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Study on flow-induced crystallization behaviour of s-PVA/SWNTs dispersion

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Abstract. In this paper, crystallization behaviour of syndiotactic poly (vinyl alcohol) (s-PVA)/single-walled carbon nanotubes (SWNTs) under shear flow was studied. The flow-induced crystallization was carried out in test tubes by stirring the uniform s-PVA/SWNTs composite dispersions at high stirring speed, during which the crystalline precipitates were gradually formed as shear time goes on. The effect of flow resistance of tube walls ascribed to the tube types and the amount of SWCNTs on the crystallization, and the thermal properties and crystallinity of the precipitates were investigated. Results showed that plastic tube is easier to cause precipitates than glass tube; the amount of SWNTs has a great effect on the crystallization behaviour.

1. Introduction

It is well known that materials are inevitably exposed to various external flow fields during actual manufacturing processes (such as spinning, extrusion, coating, etc.) [1], the crystallization behaviour of polymer will be greatly influenced by the shear flow [2, 3]. Since polyethylene crystals working with its stirred dilute solution was first observed at 1965 [4], flow-induced polymer crystallization has attracted wide attention of researchers, and the crystallization of syndiotactic poly (vinyl alcohol) (s-PVA) under flow were obtained extensive investigation [5, 6]. It was found that the crystallization behaviour of s-PVA is largely affected by temperature, concentration and flow conditions, etc.

Due to the nucleation and template effect of CNTs, the crystallization behaviour of polymer under flow in presence of CNTs will be much complex, and the research on crystallization of polymer/CNTs under flow are widely reported [7]. A distinct increase of nucleation density in polylactic acid/CNTs nanocomposite was observed even at a high cooling rate in shear field [8]. The crystallization on PVA containing single-walled carbon nanotubes (SWNTs) under shear flow gains more research attentions owing to the excellent thermal performance and more development potential of PVA. A continuous shearing on PVA/SWNTs showed that with the incorporation of SWNTs, the PVA/SWNTs exhibited an improved orientation and crystallization compared with pure PVA. Moreover, self-assembled PVA/SWNTs short ribbons with diameter/width of 3-45 μm and length of 0.5-3 mm was obtained from dispersions by this shear process [9]. However, the stirring speeds were only 500 and 800 rpm, and the loading level of SWNTs was relatively low (1 wt%).

In this paper, uniform s-PVA/SWNTs dispersions were prepared with the help of tea polyphenols (TP) and flow-induced crystallization of the dispersions at high stirring speed was investigated. Particularly the effect of flow resistance of tubes and the amount of SWNTs on the crystallization were studied via the observation of shear process recorded by HD camera. In addition, the thermal and crystallization properties of s-PVA/SWNTs composites obtained during the flow-induced crystallization process were characterized by differential scanning calorimeter and X-ray diffraction.

2. Experimental Section

2.1. Materials

S-PVA (degree of polymerization 1630, syndiotactic diad content 55%) was provided by Faculty of Textile Science and Technology, Shinshu University (Japan). SWNTs (diameter 50-80 nm; length 10 μm) were purchased from Hangzhou Haishun Plastic Co., Ltd., China. TP (purity 98%) was purchased from Shanghai Yuanye Biotechnological Co., Ltd., China.

2.2. Preparation of s-PVA/SWNTs Composite Dispersions

TP as dispersant was firstly dissolved in deionized water by means of sonication using an ultrasonic instrument (40 kHz, output power 70 W) for 5 min, and then SWNTs were added to the TP solution (mass ratio of SWNTs/TP = 1/3) to form mixtures that were sonicated for 1 h at room temperature to obtain uniform dispersions. s-PVA dilute solutions with concentration of 0.2 wt% were prepared by dissolving s-PVA in deionized water at 120 °C with continuous mechanical stir for 6 h. The prepared SWNTs/TP dispersions were slowly added to the s-PVA solution followed by sonication for 30 min. A set of homogeneous s-PVA/SWNTs composite dispersions with SWNTs mass fractions of 0, 0.1, 1.0 and 10.0 wt% based on s-PVA weight were prepared.

2.3. Flow-induced Crystallization of s-PVA/SWNTs Composite Dispersions

The prepared s-PVA solutions containing different amounts of SWNTs were immediately poured into a plastic test tube with a diameter of 13.2 mm and stirred with a stainless steel cylindrical stirrer 8.2 mm in diameter at 3000 rpm at 25 °C. Similarly, the shear flow was also carried out in a glass tube with the same size as the plastic tube.

