

Dry-jet Wet Spinning of Polyhydroxyamide Fibers

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Abstract: A high molecular weight polyhydroxyamide (PHA) solution in N, N-dimethyl acetamide (DMAc) was prepared from 3, 3'-dihydroxybenzidine and isophthalic chloride (IPC), which was used for spinning PHA fiber. Before spinning, the diffusion property of DMAc into various coagulants was examined. The fiber was well formed in coagulants such as water/ethanol with a composition of 5/5, ethanol, and ethanol/isopropanol with a composition of 7/3 and 5/5. However, the PHA fiber spun in the water/ethanol mixture contained voids. After the fiber spun in ethanol was annealed at over 350°C, the ultimate stress and initial modulus of the fiber increased from 75.5 MPa and 3.22 GPa to 369 MPa and 29.5 GPa, respectively. These properties of the PHA fiber spun by the dry spinning method were also enhanced, attaining 154 MPa and 5.56 GPa, respectively.

Keywords: Polyhydroxyamide fibers, Diffusion rate, Mechanical properties

Introduction

Polybenzoxazoles (PBOs) as heterocyclic polymers have attracted attention due to their excellent thermo-oxidative and hydrolytic stability, high mechanical properties, and good chemical resistance[1-3]. However, these polymers have the disadvantage of poor solubility, which makes them difficult to process. Additionally, since the glass transition temperature of the polymers is very high and decomposition of the polymers occurs before they melt, they cannot be thermally processed. Wholly aromatic PBOs, in general, are processible only in strong acids. PBOs can be prepared directly as processible liquid crystalline solutions by solution condensation polymerization using a strong acid such as polyphosphoric acid or methanesulfonic acid[4,5]. These solvents act as solvents, catalysts, and dehydrating agents. To obtain a useful form of the polymer, the PBO solution in the strong acid is cast or spun, and then the acid solvent is removed by coagulating the polymer with a non-solvent [1,6]. These drawbacks have been the driving force to obtain PBO precursor polymers, polyhydroxyamides (PHAs). PHAs have good mechanical properties and are easy to process[7-9]. When heated, the precursor polymers can be cyclized to PBOs and absorb heat during the cyclization reaction. In addition, they release a small molecule such as water during this cyclization reaction. Derivatives of the polymer may release phosphorus or fluorine compounds depending on their structures. These small molecules assist in flame retardation[10].

Our group has studied PHA and its derivatives containing phosphorus or fluorine compounds as fire-safe polymers. During heating in a fire, PHA can be cyclized to form PBO, resulting in excellent thermal properties and enhanced flame

resistance. In addition, processing of the polymers is easier due to their good solubility in aprotic solvents such as N-methyl pyrrolidone (NMP), N, N-dimethyl acetamide (DMAc), and N, N-dimethyl formamide (DMF).

In our early work, the PHA films were evaluated for thermal and mechanical properties in both the uncyclized and fully cyclized forms. In a continuation of this work, high molecular weight PHA from 3, 3'-dihydroxybenzidine (DHB) and isophthaloyl chloride (IPC) were prepared and spun into PHA fiber. We used dry-jet wet spinning system to make a fiber because this method is effective to draw a fiber during spinning when a coagulation rate is expected to be crucial to obtain an as-spun fiber with high mechanical properties. The tensile properties of fiber spun under various conditions were examined. Before spinning the fiber, the diffusion rate of the solvent into various coagulants was investigated.

