

Structure development and properties of high-speed melt spun poly(butylene terephthalate)/poly(butylene adipate-*co*-terephthalate) bicomponent fibers

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Abstract

Ultra-high-speed bicomponent spinning of poly(butylene terephthalate) (PBT) as sheath and biodegradable poly(butylene adipate-*co*-terephthalate) (PBAT) as core was accomplished with the take-up velocity up to 10 km/min. The structure development of the individual component and the properties of PBT/PBAT fibers were investigated through the measurements on differential scanning calorimetry, wide-angle X-ray diffraction, birefringence and tensile test. Due to the mutual interaction between two polymer-melts along the spinline, the processability of both components in PBT/PBAT bicomponent spinning was improved compared with those of corresponding single component spinings. Furthermore, in PBT/PBAT fibers, the structure development of PBT component was found to be greatly enhanced, which led to the improvement in its thermal and mechanical properties; whereas the structure development of PBAT component was significantly suppressed, in which nearly non-oriented structure was observed in both crystalline and amorphous phases.

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1. Introduction

In bicomponent melt-spinning process, two kinds of polymers are brought in contact as separate melt streams just before the spinneret and to form a single filament with designed cross-section arrangement. Bicomponent melt-spinning has been widely applied to produce functional and novel fibers like hollow fibers, electrically conductive fibers, micro/nano fibers and thermal bonding fibers, etc. [1–4]. Furthermore, due to the mutual interaction between two polymer-melts along the spinline, suitable combination of polymers with different inherent properties can also lead to unique structure development of the individual component and thereby the enhanced structure development and/or improved processability can be obtained if compared with single component spinning [5–8,9].

In this work, we attempted to produce sheath-core type bicomponent fibers consisting of poly(butylene terephthalate) (PBT) and a biodegradable copolyester poly(butylene adipate-

co-terephthalate) (PBAT). It is well known that PBT fibers are applied as flexible fibers because of its reversible crystal modification between α and β forms with the application and removal of tensile stress. PBAT fiber also exhibits elastic property with low modulus and high recoverability induced by its hard-soft segments consisting chemical structure [10]. Furthermore, the melting temperature of PBAT is about 100 °C lower than that of PBT [10]. Thus, PBAT (sheath)/PBT (core) bicomponent fibers would be an attractive material for thermal bonding nonwoven fabrics, especially when elastic property is desirable.

In addition, recently there are reports on fabrics woven by sheath-core type bicomponent fibers being composed of PBT and biodegradable polymers like poly(L-lactide), poly(butylene succinate) and poly(butylene succinate-*co*-L-lactide), etc. [11,12]. The main merit of such fabrics is that, with the presence of biodegradable component, denier-decreasing treatment can be conducted in an environmental friendly condition. Accordingly, PBAT/PBT fibers are also expected to be applied in those woven fabrics not only environmental friendly but also stretchable.

In this work, we first attempted to produce the bicomponent fiber PBAT/PBT with PBAT component as sheath and PBT

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component as core. However, in that case, the sheath of the filament remained tacky even down to the winding position, which made the filament difficult to be taken up. The tacky problem is due to the elastic nature and the sluggish crystallization kinetics of PBAT especially when processed with PBT. The latter factor will be explained below. In this work, PBT/PBAT fibers were produced by changing the PBAT component from sheath into core. Preparation of PBAT/PBT fibers will be our future work by applying cooling system along the spinline, i.e. water bath or cooling air, such methods have been successfully applied in the melt spinning of other elastic and tacky filaments [13].

In our previous study, PBAT fibers were unexpectedly found to have well-developed and highly oriented PBT-like crystal structure despite of its ideal randomness and the composition of 1:1, which was attributed to the unusual mixed crystallization behavior of butylene adipate (BA) and butylene terephthalate (BT) units. Interest of this work will be focused on investigating the effect of mutual interaction between PBT and PBAT melts along the spinline on their structure development and properties in PBT/PBAT fibers. This effect is believed to be roughly adaptable to the case of PBAT/PBT fibers in that sheath and core components are interchanged.