2.4. *Characterizations*

The dispersibility of SWNTs in different media was characterized on an optical microscope (OM, Olympus, OPTEC BK-POL). The shear flow of s-PVA/SWNTs composite dispersions were recorded on a HD camera (GOM, ARAMIS). Thermal properties were measured using differential scanning calorimeter (DSC, Mettler, TA Q200) at a heating and cooling rate of 10 °C/min under nitrogen atmosphere. X-ray diffraction analysis was taken on a diffractometer (Panalytical X'Pert-Pro MPD) with a Cu Kα radiation beam.

3. Results and Discussion

The s-PVA/SWNTs composite dispersion was prepared with the assistance of TP and the improved dispersibility of SWNTs in s-PVA solution was demonstrated by optical micrographs. It can be seen from Figure 1 that SWNTs without modification aggregated seriously either in water or in s-PVA aqueous solution, while the s-PVA/SWNTs dispersion added TP is very uniform and almost no particles, indicating the bridge effect of TP on improving the compatibility between SWNTs and s-PVA [10].

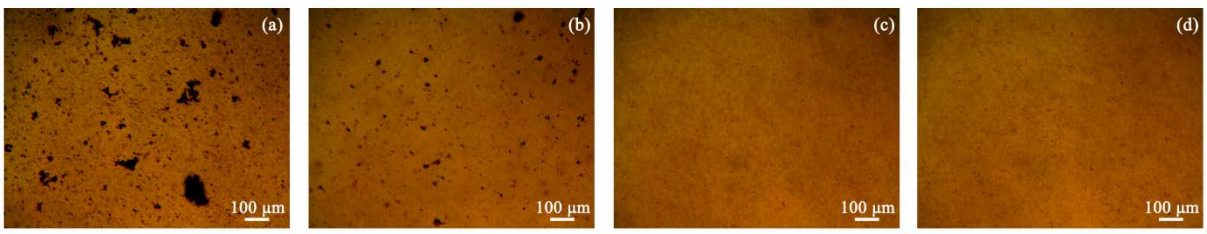

Figure 1. Optical micrographs of (a) SWNTs/H_2O, (b) s-PVA/SWNTs/H_2O, (c) SWNTs/TP/H_2O and (d) s-PVA/SWNTs/TP/ H_2O dispersions.

The well-dispersed s-PVA/SWNTs dispersions obtained above were then transferred into test tube and subjected to a high speed shear flow at a stirring speed of 3000 rpm. Figure 2a shows the HD

photos of shear flow of s-PVA/SWNTs dispersions in glass tube, small numbers of lumps were formed from dispersion and wound around stirrer after shear flow for 2 h, the precipitates seemed to be irregular and disordered due to the random rotation of molecular chains in glass tube. By comparison, when the shear flow of s-PVA/SWNTs was carried out in plastic tube as shown in Figure 2b, the precipitates arrange relatively ordered along the flow direction, indicating the effect of flow resistance on orientation of s-PVA chains and SWNTs. Moreover, the precipitates of s-PVA appear to be increased with the increasing amounts of SWNTs. The precipitate samples mentioned below are all formed from plastic tube.

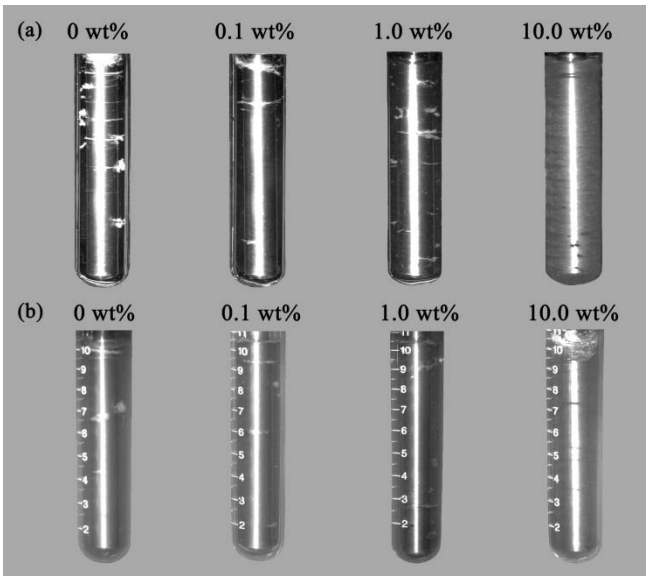

Figure 2. HD photos of shear flow of s-PVA solution containing different amounts of SWNTs at a stirring speed of 3000 rpm in glass (a) and plastic (b) tubes, respectively.