Experimental

Materials

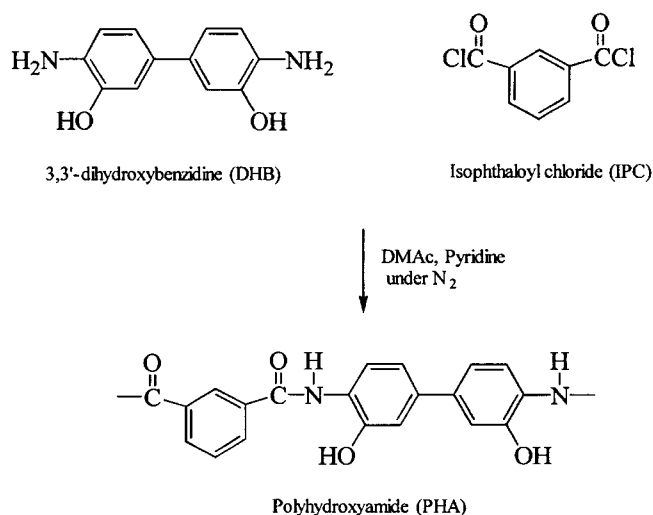
N, N-dimethyl acetamide (DMAc) was distilled over phosphorus pentoxide under reduced pressure. 3, 3'-dihydroxybenzidine (DHB) was recrystallized from water/DMAc cosolvent and dried at 60°C *in vacuo*. Isophthalic chloride (IPC) was purified by vacuum distillation at 100°C. All monomers and solvents were kept in a desiccator before use. Other reagents were used as received.

Preparation of PHA solution (Scheme 1)

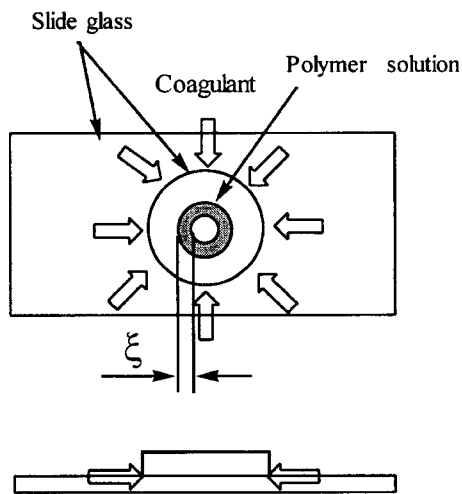
After 4.1261 g (19.1 mmol) of DHB was completely dissolved in 100 ml of DMAc under nitrogen, 4.5 ml of an anhydrous pyridine was added to the solution. The solution was allowed to cool to around -5°C and then 3.8739 g (19.1 mmol) of IPC was introduced into the solution with vigorous stirring. The temperature of the viscous solution was slowly increased to room temperature and maintained for 24 h. The resulting polymer solution was used for fiber spinning dope.

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Scheme 1. Preparation of PHA solution.



Scheme 2. Measurement of coagulation power.

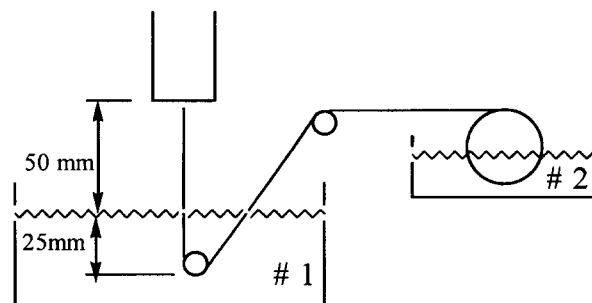
To measure the inherent viscosity of the polymer, the polymer solution was poured into methanol and the precipitate was filtered, washed with excess methanol, and dried at 60°C under vacuum until no weight change was observed.

Measurement of coagulation power

PHA solution was dropped onto a glass slide and covered with another slide. A coagulant was then introduced into the capillary between the two slides (Scheme 2). The diffusion rate of coagulant fronts was monitored by an optical microscope.

Fiber spinning equipment

PHA fiber was produced using the equipment shown in Scheme 3. The highly viscous PHA polymer solution was poured into a stainless-steel extrusion cylinder/piston assembly and extruded through a spinneret with a single



Scheme 3. Spinning equipment.

hole of 100 μm diameter. The diameter of the cylinder was around 12 mm. About 10 ml of PHA solution was used for the fiber spinning. The rate of piston movement into the extrusion cylinder was controlled by nitrogen pressure and the PHA fiber emerged from the spinneret at 200-250 psi. The spinning solution was filtered before it reached the spinneret. The extruded PHA fiber went downward through the air prior to entering a coagulation bath. The fiber stream went into the coagulant to a depth of 25 mm and then emerged from the coagulant bath (#1) and was taken up by a winder of about 110 mm in diameter. The air gap was 50 mm. The PHA fiber was well formed and could be taken up easily. While being taken up, the solidifying filament was immersed into a second coagulation bath (#2) of the same composition, to prevent it from sticking together, and kept there for 1 h. The coagulant temperature was around 25°C. The fiber was dried at room temperature.

