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Papyrus reinforced poly(L-lactic acid) composite

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Abstract—Mechanical reinforcement of an all-sustainable composite, composed of papyrus stem-milled particles as reinforcement and poly-L-lactic acid (PLLA) resin as matrix, was investigated. The papyrus particles (average diameter of 70 μm) could be well dispersed in PLLA resin up to 50 wt% without any surface modification. Young's modulus of the composite was 4.2 GPa at 50 wt% of the papyrus content. This is a two-fold increment in modulus as compared to that of the PLLA matrix. The tensile strength of the composite was almost constant around 48 MPa irrespective of the papyrus content. Temperature dependence of the storage modulus demonstrated that the incorporation of papyrus restricts the large drop in the modulus above the glass transition of PLLA.

Keywords: Papyrus; sustainable composite; poly-L-lactic acid; mechanical properties; reinforcement.

1. INTRODUCTION

The utilization of biomass has attained increased importance due to threats of uncertain petroleum supply in the near future and concerns about environmental pollution. Most sustainable plastics cannot compete economically with conventional petroleum-derived plastics in their present state. Economically favorable and environmentally friendly composites, therefore, are expected to be made from costly crop-derived sustainable plastics in combination with inexpensive natural fibers [1].

Cellulose is the most abundant form of biomass. The form most likely to be used is as reinforcement fiber, not only for ecological and economical reasons, but also because of the high mechanical and thermal performance of the resulting composite. Many kinds of natural cellulose fibers, such as flax, hemp, jute, etc., have been selected as the reinforcement [2]. We also reported on the composite with kenaf bast fibers as reinforcement [3]. It was found that kenaf fiber possesses the potential to replace glass fiber, and it shows promise as the reinforcement fiber of

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high performance composites. In this study, we selected papyrus as an alternative for the reinforcement. It is believed that papyrus was first used in *ca.* 4000 BC, where the Egyptians used papyrus bundled together for boat making; they also wove the papyrus fibers into water resistant ropes, mats, baskets, tables and so on [4]. In addition, the root was used as fuel and the stalk was used as a food. However, Egypt's greatest gift to the ancient world was the fabricated papyrus sheet made from the pith of this reed, which is the source of English word ‘paper’. Thus papyrus with its Latin name, *Cyperus papyrus* L., has been famous for a very long time; however, only few studies have been carried out concerning its nature, chemical, physical and mechanical properties as a natural plant. Papyrus is a plant that grows to 4 m at maximum. During growth, papyrus absorbs nitrogen and phosphorus from the soil and water [5, 6]. Compared with other natural plants, it also accumulates carbon dioxide at a significantly high rate [7] as a variety of C4 plants [8]. These suggest papyrus can be very environmentally friendly plant among many other natural plants. Accordingly, from the viewpoint of environmental issues, it is important to find practical ways to utilize papyrus as source material. Among many applications, we here report papyrus as a good candidate for an environmentally friendly reinforcement.

For the matrix resin, poly-L-lactic acid (PLLA) was used. PLLA is the most popular synthetic sustainable polymer; originated from natural products, stable in the lifetime of their use and storage, but degrade which microbially and/or environmentally after disposal. PLLA possesses relatively high melting point (usually around 160°C) [9] and high mechanical performance [10, 11] compared with other biodegradable aliphatic polyesters such as poly(ε-caprolactone), poly(butylene succinate), etc. However, relatively low glass transition temperature restricts the thermal resistance of PLLA [12]. In order to overcome thermal resistance, PLLA-based composites were developed. For example, PLLA-organically modified layered silicate nanocomposite was successfully prepared, where storage enhancement of storage modulus was observed [13].

In this study, papyrus/PLLA composite was prepared, and the mechanical and thermal properties of the composites were investigated. Through these investigations, we reported the capability of papyrus to function as a useful and environmentally friendly reinforcement without any surface modification and without incorporating additives.

2. EXPERIMENTAL

2.1. Materials and sample preparation

The papyrus used in this study was cultivated in Kobe, Japan, and was kindly supplied from the Kobe Papyrus Institute, NPO established at 1990 in Kobe.

