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Preparation and Characterization of Nylon 6-Clay Hybrid/Neat Nylon 6 Bicomponent Nanocomposite Fibers

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Abstract**—**Nylon 6-clay hybrid/neat nylon 6, sheath/core bicomponent nanocomposite fibers containing 4 wt% of clay in sheath section were melt spun at different take-up speeds. Their orientation and crystalline structure were compared to those of neat nylon 6 fibers. Birefringence measurements showed that the orientation development in sheath and core parts of bicomponent fibers was different. Crystallinity results showed that clay did not act as a nucleating agent for bicomponent fibers. The neat nylon 6 fiber had a smooth surface while striped pattern was appeared on the surface of bicomponent fiber containing clay due to thermal shrinkage of the core part.

Keywords**—**Bicomponent fiber, High speed melt spinning, Nylon 6-clay hybrid, Nylon 6.

I. INTRODUCTION

IN recent years, polymer based composite hybrid materials have attracted significant interests and numerous studies have been devoted to this subject. Modification of polymer by adding nanofiller becomes a practical strategy to improve the parent polymer material properties. Among the nanofillers, nano layered silicate (clay) has been received much attention and wide range of thermoplastics have been reinforced with this material [1]-[5].

Nylon 6 is a semicrystalline polymer possessing outstanding physical and mechanical properties. So, many researchers have studied the influence of nanoclay additive on the processing, structure and morphology of nylon 6-clay hybrid. Nevertheless, studies on the nylon 6-clay hybrid fiber are limited. Giza et al. compared the structures of neat nylon 6 and nylon 6-clay hybrid fibers prepared at different take-up speeds and draw ratios [6], [7]. Ibanes et al. described the microstructure changes and deformation mechanisms in spun and drawn nylon 6 fiber containing clay [8], [9]. Recently, Joshi et al. prepared nylon 6-clay nanocomposite filaments and their cord with two different clays [10]. The drawing and ultimate tenacity properties of the nylon 6/nylon 6-clay (NYC) composite fiber prepared at varying NYC contents and drawing temperatures was systematically investigated by Yeh et al. [11].

As per our knowledge, no literature is available to the effect of clay in bicomponent nylon 6-clay hybrid/nylon 6 fibers. In this work, we have fabricated nylon 6-clay hybrid/nylon 6 bicomponent fibers via melt spinning at different take-up speeds and the structural changes of neat nylon 6 and bicomponent fiber were investigated.

II. EXPERIMENTAL

A. Materials

The materials used in this study, neat nylon 6 and nylon 6-clay hybrid masterbatch containing 4wt% clay, were provided by Nanopolymer Composites Corporation, Taiwan. The nylon 6-clay hybrid masterbatch under commercial name of NE2640 were produced via in-situ polymerization with a montmorillonite modified by methyl, tallow, bis-2-hydroxyethyl quaternary ammonium chloride Cloisite 30B from Southern Clay Products, Inc. The nylon 6 pellets with a commercial name of A2500 had a relative viscosity of 2.5.

B. Melt Spinning of Filaments

The polymer chips were dried in a vacuum oven for at least 12h at 110°C prior to spinning. Melt spinning was carried out using a spinning apparatus (Musashino Kikai Co., Ltd., Japan). Filaments were extruded from the spinneret through a single-hole nozzle with a diameter of 1mm and were taken up by the high-speed winder located 330cm below spinneret. No spin finish and external quench cabinet was used. The take-up velocity was changed from 25m/min to 5000m/min. The bicomponent fiber was produced in sheath-core form in which the sheath and core parts were nylon 6-clay hybrid (NCH) and neat nylon 6, respectively. The weight fraction of both parts was the same (50/50). Hereafter, this fiber is named BiCo.

C. Measurements

The birefringence of fibers was obtained using an interference microscope (Carl Zeiss Jena, Germany). The average of the measurements for ten individual fibers is reported.