Characterization

The PHA fiber was cut into segments 30 mm long. The samples were tested with a Merlin Instron 5564 at room temperature to determine their mechanical properties. The extension rate was 3 mm/min. Scanning electron micrographs were obtained on a Jeol 35CF scanning electron microscope. Inherent viscosity of the PHA polymers was determined at 0.5 g/dl in DMAc at 25°C with an Ubbelohde viscometer.

Results and Discussion

In order to obtain high molecular weight PHA, the monomers and solvent had to be carefully purified. DHB was purified by recrystallization with water and DMAc cosolvent. IPC was purified by vacuum distillation and DMAc by fractional distillation under vacuum. The solution colors varied from yellow to dark brown depending on monomer purity. The better the monomer purification, the more yellowish the solution color, because oxidization changes the color of DHB to brown. The polymer concentration was adjusted to 8% (w/v). Thus, over 100 grams of the light yellow PHA, with an inherent viscosity of 2.28 dl/g, solution was obtained. The chemical structure of PHA is shown in Scheme 1. The PHA polymer solution was

used for fiber spinning.

Before spinning of PHA fiber, the diffusion rate of DMAc into various coagulants was investigated to choose the best coagulant for PHA fiber formation. In our preliminary experiments, PHA coagulated faster in water than in alcohol. Thus, we measured the specific growth rate of the solid layer forming on the surface of PHA solution treated with various coagulants. The thickness of the solidified layer is proportional to the square root of time according to the following equation[11]:

$$\Xi = 1/4 \lim_{t \rightarrow 0} (d\xi^2/dt) \quad (1)$$

where Ξ : initial boundary growth rate

ξ : thickness of solidified layer

t : time

It is well known that the experimental values of Ξ are reproducible and reflect the effects of spinning dope, coagulation bath composition, temperature, etc. Ξ does not depend explicitly on the radius of the sample and spinning velocity, but only on the rate of mass transfer and phase separation.

The diffusion rates of DMAc into various coagulants are shown in Figure 1 and the initial boundary growth rates are summarized in Table 1. As shown in our preliminary experiments, the diffusion rate of DMAc in PHA solution

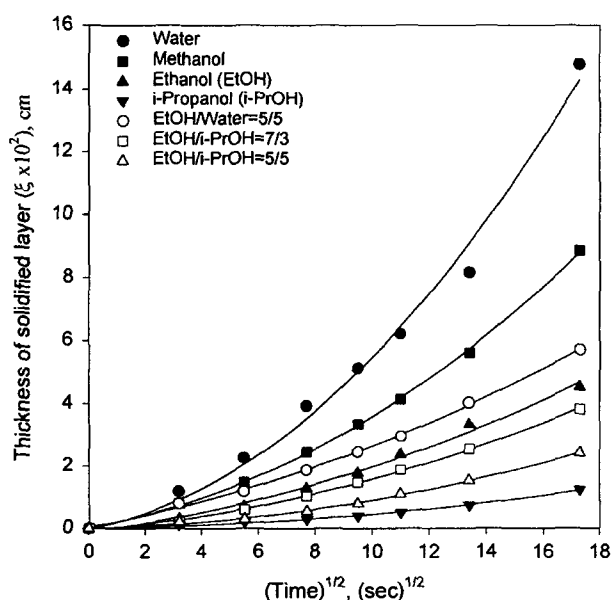


Figure 1. Diffusion rate of various coagulant fronts.