2. Experimental

2.1. Bicomponent spinning

Sheath-core type PBT/PBAT bicomponent fibers were produced by extruding the melts of PBT (intrinsic viscosity = 0.88 dL/g) as the sheath and PBAT (melt volume-flow rate = 3–6 ml/10 min) as the core using two different extrusion systems. Each extrusion system consists of an extruder and a gear pump. The co-axially combined polymer melts were extruded through an annular-type spinneret with a single hole (ϕ 1 mm) at a temperature of 260 °C, and the mass flow rate was controlled at 3 g/min for each component. Fiber samples with take-up velocities from 1 to 10 km/min were obtained, where 10 km/min is the maximum velocity of our present winding equipment. In our previous work, the attainable highest velocities for PBT and PBAT single component spinning were 8 and 5 km/min, respectively. Therefore, the processability of both components was improved in PBT/PBAT bicomponent spinning if compared with the corresponding single component spinning.

2.2. Differential scanning calorimetry (DSC)

The thermal property of PBT/PBAT fibers was analyzed by using a differential scanning calorimeter. About 5 mg of fiber sample was encapsulated in aluminium DSC pan. The DSC measurement was carried out from room temperature to 250 °C at a heating rate of 10 °C/min.

2.3. Wide-angle X-ray diffraction (WAXD)

Wide-angle X-ray diffraction (WAXD) patterns of fiber samples were recorded by using an X-ray generator (Rigaku

Co., Japan) with a monochromatized Cu K α radiation and a CCD camera. The generator was operated at 40 kV and 300 mA. The camera length was 45.5 mm, and the exposure time was 25 s.

In addition to the conventional WAXD measurement, in situ WAXD measurement during the heating process was also performed. Fiber samples were set in a heating chamber with a temperature controller. The temperature was increased from room temperature to 150 °C with a heating rate of 1 °C/min. The WAXD patterns at room temperature and 150 °C were recorded.

2.4. Birefringence

Birefringence of the sheath and core components in the bicomponent fiber was measured using an interference microscope (Carl Zeiss Jena) equipped with a polarizing filter based on a method described elsewhere [6]. The refractive indices of the sheath and core parts n_{out} and n_{in} can be obtained using the Eqs. (1) and (2):

$$\frac{a_{out}}{A} \frac{\lambda}{2} = (n_{out} - N)(R_{out}^2 - R_{in}^2)^{1/2} \quad (1)$$

$$\frac{a_{in}}{A} \frac{\lambda}{2} = (n_{out} - N)(R_{out} - R_{in}) + (n_{in} - N)R_{in} \quad (2)$$

where a_{out} and a_{in} are the fringe shifts measured at the interface between the sheath and core, and at the center of the fiber, respectively, R_{out} and R_{in} are the inner and outer radii, N is the refractive index of immersion liquid, and λ is the wave length of incident light. The birefringence of the sheath and core was represented as the difference between the corresponding refractive indices in parallel and perpendicular directions to the fiber axis.

2.5. Tensile test

The stress–strain curves of the fiber samples were obtained using a tensile test machine (Toyosokki, UTM-4L). The gauge length was 20 mm and the tensile speed was 20 mm/min. A representative stress–strain curve was determined by at least 10 trials for each kind of fiber. Initial tensile modulus, tensile strength and elongation at break were obtained analyzing the stress–strain curves.