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Differential scanning calorimetry (DSC) was carried out by using a Q100 (TA Instruments, USA) device with a heating rate of 10 °C/min in the range of 0-250 °C under nitrogen atmosphere. The crystallinity of sample was calculated according to the following formula:

$$X_C(\%) = \frac{\Delta H_f}{\Delta H_f^{\circ}} \times 100 \tag{1}$$

where X_C is crystallinity percentage, ΔH_f refers to the measured melting enthalpy and ΔH_f° is the enthalpy of fusion of completely crystalline nylon 6 (ΔH_f°=213J/g) [12].

The morphology of the fiber surface was studied using a scanning electron microscopy – SEM (SM-200, Topcon, Singapore) operated at 15kV.

III. RESULTS AND DISCUSSION

A. Birefringence

The dependence of fiber birefringence on take-up speed is plotted in Fig. 1. As expected, birefringence of neat nylon 6 fiber increased monotonically with take-up speed up to 3000m/min, then reached to a saturation point. The development of molecular orientation in fibers leads to an increase in birefringence. Similar behavior was observed in the sheath part of BiCo fibers, but the birefringence begins to level off at higher take-up speed (4000m/min). As seen later, these results are in agreement with the crystallinity data obtained by DSC (Table I). Moreover, at take-up speed of 500m/min, the birefringence of sheath part of BiCo fiber was higher than that of neat nylon 6 and above 1000m/min, the birefringence of neat nylon 6 fiber exceeded that of sheath part of BiCo fiber. The significant increase in both samples was observed when take-up speed increased from 1000m/min to 2000m/min. On the other hand, almost zero birefringence of core part of BiCo fibers shows that no orientation occurred in this part. By considering orientation-induced crystallization in melt spinning, it can be suggested that the core part remains in the amorphous state.

Negligibly small birefringence in nylon 6 in BiCo suggests that the solidification/crystallization of nylon 6-clay occurs firstly in the spin line, before the crystallization of neat nylon 6. Then there can be even an orientation relaxation in neat nylon 6 during the cooling of the spin line from the crystallization temperature of nylon 6-clay to Tg of nylon 6. One can say that higher viscosity in sheath part compared to core part could be regarded as the reason for appearing such a behavior in birefringence of these parts. In this case, however, it is not easy to explain why sheath part of BiCo has lower birefringence than the neat nylon 6. If viscosity of nylon 6-clay is higher than that of neat nylon 6, and if both polymers have similar stress-optical coefficient, birefringence of nylon 6-clay in BiCo fiber should be higher than that of neat nylon 6 of single component fiber.

Accordingly, in the following discussion we need to discuss the mechanism of structure formation in BiCo fiber without mentioning that nylon 6-clay has higher viscosity than neat nylon 6. On the other hand, it should be noted that nylon 6-clay tends to solidify at higher temperature than neat nylon 6. This behavior can be observed through the on-line measurement of the thinning behavior in the spin line as reported in previous research (see Fig. 7 in [6])[6]. Solidification point tends to shift to upstream with the increase of take-up velocity, while, solidification point of nylon 6-clay is always closer to the spinneret than neat nylon 6 at a certain take-up velocity [6]. This basically suggests that the variation of viscosity with temperature is more significant in nylon 6-clay. In other words, viscosity of nylon 6-clay has higher activation energy than that of neat nylon 6. Also the possibility of crystallization of nylon 6-clay under elongational flow appears to be higher than the neat nylon 6.

B. Thermal Properties

Fig. 2 shows the DSC curves of neat nylon 6 and BiCo fibers at different take-up speeds. The results obtained from DSC curves are summarized in Table I. As seen in Fig. 2, if it is assumed that the higher and lower melting peaks are related to α and γ crystal forms, respectively, the α-crystal form predominates in the BiCo fibers at all take-up speeds. For neat nylon 6, similar behavior was occurred up to take-up speed of 3000 m/min and afterward, an increase in the amount of γ-crystal form was observed.

It seems that there are γ-crystals with different perfection, size, and stability in nylon 6 in which above take-up speed of 3000 m/min, γ-crystals with higher stability were formed in the fibers. In fibers spun at lower take-up speed, the less grown, smaller crystallites of the γ-crystal form were converted to α-crystalline form with higher stability during DSC heating. This means that the melting peak temperature does not necessarily represents the original structure in the fiber.