Figure 1 shows the photographs of (a) a whole stem, (b) a cross-section of the papyrus stem and (c) a scanning electron micrograph of the pith/bast interface of

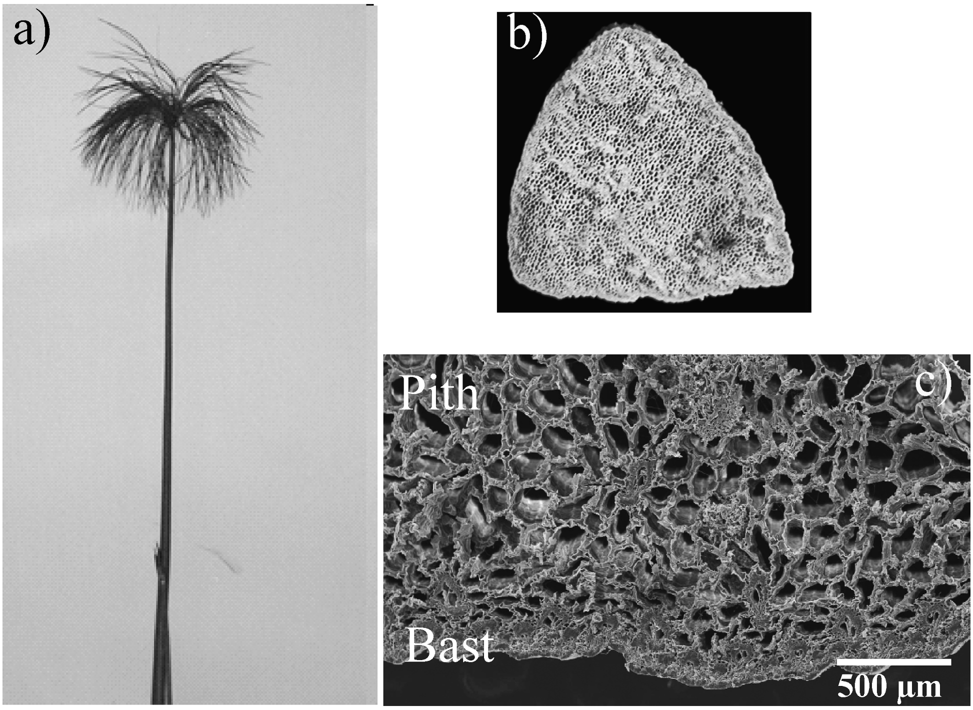

Figure 1. Photographs of (a) whole stem, (b) cross-section of papyrus stem and (c) scanning electron micrograph of the pith/bast interface of papyrus cultivated at Kobe Papyrus Institute.

papyrus. The height of the stem was 2 m in average. The stem is composed of cellulose (39.1%), hemicellulose (24.8%), lignin (18.5%) and other materials (ash, pectin, etc.) [14]. The triangular shaped cross-section of the stem can be divided into a relatively dense bast (outside) and a very porous pith (inside). The whole stem was milled using a vibrating sample mill (Heiko T1-100, Heiko Seisakusho Ltd.), then sieved through a mesh (No. 100).

Figure 2 shows the scanning electron micrograph of the milled papyrus stem used in this study. The milled sample contains some chopped short fibers, but the major part is grain-like particles. Thus the aspect ratio is almost unity with the average size of 70 µm. The crystal structure of these particles can be assigned as cellulose I, typical for natural plant fiber; however, its crystallinity seemed to be low judging from the X-ray diffraction profile. This is because the particles contain large amounts of pith, whose crystallinity was lower than that of the bast.

PLLA (Mitsui Chemicals Inc., LACEA, with viscosity average molecular weight $M_\mathrm{v} = 3.9 \times 10^4$) was used as matrix.

Both papyrus particles and PLLA were dried at 70°C in advance, then kneeded using a brabender batch-type mixer (Labo Plastomil, Toyoseiki Ltd.) at 180°C for 8 min with the rotation speed of 60 rpm. As low a temperature as possible was selected to avoid the degradation of natural plant material above the melting point of

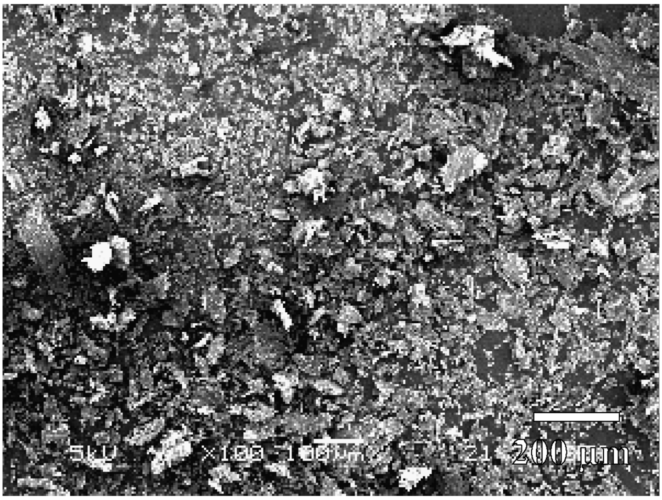

Figure 2. Scanning electron micrograph of the milled papyrus stem (Average particle size is 70 µm).