3. Results and discussion

3.1. Melting temperature (T_m)

DSC thermograms of PBT/PBAT fibers prepared at 1 km/min and 10 km/min were plotted in Fig. 1. The endothermic melting peaks at ca. 125 and ca. 230 °C are corresponding to the melting of PBAT and PBT components, respectively. It is notable that the melting peak of PBAT is smaller and broader compared with that of PBT. Furthermore, with increasing take-up velocity there is no distinct change in PBAT melting peaks, whereas the melting peak of PBT

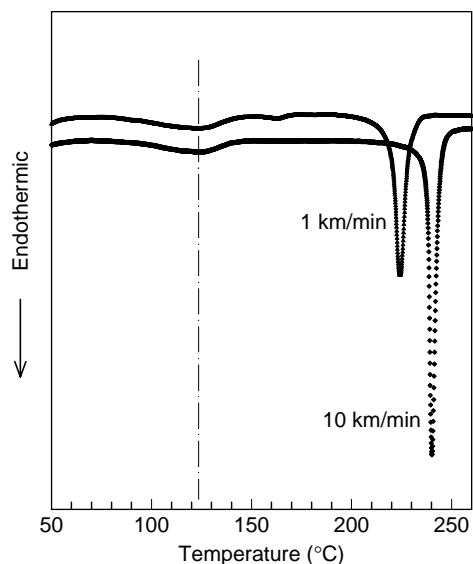


Fig. 1. DSC thermograms of PBT/PBAT fibers prepared at take-up velocities of 1 and 10 km/min.

became sharper and shifted from 223 to 240 °C, indicating that the highly ordered crystal structure of PBT was developed by ultra-high-speed bicomponent spinning with PBAT.

3.2. WAXD analysis

The crystal structure of PBT/PBAT fibers was further investigated by WAXD measurement. WAXD patterns of as-spun fibers prepared from 1 to 10 km/min are listed in Fig. 2. Diffraction arches developed into sharp diffraction spots with increasing take-up velocity; and a noteworthy observation in Fig. 2 is that there is an overlapping of diffraction rings and sharp diffraction spots. Development of sharp diffraction spots indicates the progress of orientation-induced crystallization, which leads to formation of more perfect crystallites in higher speed fibers. This agrees with the result of remarkably increased T_m revealed by DSC. Overlapping of diffraction spots and rings indicates the coexistence of both highly

oriented and non-oriented crystal structure in PBT/PBAT fibers.

Incidentally, our previous study revealed that PBAT exhibits quite similar WAXD pattern to that of PBT [10]. Hence, it is difficult to assign these two kinds of crystal structure to each component if just based on diffraction patterns. To identify these two diffraction patterns, in situ WAXD measurement was conducted at elevated temperatures. The WAXD pattern of PBT/PBAT fiber prepared at 10 km/min was recorded at 150 °C, a temperature higher than T_m of PBAT while much lower than that of PBT, as shown in Fig. 3. Based on the fact that diffraction rings totally disappeared at 150 °C in Fig. 3, the diffraction rings are undoubtedly assigned to be induced by PBAT component.

To compare the crystal structure development of the individual component in PBT/PBAT bicomponent spinning with that of the corresponding single component spinning, WAXD patterns of the as-spun fibers prepared at 3 km/min are shown in Fig. 4. Sharper diffraction spots of PBT in PBT/PBAT fibers compared with the diffraction arches of PBT in single component fibers suggest that the development of highly oriented PBT crystals was promoted in bicomponent spinning with PBAT. On the other hand, the orientation development of PBAT crystals was significantly suppressed in bicomponent spinning with PBT, which was revealed by diffraction rings of PBAT component in bicomponent spinning instead of sharp diffraction spots in single component spinning. The enhanced and suppressed crystalline orientation in PBT/PBAT fibers will be further discussed through the overall molecular orientation in terms of birefringence.