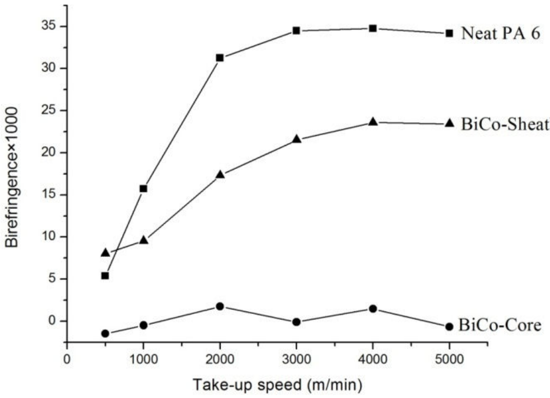


Fig. 1 Birefringence values for neat nylon 6 and BiCo fibers at different take-up speeds

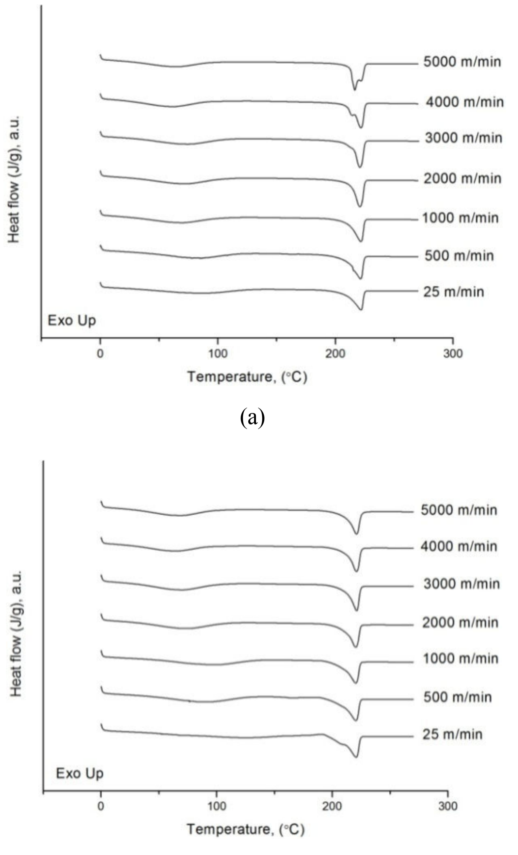
In BiCo fiber, the γ-crystals with lower stability formed because of clay particles which then can easily converted to α-crystals during heating in DSC. Crystallinity of nanocomposite sample was found to be lower than neat nylon

6 at respective take-up speeds, as revealed from DSC analysis (Table I). This suggests that less ordered polymer packing was obtained for nylon 6-clay composite with sheath-core structure. Moreover, there is a possibility that sheath part of the BiCo fiber has higher crystallinity than neat Nylon 6 because crystallinity of the core part is low.

TABLE I
THERMAL PROPERTIES OF MELT-SPUN FIBERS BASED ON DSC RESULTS

Sample	Take-up velocity (m/min)	Heating cycle		
		T_{m1} (°C)	T_{m2} (°C)	Crystallinity (%)
PA 6	25	------	221.8	34.0
	500	------	221.3	35.9
	1000	------	221.6	36.6
	2000	------	220.6	37.6
	3000	212.6	220.6	38.1
	4000	214.1	221.5	38.4
	5000	216.3	221.9	38.5
BiCo	25	------	220.5	29.9
	500	------	220.3	32.5
	1000	------	220.1	31.4
	2000	------	220.2	32.3
	3000	------	221.0	33.0
	4000	------	220.7	33.4
	5000	------	220.9	34.0