PLLA. After mixing, no significant thermal degradation was observed. The papyrus content of the composite could be changed from zero to 50 wt%, as determined from the weight loss on the thermogravimetric trace.

Then, the papyrus/PLLA blend was compression molded into a sheet at 160°C followed by quenching in ice-water. Each specimen was stored in a desiccator till used.

2.2. Measurements

The stress–strain curve for the composite was measured by a tensile tester (Shimadzu, Autograph AGS-1kND) at room temperature. Rectangular specimens with a length of 50 mm, a width of 5 mm and thickness of 0.5 mm were tested. The initial length of the specimen was 20 mm and the extension rate was 2 mm/min. The average values of the Young's modulus and tensile strength were evaluated for 5 tested specimens.

The dynamic storage modulus was measured using a dynamic mechanical analyser (DVA-220S, ITK Ltd.) from 20 to 130°C. A heating rate of 6°C/min, an original length of 10 mm, and a frequency of 10 Hz were employed.

The cross-section of the stem, and the fractured surfaces of the composites were observed using a scanning electron microscope (SEM, JEOL Ltd., JSM-5610LVS) at the accelerating voltage of 5 kV. Pt/Pd was deposited on the surface prior to the observation.

3. RESULTS AND DISCUSSION

Figure 3 shows the effect of the papyrus content on the Young's modulus of the papyrus/PLLA composite. The Young's modulus increased monotonically with

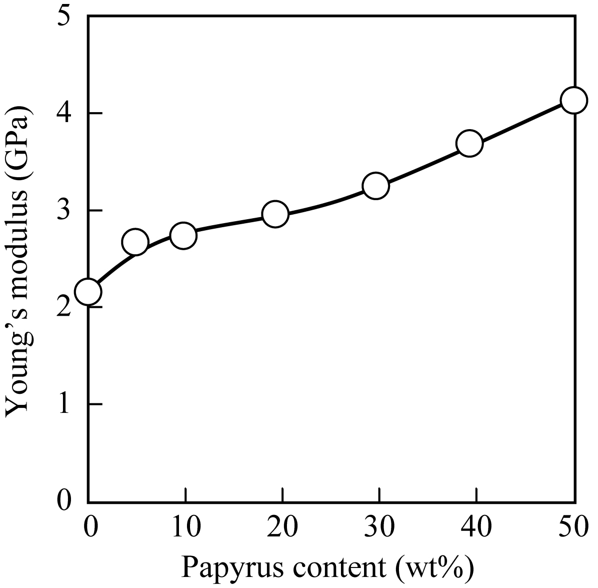

Figure 3. Relationship between Young's modulus and the papyrus particle content of the papyrus/PLLA composite.

increasing papyrus content, and it reached 4.2 GPa at 50 wt% papyrus content, i.e. twice the modulus of the PLLA matrix. This shows that papyrus particles are effective for the mechanical reinforcement of PLLA. The increase of Young's modulus almost corresponds to that predicted using Smallwood's equation: $E = E_o(1 + 2.5V_f)$, where E, E_o are Young's modulus of the composite, and that of the matrix, respectively, and V_f is the volume fraction of the filler [15]; $E = 4.5$ GPa at 50 wt% papyrus content. In this equation, perfect adhesion and enough high filler modulus compared with the matrix modulus are assumed as preliminaries. This implies that the mechanical reinforcement is due to the high interfacial adhesion between the papyrus and PLLA.

Figure 4 shows the effect of the papyrus content on the tensile strength of the papyrus/PLLA composite. The experimental tensile strength of this composite was almost constant at around 48 MPa up to the papyrus content of 50 wt%. The change of the tensile strength with increase of filler content is very complicated for a particulate filled composite: it depends on the matrix/filler combination, interfacial adhesion, filler size, shape, dispersion and so on. Many formulae have been proposed to express the relationship between the tensile strength and the filler content [16, 17]. For example, Nielsen predicts the tensile strength with the following equation assuming no-interfacial adhesion [17]:

$$(\sigma/\sigma_o) = \left(1 - V_f^{2/3}\right) \cdot S,$$

where σ, σ_o are the tensile strength of the composite, and that of the matrix, respectively. S is a stress concentration factor between 0.5 and 1.0. As revealed