Further evaluation on the crystal structure development was conducted by analyzing the degree of crystallinity (X_c) of each component in PBT/PBAT fibers using Eq. (3).

$$X_c = \frac{\int_{2\theta_1}^{2\theta_2} \cos \theta \int_0^{\pi/2} I_c(\delta, \theta) \sin \delta \, d\delta \, d(2\theta)}{\int_{2\theta_1}^{2\theta_2} \cos \theta \int_0^{\pi/2} I(\delta, \theta) \sin \delta \, d\delta \, d(2\theta)} \quad (3)$$

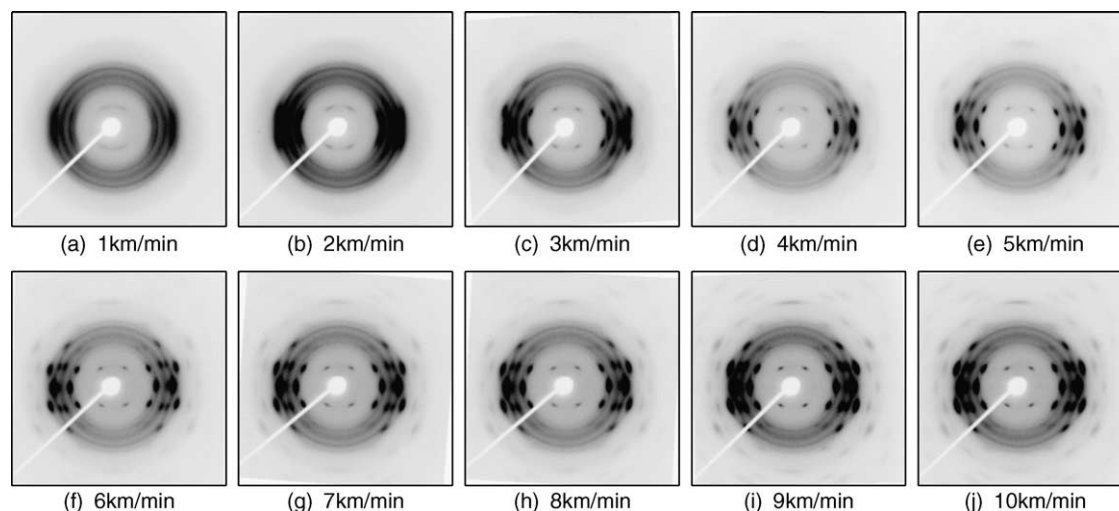


Fig. 2. WAXD patterns of PBT/PBAT bicomponent fibers. The take-up velocity is as indicated.

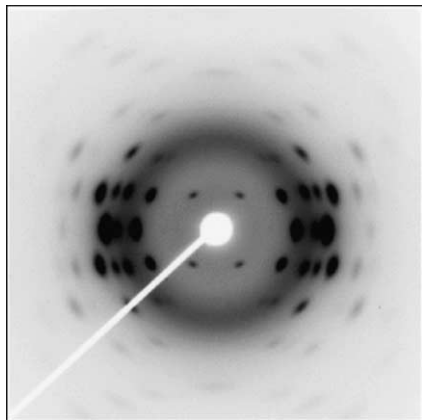


Fig. 3. WAXD pattern of PBT/PBAT fibers recorded at 150 °C. The take-up velocity is 10 km/min.

where 2θ is diffraction angle, in this work, $2\theta_1 = 5^\circ$, and $2\theta_2 = 40^\circ$; δ is the azimuthal angle from the meridian in WAXD pattern recorded by flat CCD camera.

The estimated crystallinity of PBT/PBAT fibers (10 km/min) at room temperature and at 150 °C is 42 and 29%, respectively. Neglecting the difference in numbers of electrons per unit mass of PBT and PBAT, and considering the composition of 1:1 in PBT/PBAT fibers, the crystallinity of PBT and PBAT components were estimated to be about 58 and 26%, respectively. For semi-crystalline polyester PBT, the high crystallinity of up to 58% is a strong evidence again of its enhanced crystal structure development, which leads to a much higher T_m (ca. 240 °C) compared with the T_m (ca. 220 °C) in the literature and also the T_m of low speed fibers in this work. It is also notable that the crystallinity of PBAT component is up to 26% although its molecular orientation was significantly suppressed in bicomponent spinning with PBT. This result might be attributed to its low T_g (−30 °C) and the unusual mixed-crystallization behavior of its comonomers [10]. In other words, it can be considered that the crystallization of PBAT component proceeded after the spinning process.