T_{m1}: Lower melting temperature; T_{m2}: Higher melting temperature



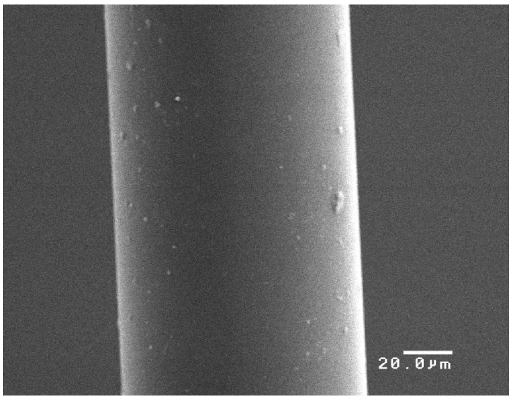
(a)

(b)

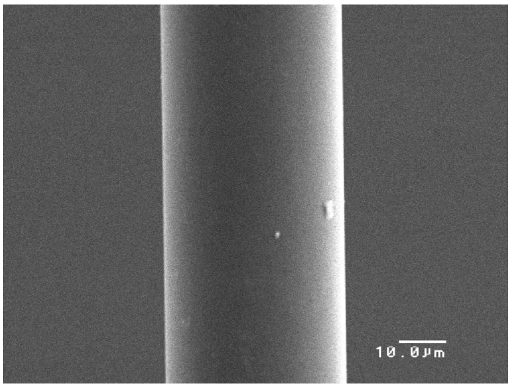
Fig. 2 DSC thermograms of (a) neat nylon 6 and (b) BiCo fibers

C. Morphology

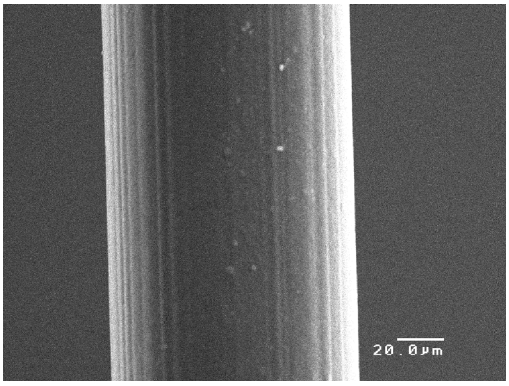
Fig. 3 shows SEM micrographs in the direction of axes of neat nylon 6 and BiCo nanocomposite fibers. A smooth surface is observed in the SEM images of the neat nylon 6 fiber while the stripe is seen on the surface of BiCo fibers. The stripe may be related to the thermal shrinkage of the core part. As described in Birefringence section, solidification (crystallization) of sheath part occurs at a temperature much higher than the Tg of nylon 6. Crystallized part supposed to have much lower thermal expansion coefficient than the polymer melt. Then the volume reduction of the core part with cooling is much more significant than that in the sheath, which leads to the development of stripe. These patterns are more pronounced in fiber spun at higher take-up speed.



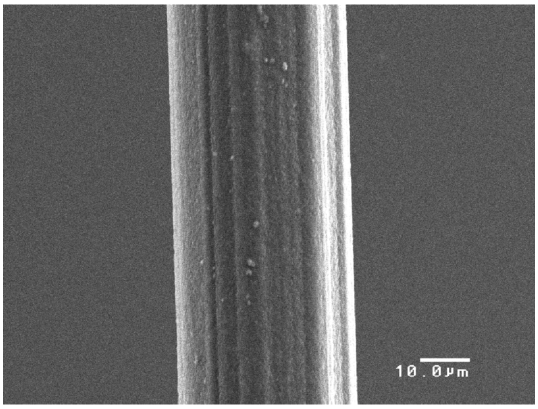
PA6-500 m/min



PA6-5000 m/min



BiCo- 500 m/min



BiCo- 5000 m/min

Fie 3 SEM micrographs along the fiber axis

IV. CONCLUSION

The results of current study illustrated that the sheath part had much higher orientation compared to core part in the BiCo fibers. The DSC curves suggested that there were γ-crystalline forms with different stabilities in BiCo fibers. The neat nylon 6 fibers showed higher crystallinity in the whole take-up speed range, indicating that the presence of clay reduced the crystallizability of polymer chains in BiCo fibers. The difference in crystallization rate of sheath and core parts in BiCo fibers resulted in the core part remained in the amorphous state. The striped pattern on surface of BiCo fibers was developed and had more obvious at higher take-up speed.

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