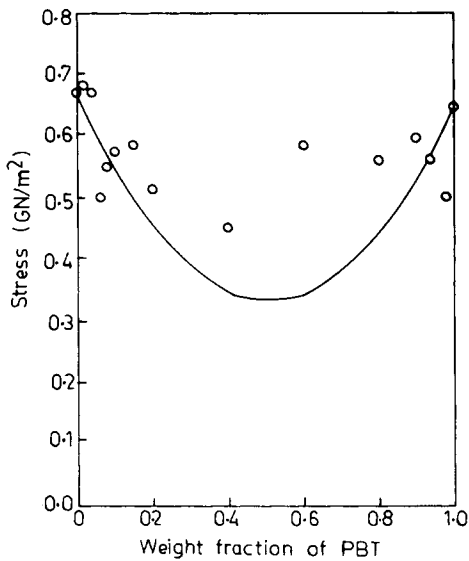Fig. 6.   Sonic modulus of set yarns with calculated values as continuous lines.

Fig. 7.   Breaking stress of drawn fibers. The continuous line shows the theoretical predictions by Paul.[33]
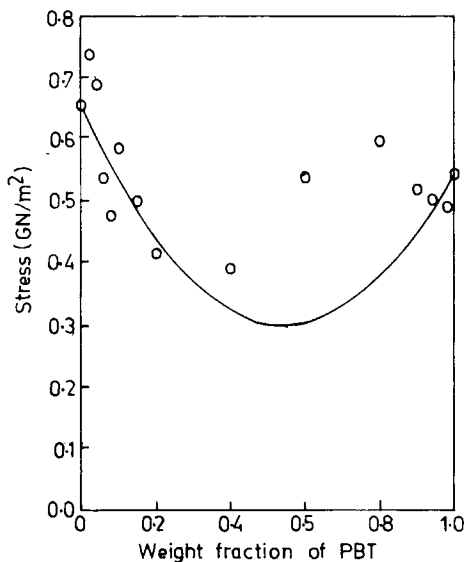
Fig. 8.   Breaking stress of set yarns. The continuous line shows the theoretical predictions by Paul.[33]

observed small modulus value for PBT means that the chain conformation in the crystalline region of PBT is more contracted than that of PET.[25]

The calculated values of modulus [Eqs. (1) and (2)] and calculated values of strength [Eq. (5)] are applied to undrawn, drawn, and set yarns. Figures 1 and 2 show the modulus and strength of undrawn fibers. Both figures show incompatibility of as-spun fibers, when PBT is approximately 10–40%. This is the region where PBT is the minor amount. In this range, crystallization of PBT takes place in a state, where PET is already crystallized. On the other hand, this type of incompatibility behavior is not present where PBT is the major component. There is a synergistic effect in the range when the second component (either PET or PBT) is minimum. Our theoretical predictions indicate these regions as compatible regions.[13]

Orienting the as-spun fibers minimizes both the incompatibility effect as well as the synergistic effect, as seen from both sonic and initial modulus (Figs. 3 and 5). Both initial modulus and sonic modulus show similar behavior, but it is not identical due to large strain differences between the two measurements. Kleiner[22] shows that the sonic modulus analysis would lead to greater accuracy. The strength of the drawn yarns (Fig. 7) shows similar modifications. After heat setting, modulus and breaking stress decrease (Figs. 4, 6, and 8). Most primary crystallization takes place during heat setting, where small crystals melt and merge in bigger crystals,[34] which decreases modulus and strength.[35] The experimental values of breaking stress are higher than those of the calculated values, showing partial compatibility. Also, the modulus values are in between the upper bound and lower bound of the calculated values.

Modulus of blends of 94/6 and 92/8 blends shows lower values. The breaking stress of this two blends and 2/98 PET/PBT blend are less than

those of the calculated values. At 92/8 blend, the components are about to phase segregate, as per differential scanning calorimetry (DSC) analysis.[17] Paul[33] showed that if the experimental value is less than the calculated value, there is a compatibilizing effect. PET/PBT 98/2 fiber shows a high initial modulus, sonic modulus, and strength, indicating a synergistic effect. The rheological behavior for this blend system shows higher chain entanglement.[16] Our previous results[17] for this blend show that PBT molecules are uniformly distributed in PET. The entanglement may result in higher crystalline links as changes introduced in the supermolecular structure of a polymer melt may be reflected in the solid state.[26] This may account for high modulus and strength.[27-29] Lovinger and Williams[18] have shown that the improvement in the properties of the PP/PE blend is due to the formation of intercrystalline links.

Modulus and strength at 90/10 fiber is high. At this ratio, the two components phase segregate and crystallize independently. The high modulus is more pronounced in drawn and set yarns, as evidenced from sonic modulus values, than that of the as-spun fibers. So the high strength and modulus may possibly be due to a fine grain structure, which on drawing produces a interconnected structure with high density of tie molecules and fewer defects in terms of microfibril ends.[2,30-32]

CONCLUSION

1. PET and PBT have different modulus values due to structural differences. The modulus values of the blends are within the limits of the values proposed by Nielson.[21]

2. The model proposed by Paul[33] to interpret strength shows that the blend fibers have at least partial compatibility in the whole range. When the phase segregation is just operative, the blends have low strength and modulus values.

3. 98/2 Blend shows a higher modulus and strength value due to high intercrystalline links.

4. 90/10 Blend probably has a fine grain structure, which on drawing produces an interconnected structure with high density of tie molecules, resulting in high modulus and comparatively high strength.

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