Table 1. Initial diffusion rates of various coagulant fronts

Coagulant	Water	Methanol	Water/Ethanol		Ethanol / Isopropanol		
			5/5	0/10	7/3	5/5	0/10
$\Xi \times 10^6(\text{cm}^2/\text{s})$	6.64	5.92	5.23	3.18	1.46	0.26	0.023

into water was faster than into alcohol. The transfer rate of DMAc out of PHA solution increased in the order; isopropanol (i-PrOH) < ethanol (EtOH) < methanol < water. The boundary growth rate does not represent the real diffusivity of solvent into coagulant, but it can be considered as a measure of diffusivity. Initial boundary growth rates of PHA solution coagulated in water, methanol, water/EtOH with a composition of 5/5 (v/v), EtOH, EtOH/i-PrOH (7/3 and 5/5, v/v), and i-PrOH were 6.64×10^{-6} , 5.92×10^{-6} , 5.23×10^{-6} , 3.18×10^{-6} , 1.46×10^{-6} , 0.26×10^{-6} , and 0.023×10^{-6} cm^2/sec , respectively. The magnitude of Ξ depends on the rate of mass transfer and phase and structural transitions in the polymer-solvent-non-solvent system in exactly the same way as does the solidification rate in the real wet-spinning process. In our system, PHA fiber was well spun in the coagulation bath with water/EtOH (5/5), EtOH, and EtOH/i-PrOH (7/3, 5/5). This means PHA fiber would be spun in coagulants with Ξ ranging from ca. 5×10^{-6} to 0.3×10^{-6} cm^2/sec . It would be possible to spin PHA fiber in a water/DMAc coagulant, as a well known solvent-non-solvent system, with this range of Ξ . For example, the Ξ of PHA solution immersed in water/DMAc with a composition of 6/4 is similar to that of PHA solution coagulated in EtOH, 3.45×10^{-6} cm^2/sec . In our preliminary experiments, the PHA fibril was well formed in a coagulant with a water/ethanol mixture (2/8, 3/7, 5/5) when the PHA solution was dropped into the coagulant with vigorous stirring. From these results, water/EtOH, EtOH, and EtOH/i-PrOH mixtures were selected as coagulants.

The tensile properties of PHA fibers spun in various coagulants are summarized in Table 2. In the case of PHA fiber spun in water/EtOH with a composition of 5/5, the fiber stream was frequently broken over a winder speed of 40 rpm. This might be due to the fast coagulation of PHA fiber in the coagulant. The fiber was taken up at 70-75 rpm in all other coagulants. The average diameters of PHA fibers spun in water/EtOH with a composition of 5/5, EtOH, and EtOH/i-PrOH with compositions of 3/7 and 5/5 were 83.3, 54.0, 51.5, and 52.2 μm , respectively. The fiber spun in

Table 2. Tensile properties of PHA fiber

Coagulant	Ultimate stress (MPa)	Initial Modulus (GPa)	Elongation at break (%)
EtOH/Water (5/5)	25.0	1.33	1.9
EtOH	75.5	3.22	3.6
EtOH/i-PrOH (7/3)	73.1	2.78	4.9
EtOH/i-PrOH (5/5)	74.9	3.11	5.7

water/EtOH with a composition of 5/5 was taken up at 38 rpm. The final fiber diameters are determined by the solution viscosity, the rate of resin extrusion, the spinneret hole diameter, and the difference in velocity between the dope leaving the spinneret and the winder, called the spin-draw ratio or the spin-stretch factor[12]. In our system, the spin-draw ratio was varied only depending on the coagulant. The diameter of the fiber spun in the water/EtOH coagulant with a composition of 5/5 is greater than that of the fiber spun in the EtOH or EtOH/i-PrOH mixed coagulants, indicating that water hindered drawing of the fiber because of the fast diffusion rate of DMAc. The ultimate strength, initial modulus, and elongation at break of the PHA fibers spun in water/EtOH with a composition of 5/5, EtOH, and EtOH/i-PrOH with compositions of 7/3 and 5/5 were 25.0, 75.5, 73.1, and 74.9 MPa; 1.33, 3.22, 2.78, and 3.11 GPa; and 1.9, 3.6, 4.9, and 5.7%, respectively. The tensile properties of the fiber spun in water/EtOH with a composition of 5/5 were much lower than those of any other fibers spun in EtOH/i-PrOH mixed coagulants. However, the ultimate strength and initial modulus of the fiber spun in an EtOH/i-PrOH mixed coagulant was almost the same for all compositions, ca. 74 MPa and 3 GPa. The fiber spun in water/EtOH with a composition of 5/5 was more brittle than that of PHA fiber spun in EtOH or EtOH/i-PrOH mixed coagulant. Elongation of PHA fiber spun in water/EtOH with a composition of 5/5 was only 1.9%. Cross-sections of fractured fibers spun in the coagulants with water/EtOH (5/5), EtOH, and EtOH/i-PrOH (5/5) are shown in Figure 2, demonstrating the basis for the difference in tensile properties between the fiber spun in water/EtOH and EtOH/i-PrOH mixed coagulants. The fiber spun in water/EtOH with a composition of 5/5 exhibited a very porous structure, which is mainly due to fast solvent exchange with the coagulant. The diameter of voids that this fiber contained were about 10 μm . However, fiber spun in the EtOH or EtOH/i-PrOH mixed coagulant was void-free. This difference affected the mechanical properties of the PHA fibers. As shown in Table 2, the mechanical properties of fibers spun in the EtOH or EtOH/i-PrOH mixed coagulant