3.3. Birefringence

The structure development of the individual component in PBT/PBAT was also evaluated by overall molecular

orientation represented by birefringence. The birefringence of PBT and PBAT component in bicomponent fibers as a function of take-up velocity is plotted in Fig. 5, and the birefringence of PBT and PBAT single-component fibers was incorporated. In Fig. 5, birefringence shows a tendency of increase with increasing take-up velocity. This is because of the higher elongational stress applied to the spinline at a higher take-up velocity, which induces higher molecular orientation.

In Fig. 5, the birefringence of PBT component in PBT/PBAT fibers shows a higher value than that of the corresponding PBT single component fibers. Especially, significant difference can be observed in the low take-up velocity range of 1–4 km/min, indicating the structure development of PBT component is greatly promoted there. On the other hand, compared with the fairly high birefringence of PBAT single component fibers, the birefringence of PBAT component in PBT/PBAT fibers is close to zero regardless of take-up velocity. It is unquestionable that the structure development of PBAT component was greatly suppressed in the bicomponent spinning with PBT. The close to zero birefringence value suggests that the amorphous phase of PBAT component is also close to random, same as in the case of its crystal structure revealed by diffraction rings in WAXD measurement.

The remarkable difference in structure development between the individual component in A/B bicomponent spinning, and in A (or B) single-component spinning has been also reported in bicomponent spinning of PET/PP, PET/LCP, and PET/PS, etc. The mechanism has been clarified using numerical simulation on the mutual interaction between two polymer melts during bicomponent spinning [5,6]. If two polymers (A and B) have a difference in activation energy of elongational viscosity or solidification temperature or initial elongational viscosity, then one polymer (assuming A) will undergo concentrated thinning behavior in up-stream (near to spinneret) than that of the other (B) in their respective single-component spinning. If we carry out A/B bicomponent spinning, the thinning curve of the spinning line should be in-between the thinning curves of their single-component spinning. Therefore compared with single-component spinning, A will experience higher stress near to solidification point in spinline due to larger strain rate, and thereby enhanced structure development, while B will be just the opposite.

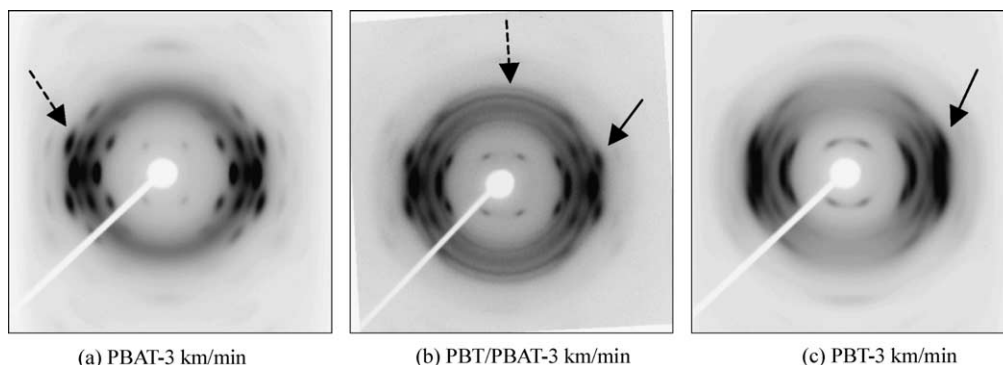


Fig. 4. WAXD patterns of PBT, PBAT single component fibers and PBT/PBAT bicomponent fibers. The take-up velocity is 3 km/min.

