Development of Novel Film Using Paramylon Prepared from *Euglena gracilis*

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ABSTRACT: A novel film was developed using paramylon from *Euglena gracilis* and its physical properties were investigated. Formic acid was suitable for the preparation of a solution of paramylon, and a transparent even yellow film was obtained by casting the solution on a glass plate and drying the cast film in air without using coagulation bath. However, the spinability of a paramylon solution was fairly low. The spinability was a little enhanced by blending polyvinyl alcohol (PVA) up to 70%. The paramylon/PVA blend fibers were produced through wet spinning using coagulation bath of conc. Na_2SO_4 at a room temperature. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3495–3497, 2006

Key words: paramylon; euglena; film; fiber

INTRODUCTION

The *Euglena* family, classified in both vegetable and single cellular animal, is a monad that can move with its tail using like a screw and synthesizes paramylon as storage polysaccharide from CO_2 and solar energy. The polysaccharide consists of triple helical structure of (1→3)-β-D-glucans and has crystallinity more than 90% though the degree of polymerization (DP) is no more than 700.[1,2] Such specific properties of paramylon, that is, high crystallinity and low DP, are unwelcome from a viewpoint of polymer processing. However, it is important to establish a new production system using renewables from environmental point of view.

In this study, the wet process was applied to paramylon to produce stable films, and their physical properties were investigated. In addition, an attempt was made to spin the paramylon fibers by blending polyvinyl alcohol (PVA).

EXPERIMENTAL

Materials

Spray-dried powder like *Euglena gracilis* was furnished from Kanai Juyo Kogyo, Japan. The powder was soaked in a NaOH aqueous solution of 0.25*N* and shaken for 5 h, and then settled for 1 day. The settlement was centrifuged and filtered off. The obtained powder was neutralized with acetic acid and washed in water. Then, the paramylon powder, Eg, was prepared. Other chemicals used were all laboratory grade and were purchased from Wako Pure Chemical Industries, Japan.

Preparation of film and fiber

Eg powder was dissolved in 90% formic acid after constant stirring for at least 36 h, and then the solution of 0.15 g/mL was prepared. The paramylon cast film was obtained by casting the solution on a glass plate and drying in air at a room temperature. The paramylon fiber was tried to be produced using a wet spinning process. However, the spinability of the paramylon solution was too low. The spinability was a little enhanced by blending PVA up to 70% keeping the total concentration of solution at 0.15 g/mL. The paramylon/PVA blend fibers were produced through wet spinning using a nozzle of 0.4 mm in diameter and a coagulation bath of 30–40% Na_2SO_4 at a temperature of 20–30°C.

Relative viscosity

A regenerated film of 0.1 g was dissolved in dimethyl sulfoxide of 10 mL and the relative viscosity, t/t_0 at 30°C was measured using an Ostwald type viscometer. t and t_0 are the passing times for the sample solution and its solvent.

Tensile tests

Tensile tests were made using an automatic Tensilon Tester (A and D, type STA-1150, Japan) at 20°C and

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65% RH. The measurements conditions were as follows. As for the film sample, the gauge length was 20 mm, the cross-head speed 2 mm/min, and the sample was cut into a rectangular shape of 30 mm in length and 5 mm in width. The values were the average of 10 tests. As for the fiber sample, the gauge length was 10 mm, the cross-head speed 1 mm/min, and the sample was cut into 30 mm in length. The values were the average of 20 tests.

X-ray measurements

The WAXD profiles for the regenerated films and fibers were measured using a diffractometer (RINT2100FSL, Rigakudenki, Japan) and pinhole-collimated Cu Kα X-rays. X-ray specimens were prepared by laminating the cast film or aligning the fibers into a bundle to a desirable thickness, so that the volume of the specimen irradiated by the X-ray beam was kept approximately constant.

RESULTS AND DISCUSSION

Film

The cuticle of spray-dried *Euglena gracilis* is shown in Figure 1(a). The paramylon powder can be seen across the broken cuticle. In Figure 1(b), the paramylon powder prepared is shown. WAXD profile for the powder was measured and was compared with previous works.[3,4] The profile showed similar characteristics. Thus, the separation process proposed in this study is applicable and will not degrade the paramylon molecules seriously.