were better than those of the fiber spun in water/EtOH with a composition of 5/5. The fractured cross-sections of the PHA fibers spun in EtOH and EtOH/i-PrOH with a composition of 5/5 were almost the same, i.e; void-free. This means that PHA fibers spun in a coagulant in which the Ξ of the PHA solution immersed was below around $3 \times 10^{-6} \text{ cm}^2/\text{s}$ are void-free. No difference in mechanical properties was observed for the fibers spun in the coagulants with EtOH and EtOH/i-PrOH (7/3 and 5/5). In order to obtain PHA fiber with excellent mechanical properties, the fiber must be drawn fully before coagulation. Therefore, the diffusion rate of DMAc into a coagulant must be as low as possible.

The PHA fiber was annealed under vacuum for 30 min at each temperature without tension. After annealing at temperatures above 250°C, the yellow fiber turned dark brown. The tensile properties of the PHA fiber before and after annealing are summarized in Table 3. For the fibers annealed at 250, 350, and 450°C, the ultimate stress and initial modulus increased to 127, 286, and 369 MPa; 3.68, 24.2, and 29.5 GPa, respectively. Also, the elongation (%) at break was somewhat increased. Annealing the PHA fiber at 250°C did not significantly affect the mechanical properties of the control PHA fiber. However, the tensile properties of the fiber were dramatically enhanced by annealing at 350 and 450°C, because the PHA fiber was rearranged to the corresponding PBO fiber over 250°C. According to our previous results, the rearrangement of PHA films to their corresponding PBO films begins at about 260°C and is completed over 400°C[7-9]. Therefore, the PHA fiber might

Table 3. Tensile properties of annealed PHA polymer spun in EtOH

Annealing temperature(°C)	Ultimate stress (MPa)	Initial Modulus (GPa)	Elongation at break (%)
Control	75.5	3.22	3.6
250	127	3.68	6.4
350	286	24.2	4.2
450	369	29.5	7.1