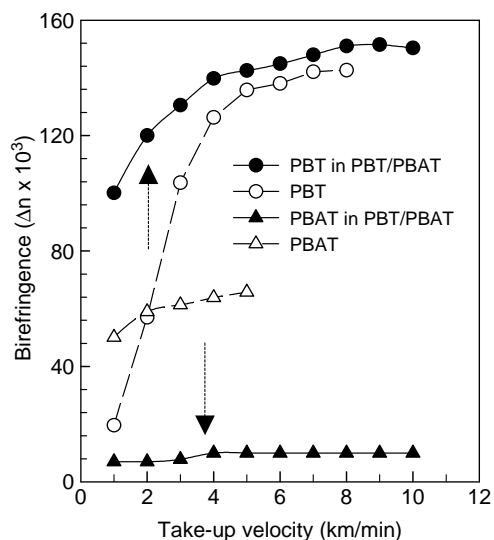


Fig. 5. Comparison of the birefringence of PBT and PBAT components in bicomponent fibers with that of their respective single component fibers. The take-up velocities are as indicated.

Accordingly, in the case of PBT/PBAT fibers, PBT component underwent solidification at the point where PBAT was still in melt state, and thereby PBAT underwent orientation relaxation and remained in close to random state. This is the reason that PBAT remained tacky along the spinline and made the filament difficult to be taken up when it was arranged in sheath part. Non-oriented crystal structure of PBAT is speculated to be formed off spinline as its glass transition temperature (ca. $-30\text{ }^{\circ}\text{C}$) is much lower than room temperature.

3.4. Mechanical properties

Fig. 6 shows the stress–strain (*s–s*) curves of PBT/PBAT bicomponent fibers and the corresponding single-component

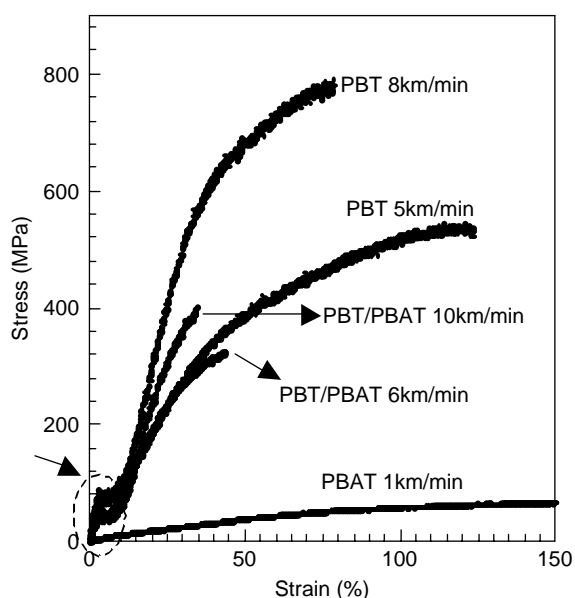


Fig. 6. Stress–strain curves of PBT/PBAT bicomponent fibers, PBT fibers, and PBAT fibers. Take-up velocity of each kind of fiber is as indicated.

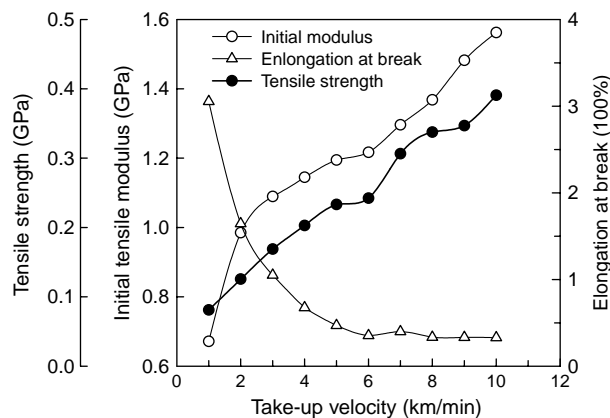


Fig. 7. Mechanical properties of PBT/PBAT bicomponent fibers as a function of take-up velocity.