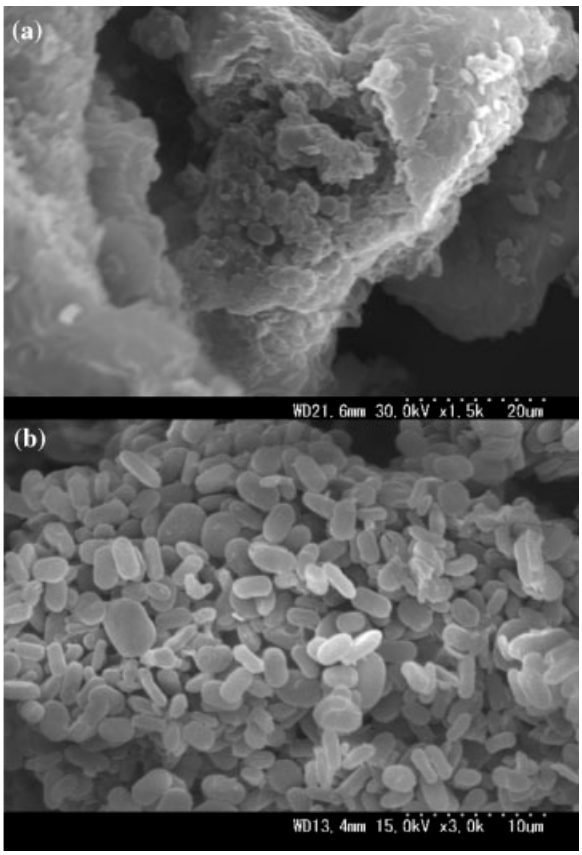

Figure 1 Aspects of paramylon powder: (a) observed across the broken cuticle of Euglena gracilis; (b) separated powder.

TABLE I
Mechanical Properties for Paramylon Films

Sample	Strength (MPa)	Elastic modulus (GPa)	Elongation (%)
As-cast	33.9	1.13	14.2
Steamed	49.9	1.99	10.3

For the production of cast film, we used 90% formic acid for the solvent. Such strong acid tends to bring about hydrolysis reaction. Therefore, the change in a relative viscosity was measured with respect to the time for the preparation of paramylon solution. A relative viscosity monotonously decreased with increasing time. It is seen that the molecular weight of paramylon became smaller through the hydrolysis reaction with formic acid. The tensile properties for the regenerated paramylon film obviously lowered when the time for the preparation of solution became longer than 72 h.

To regenerate a cast film from a polymer solution, a coagulation bath of nonsolvent is often used. In a case of a paramylon solution, however, rapid coagulation using hot water made the cast film wrinkled and dull. Slow drying in a draft chamber is effective for the production of a transparent and even film. The tensile strength for the regenerated paramylon film reached to 33.9 MPa (Table I).

For the enhancement of tensile properties, a post curing treatment using hot steam at 135°C for 2 h was applied to the as-cast film. The changes in tensile properties are shown in Table I. It is seen that this treatment was effective to enhance the tensile properties. The changes in WAXD profiles by the treatment are shown in Figure 2. After the treatment, a shoulder at $\sim 18^\circ$, and peaks at $\sim 30^\circ$ and 41° became distinguishable. It is seen that the hot steam treatment promoted the crystallization of as-cast film. Therefore, the treated film showed superior tensile properties.

The primary structure of paramylon is the same as that for biodegradable curdlan.[5] Thus, the paramylon film will be utilized for a biodegradable material. However, the ductility of the paramylon film is needed to be enhanced by mixing a suitable plasticizer.