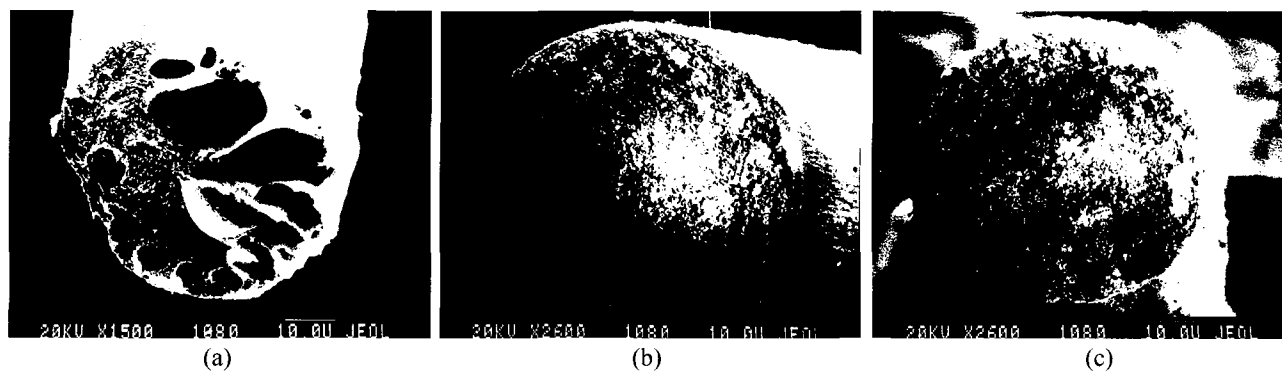


Figure 2. Cross-section of fractured PHA fibers spun in (a) water/ethanol (5/5, v/v), (b) ethanol, and (c) ethanol/i-propanol (5/5, v/v).

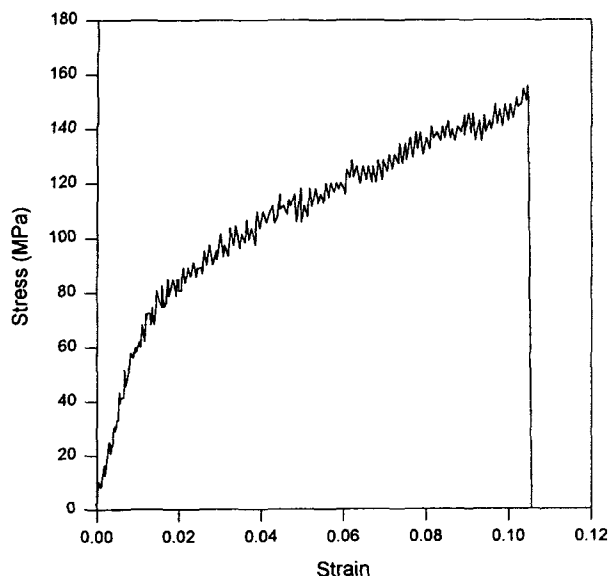


Figure 3. Stress-strain curve of PHA fiber spun by pulling out PHA solution.

be slightly rearranged to the corresponding PBO by annealing at 250°C for 30 min. In the case of annealing at high temperatures (above 350°C), the annealing effect on the tensile properties of the PHA fiber decreases.

Even though the tensile properties of PHA fiber spun in EtOH/*i*-PrOH mixed coagulants were better than those of the fiber spun in water/EtOH with a composition of 5/5, these properties are not good enough for real applications. Figure 3 shows the stress-strain curve of the PHA fiber made by stretching the PHA solution. The PHA fiber was drawn while being dried in air for 10 min and then immersed into a coagulation bath with EtOH. The diameter of the PHA fiber was 24.8 μm . The ultimate stress, initial modulus, and elongation at break of the fiber were 154 MPa, 5.56 GPa, and 10.1%, respectively. According to our previous results, these values are equal to those of PHA films, 137 MPa, 5.94 GPa, and 9%. To obtain a PHA fiber with high mechanical properties, therefore, the diffusion rate of the solvent out of PHA fiber must be decreased as much as possible and the fiber fully drawn during spinning. In the future, attempts to spin PHA fiber by a dry spinning method will be tried.

Conclusions

In order to spin PHA fiber, the diffusion rate of DMAc from a PHA solution into various coagulants was examined. The diffusion rate of DMAc out of PHA solution increased in the order *i*-PrOH < ethanol < methanol < water. PHA fiber with good mechanical properties was successfully obtained in EtOH and EtOH/*i*-PrOH mixed coagulants. In the case of PHA fiber spun in water/EtOH coagulant, fiber formation was good, but the mechanical properties were poor due to

fast diffusion of solvent out of the PHA fiber. The tensile properties of PHA fiber spun in EtOH coagulant were increased by annealing over 250°C because of the rearrangement of PHA to PBO. The PHA fiber spun by pulling out the PHA solution and then drawn in the air had high mechanical properties.

Future work will focus on examining a dry spinning method to make PHA fiber with excellent mechanical properties. Also, the chemical cyclization of PHA fiber during spinning will be investigated to allow sufficient stretching of the fiber, because drawing the fiber is also important for obtaining PHA fiber with high mechanical properties in this system.

Acknowledgments

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