Figure 3 shows DSC heating and cooling curves of the precipitate samples obtained from sheared s-PVA solution containing different amounts of SWNTs. The first heating process was conducted from 50 to 250 °C at a heating rate of 10 °C/min. As shown in Figure 3(a), all the samples have only one endothermic peak, and the melting temperature (Tm_1) gradually decreases from 244.32 to 236.72 °C (summed in Table 1) as the SWNTs loadings increase. Then the cooling process was conducted from 250 to 50 °C at a cooling rate of 10 °C/min, the crystallization temperature (Tc) of the samples shows the declining trend from 216.95 to 149.81 °C. The second heating curve was obtained by heating at the same heating rate, showing that the melting temperature (Tm_2) decreases from 238.70 to 187.74 °C with the increasing SWNTs loadings.

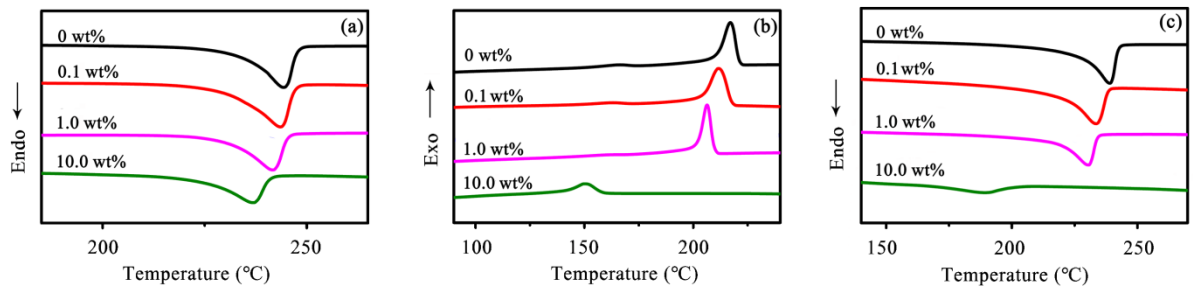

Figure 3. DSC curves (a) first heating curves, (b) cooling curves and (c) second heating curves of s-PVA with different SWNTs loadings.

Further, as shown in Figure 4, the pure s-PVA shows a sharp peak in the XRD pattern, while the increasing loadings of SWNTs lead to a wide peak and decreased peak intensity. The calculated crystallinity (Xc) based on the XRD pattern summered in Table 1 shows that the crystallinity of pure s-PVA is 88.57%, while that of the composites containing 10.0 wt% SWNTs decreases to only 62.13%. These results indicate that although the introduction of large amounts of SWNTs in s-PVA can provide more nucleation sites, the formed SWNTs network may restrict to the mobility of polymer chains and weaken the ability of polymer to crystallize, which is consistent with the reported findings [11]. With the addition of SWNTs, the precipitates of s-PVA from the solutions containing different amounts of SWNTs increase from 40.8 to 69.3%. Hence, although the formed crystals are not so regular and perfect, the introduction of SWNTs increases the precipitates is valuable.

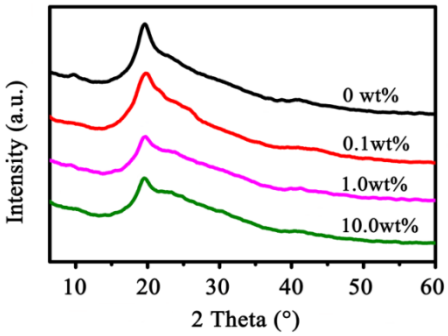

Figure 4. XRD patterns of s-PVA containing different amounts of SWNTs.

Table 1. Thermal properties, crystallinity and precipitate rate of s-PVA/SWNTs

SWNTs (wt %)	Tm_1 (°C)	Tc (°C)	Tm_2 (°C)	$_{Xc}$ (%)	Precipitate rate (%)
0	244.32	216.95	238.70	88.57	40.8
0.1	243.44	211.80	233.26	79.43	48.0
1.0	241.70	206.34	230.43	76.64	54.9
10.0	236.72	149.81	187.74	62.13	69.3

4. Conclusion

The crystallization behaviour of s-PVA/SWNTs under high speed shear flow was investigated in this paper. The uniform s-PVA/SWNTs dispersions were prepared with the assistance of TP. Through the shear process recorded by HD photos, s-PVA/SWNTs composite dispersions are easier to precipitate in plastic tube and the precipitates are more orderly arranged than in the glass one, indicating the facilitation of flow resistance on s-PVA crystallization. In addition, although the introduction of SWNTs may reduce the crystallinity, the increase of the precipitate amount is still valuable. This study improves our understandings on crystallization behaviour of polymer/SWNTs under shear flow and the preparation of polymer/CNTs composites materials based on these will be further researched.

Acknowledgments

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