



# Dual effects of compatibilizer on the formation of oriented ribbon-like dispersed phase domains in polystyrene/polyamide 6 blends



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## HIGHLIGHTS

- Polymer blend with highly oriented ribbon structure was prepared by tape extrusion.
- Compatibilizer shows dual effects on the formation of oriented ribbon structure.
- Formation mechanism of ribbon in the presence of compatibilizer was put forward.

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## ABSTRACT

Polymer blends with oriented ribbon-like dispersed phase were prepared via tape extrusion. Two specially designed compatibilizers, one being non-reactive and another reactive, were used to examine their influence on the formation of oriented ribbon-like dispersed phase in polystyrene (PS)/polyamide 6 (PA6) blend. Results show that both compatibilizers can decrease interfacial tension and produce vinculum effect to strengthen the deformation of dispersed phase. Moreover, the stretching force of tape extrusion pushes the compatibilizer molecules towards the tips of dispersed phase causing a non-uniform distribution along the surface of dispersed phase. At a low loading concentration of compatibilizer, the deformed dispersed phase particles can connect each other from their middle part and merge into long and even endless ribbons. However, when the loading of compatibilizer exceeds a certain level, the formation of ribbon-like dispersed phase will be impeded because all surfaces of dispersed phase are completely covered by the compatibilizer so that the coalescence of dispersed phase cannot occur.

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## 1. Introduction

Blending has been a very attractive and inexpensive approach to modification of polymer materials (Cartier and Hu, 1999; Su et al., 2011). Final properties of those polymer blends strongly depend on the morphology and dimension of the dispersed phase (Cheng et al., 2013; Ramirez-Arreola et al., 2008). Recently, polymer blends with a ribbon-like dispersed phase have shown potential for significant enhancement of mechanical strength (Li et al., 2014; Ma et al., 1990), barrier to gases (Xie et al., 2015; Zhou et al., 2016), electrical conductivity (Gao et al., 2014; Yu et al., 2013) and optical performance (Tangirala et al., 2004). In our previous paper, we reported a structural color effect occurring in ribbon-matrix polymer blend of polystyrene (PS) and polypropylene (PP) (Wang et al., 2014b).

The deformable nature of dispersed phase during melt blending of polymers makes it possible to create various morphologies such as ellipsoidal, fibrillar, and ribbon-like structure in polymer blend. Currently, ultrasonic extrusion (Gunes and Isayev, 2011), co-extrusion (Wang et al., 2014a), in-situ fibrillation (Jiang et al., 2009; Shen et al., 2011) have been employed to control the morphology of polymer blend. Among those methods, the way to deform dispersed polymer particles by drawing the extrudates along extrusion direction has attracted increasing attention owing to its easy operation and high efficiency. In the drawing process, the dispersed polymer particles are elongated and then connect to form various morphologies, depending on the initial size of dispersed phase (Wang et al., 2007), viscosities of the matrix ( $\eta_m$ ) and the dispersed phase ( $\eta_d$ ) (Delaby et al., 1994; Wanno et al., 2000), draw ratio (Liu et al., 2014; Jayanarayanan et al., 2009) and composition (Wang et al., 2015). Among those factors, the viscosity ratio ( $\lambda = \eta_d/\eta_m$ ) is one of the most important parameter governing the resultant morphology of polymer blend. Both experimental and numerical results have indicated that lowering the viscosity ratio

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facilitates the drawing deformation of spherical dispersed phase and formation of smaller and more uniform elongation shapes (Bazhlekov et al., 2006; Yi et al. 2010; Wang et al., 2015).

Besides the viscosity ratio, the capillary number ( $Ca = R\eta_m\dot{\gamma}/\sigma$ , where  $R$  is the initial radius of the dispersed phase,  $\dot{\gamma}$  is the shear rate, and  $\sigma$  is the interfacial tension) is another significant dimensionless parameter controlling the morphology of polymer blend. It is well known that an increase of  $Ca$  can promote the deformation of dispersed phase particles. Thus, it seems that increasing drawing ratio and lowering interfacial tension are beneficial to produce various morphologies. As expected, much research work has confirmed that high drawing ratio is conducive to the formation of long and even endless fibril or ribbon within the polymer blend (Dai et al., 2008; Jayanarayanan et al., 2009; Li et al., 2003; Wang et al., 2007).

A compatibilizer of type block or graft copolymer pre-made or generated in-situ whose segments are chemically identical to or have affinity with the polymer components is most effective additive to reduce the interfacial tension of immiscible polymer blend (Bahrami et al., 2014; Li and Hu, 2001; Wang et al., 2011; Zhang et al., 2012a). Nevertheless, Jayanarayanan (Jayanarayanan et al., 2010) reported that the presence of 5% polyethylene grafted with maleic anhydride (PE-g-MA) in low density polyethylene/poly(ethylene terephthalate) (PET) (85/15 by mass) blend reduced the aspect ratio and continuity of formed PET fiber by the way of drawing. They thought that since the compatibilizer was located in the surface of the dispersed phase and restrains the coalescence of the dispersed phase, long microfibrillar or ribbon-like structures cannot be formed. Numerical simulations (Pawar and Stebe, 1996), however, showed that an extension flow could push the compatibilizers towards the ends of dispersed phase particles, which causes a gradient in the concentration of the compatibilizer along surfaces of dispersed phase particles, i.e., a high compatibilizer concentration at the ends and a low one or even none at the middle part. This inhomogeneous distribution of the compatibilizer may not only promote the deformation of dispersed polymer particles at the ends and but also offer an opportunity of coalescence at the middle part, which should result in a much more complicated picture for the formation of highly-oriented fibrils or ribbons via a combination of deformation and coalescence. Therefore, it is necessary to understand the role of compatibilizer in a polymer blend during drawing.