fibers. Take-up velocities are as indicated. The unique plateau in stress–strain curves of PBT can be observed in the strain range of 4–15%, and at a stress of ca. 78 MPa regardless of take-up velocity. This plateau is well-known to be the region where crystal form transition (α to β) occurs [14]. Similar plateau can be also observed in PBT/PBAT *s–s* curves; however it is located at a stress of ca. 40 MPa. Since the crystal form transition in PBT only occurs at a critical stress of ca. 78 MPa at room temperature [21], considering the component ratio (1:1) in PBT/PBAT, it can be speculated that the stress applied to PBT component might be close to twice of the apparent stress value, indicating only PBT component bears the load in that strain region. This speculation is strongly supported by the significantly low modulus of PBAT single component fibers as revealed by its rubbery-like *s–s* curve in Fig. 6. Compared with the PBAT single component fibers with fairly high molecular orientation, the nearly non-oriented PBAT component in bicomponent fibers should have even lower modulus. Therefore the response of PBAT component in the low strain region is almost negligible when a load is applied to PBT/PBAT fibers.

The initial tensile modulus, tensile strength and elongation at break of PBT/PBAT fibers are plotted as a function of take-up velocity in Fig. 7. It suggests that the development of mechanical properties is enhanced by increasing take-up velocity. The comparison of mechanical properties of PBT/PBAT fibers with that of PBT fibers is given in Fig. 8. Due to negligible response from PBAT component in the initial deformation region as explained above, the initial modulus of PBT/PBAT fibers keeps being about half of that of PBT fibers regardless of take-up velocity. This tendency also appears in tensile strength when take-up velocity is beyond 5 km/min, whereas these two types of fibers show a comparable tensile strength in the low take-up velocity range. Considering the component ratio of PBT in PBT/PBAT fibers, in the low velocity region, tensile strength of PBT component is nearly two times enhanced when bicomponent spun with PBAT. This enhancement is attributed to the significantly enhanced molecular orientation of PBT component as revealed by birefringence in Fig. 5. The results here suggest that the

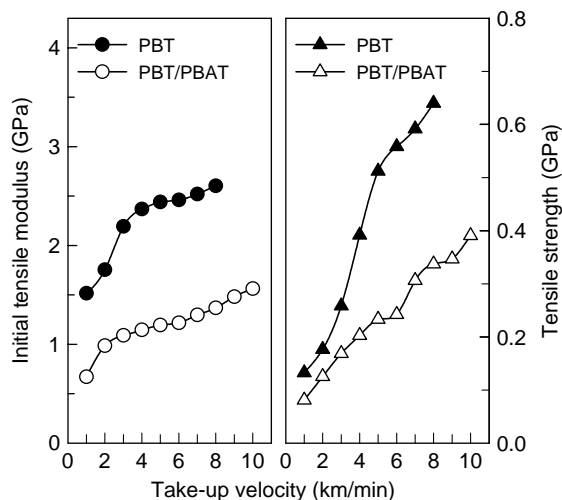


Fig. 8. Comparison of initial tensile modulus and tensile strength of PBT/PBAT fibers with those of PBT fibers.

dependency of initial modulus and tensile strength on molecular orientation is different. In this study, tensile strength appears to be more directly influenced by molecular orientation, though in general modulus is believed to be more directly influenced by molecular orientation.

4. Conclusions

Ultra-high-speed bicomponent spinning of PBT (sheath) and biodegradable PBAT (core) was accomplished with the take-up velocity up to 10 km/min. The spinnability of PBT/PBAT fibers is improved compared with the single component spinings of PBT and PBAT.

The structure development of the individual component and the properties of PBT/PBAT fibers were investigated. Compared with respective single component fibers, in

PBT/PBAT fibers, the molecular orientation and crystalline structure development of PBT component was greatly enhanced, whereas the molecular orientation of PBAT component was greatly suppressed. The enhanced structure of PBT component leads to the improvement in both thermal property and tensile strength, suggesting that it is an effective way to promote the structure development of PBT through the bicomponent spinning with PBAT. On the other hand, PBAT component was found to have nearly non-oriented structure in both crystalline and amorphous phases, which is a desirable feature for the following denier-decreasing treatment in fabric applications.

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