Fiber

We tried to produce regenerated fibers from a paramylon solution. However, the spinability of the solution was fairly low. The spinability was a little enhanced by blending PVA up to 70%. The paramylon/PVA blend

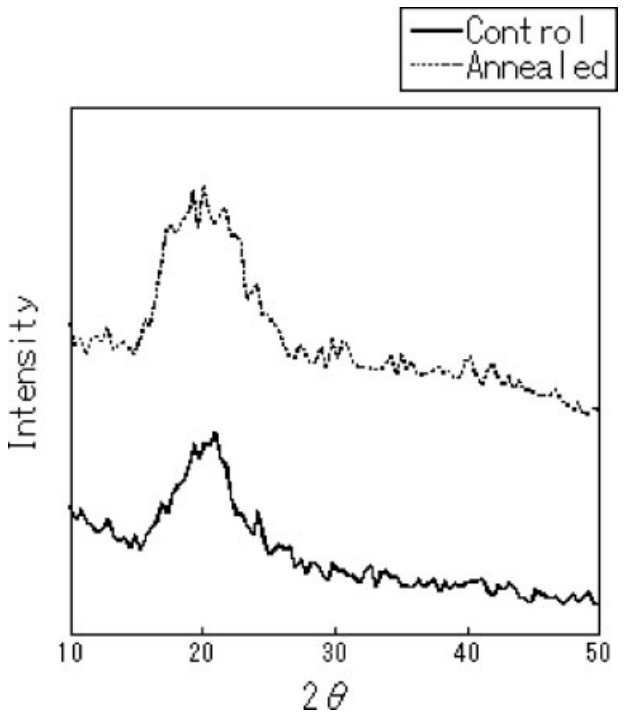

Figure 2 WAXD profiles for as-cast film and steam treated one.

fiber was produced through wet spinning using a coagulation bath of conc. Na_2SO_4 at nearly room temperature. When the blend ratio of PVA was smaller than 50% or a temperature of coagulation bath was higher than 50°C, the wet spinning could not be made.

The PVA fractions of as-spun blend fibers are still soluble in water. Thus, the PVA fractions were crystallized by heatsetting the blend fibers using an air-oven

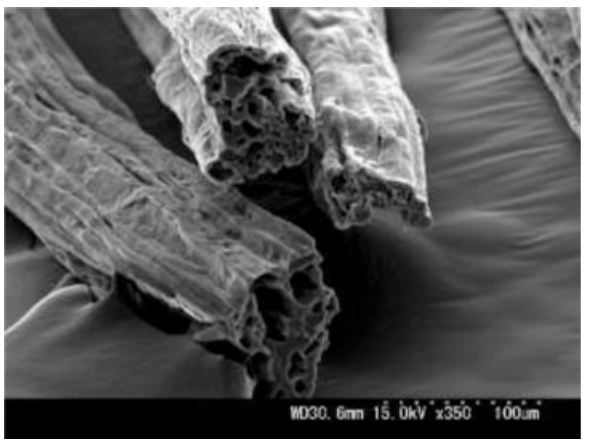

Figure 3 Scanning electron micrograph for the paramylon/PVA (30/70) blend fibers heatset at 200°C.

TABLE II
Tensile Properties for Paramylon/PVA (30/70) Blend Fibers Heatset at Various Temperatures

Temperature (°C)	Strength (cN/dtex)	Elongation (%)
160	0.19	19.6
180	0.28	19.8
200	0.33	19.3

at 160–200°C for 5 min with fixing the ends of fibers. The crystallization of PVA was confirmed from WAXD profiles, and the blend fibers did not show a fiber diffraction pattern. The molecular orientation seems to be fairly low. The aspects of fibers heatset at 200°C are shown in Figure 3. It is seen that the structure of the fiber became porous. It seems that a coagulation rate was still too rapid. The tensile properties are shown in Table II. The tensile strength of heatset blend fiber was no more than 0.33 cN/dtex.

To check the miscibility between PVA and paramylon, the blend cast films having the fractions of PVA more than 50% were produced. The films showed islands-in-a-sea type structure, and the islands were rich in paramylon. When the shear stress was applied at the interface, cracks were easily generated. Therefore, the tensile properties for the blend fibers became small.

CONCLUSIONS

A novel film was developed using paramylon from *Euglena gracilis* and its physical properties were investigated. Formic acid was suitable for the preparation of a paramylon solution, and the film was prepared by casting the solution on a glass plate and drying the cast film in air without using coagulation bath. The film was strengthened through a hot steam treatment. The spinability of a paramylon solution was fairly low. The spinability was a little enhanced by blending PVA up to 70%. However, poor miscibility between paramylon and PVA affected the tensile properties of blend fibers.

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