In this work, two specially designed compatibilizers, one being non-reactive and another reactive, were used to investigate their effect on the formation of highly-oriented ribbon in polymer blend via tape extrusion. The results showed that compatibilizer at a low concentration could promote the deformation of spherical dispersed phase into the ribbon-like morphology. Moreover, the deformation degree of dispersed phase particle is related to the compatibilizing efficiency of the compatibilizer.

## 2. Experimental

### 2.1. Materials

Polystyrene (PS) and Polyamide 6 (PA6) were used as the matrix and the dispersed phase, respectively. Table 1 lists their selected characteristics. Two types of compatibilizers were synthesized in

our lab, and they were used to decrease the interfacial tension between PS and PA6. One was a random copolymer of styrene (St) and 3-isopropenyl- $\alpha,\alpha$ -dimethylbenzene isocyanate (TMI) denoted as P(St-co-TMI) which bring reactive groups; and the other was a graft copolymer of PS and PA6 (PS-g-PA6), which brings no reactive groups. PS-g-PA6 was synthesized by the anionic polymerization of  $\epsilon$ -caprolactam (CL) onto P(St-co-TMI). The molecular weight and TMI content of the reactive compatibilizer P(St-co-TMI) were 40.7 kg/mol and 3.4 wt%, respectively.

Fig. 1 shows the molecular architectures of two PS-g-PA6 graft copolymers as the non-reactive compatibilizers. They had similar PS backbone and PS/PA6 ratio but differed in the PA6 graft length and/or in number of grafts per PS backbone. More specifically, the PA6 graft length of PS-g-PA6-b was only half of PS-g-PA6-a. Details on the preparation of those interfacial compatibilizers can be found elsewhere (Hu et al., 2002; Hu et al., 2005; Zhang et al., 2006; Zhang et al., 2012b).

### 2.2. Preparation of polymer blend with oriented ribbon-like dispersed phase

Prior to tape extrusion, PS, PA6, and PS-g-PA6 or P(St-co-TMI) pellets dried at 80 °C in a vacuum oven for 24 h were compounded at 230 °C in a twin-screw extruder with a diameter of 25 mm and a length-to-diameter ratio of 60. The mass ratio of PS and PA6 was fixed at 80/20. Feeding rate and screw speed were set at 6.9 kg/h and 150 rpm, respectively. After going through an aperture die, the extrudate was cooled and cut into chips.

After drying at 80 °C for 12 h in a vacuum oven, those obtained chips were gravimetrically fed into a single-screw extruder (Brabender Measurement and Control System) with a diameter of 25 mm and a length-to-diameter ratio of 19 for the tape extrusion. The barrel temperature and screw speed were set at 230 °C and 100 rpm, respectively. The extrudate from the outlet of slit die was drawn, and then was pressed by two water-cooled steel rollers. The drawing speeds were controlled by two running rollers coupled to an electric motor with different variables. Finally, the extruded blends were collected after being cooled to room temperature.

### 2.3. Quiescent annealing process

The obtained PS/PA6 blends were fixed between two glass slides, and then were annealed in an oven preheated to 230 °C. After various annealing time (from 2.5 to 10 min), those samples were taken out and then quenched immediately by liquid nitrogen to freeze their morphologies.

### 2.4. Characterizations

Thermo Scientific HAAKE MARS rotational rheometer (RS6000) was used to characterize the rheological behavior of PS and PA6. Prior to the measurement, the samples were pressed into disks of 20 mm diameter and 1 mm thickness. The test was performed using a dynamic mode in a frequency range from 100 to 0.1 Hz at 230 °C.

Scan electron microscopy (SEM, Spura 55Vp) was used to observe the morphologies of the obtained blends. Before the SEM observations, the surfaces of samples fractured in liquid nitrogen were immersed in formic acid at room temperature for 12 h to etch the dispersed PA6 phase, and then they were dried in a vacuum oven at 80 °C for 12 h. After sputtering the gold, the morphologies of samples without and with etching dispersed PA6 phase were obtained by SEM at an acceleration voltage of 5.0 kV. A semiautomatic image analysis method was used to determine the diameter of the dispersed phase domain. The volume average particle

**Table 1**  
Selected information of PS and PA6 used in this work.

Material	Supplier	$M_n$ (kg/mol)	$M_w$ (kg/mol)
PS	Yangzi-BASF Styrenics Co., Nanjing, China	101.3	228.8
PA6	UBE Industries Ltd	19.4	49.4

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