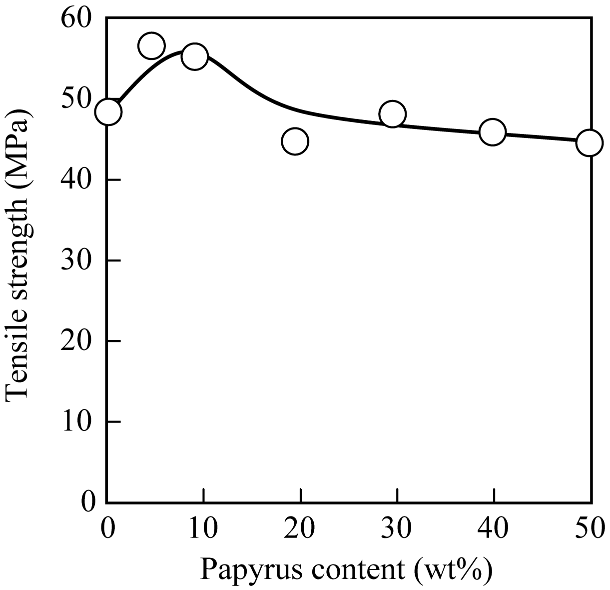

Figure 4. Relationship between the tensile strength and the papyrus particle content of the papyrus/PLLA composite.

with this equation, the tensile strength often tends to decrease by the incorporation of the filler for the conventional particulate filled composites. Takase and Shiraishi reported that the tensile strength of polypropylene (PP)/pulp composite decreased with the pulp content. On the contrary, the increase of the tensile strength could be only observed when PP was modified with maleic anhydrite (MA) [18], where MA interacts with the OH group of pulp. This shows that high interfacial adhesion is required for the increase of the tensile strength. As shown in Fig. 4, the tensile strength remained unchanged up to the papyrus content of at 50% concentration. This again suggests relatively high interfacial adhesion between papyrus and PLLA, even without special surface modification.

Figure 5 shows the scanning electron micrograph of the tensile fractured surface of the papyrus/PLLA composite (papyrus content = 20 wt%). Cellulosic fibers are well known not to easily disperse in non-polar polymers. The main problem in processing is the tendency of natural fibers to form large aggregates due to high intermolecular bonding among the fibers. However, the dispersion of the particles seemed to be good for the combination between papyrus and PLLA spontaneously without any special surface modification. Ancient papyrus sheet was manufactured only by stacking the strips of the pith without adding adhesive. In this case, the sap of the papyrus is believed to effect adhesion [19]. The papyrus pith contains a large amount (2.1 wt%) of pectin compared with hard wood (0.1 wt%), which may account for the high dispersibility of papyrus particles in PLLA. In Fig. 5 it may be seen that part of the papyrus surface was exposed, and another part was wrapped with the matrix resin. This observation reveals that the interfacial adhesion in the

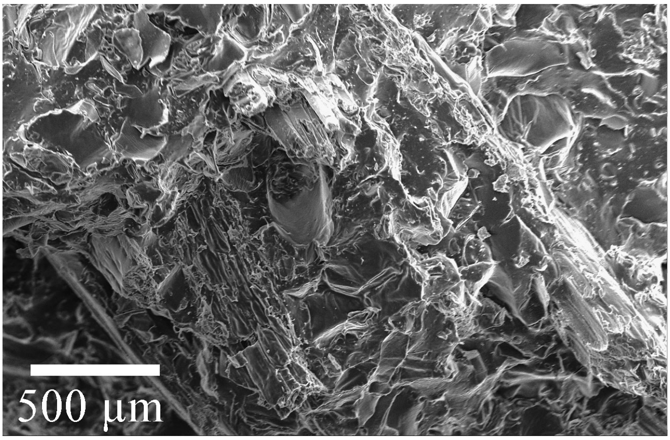

Figure 5. Scanning electron micrograph of the fractured surface of the papyrus/PLLA composite (Papyrus content = 20 wt%).

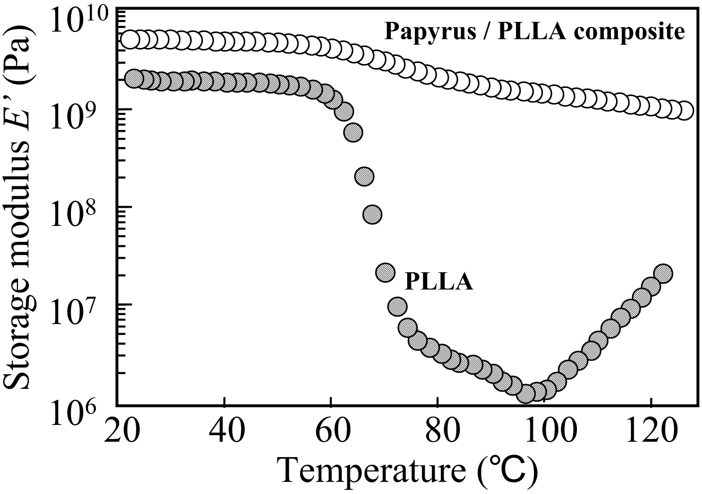

Figure 6. Temperature dependence of the storage modulus E' for PLLA and the papyrus/PLLA composite (Papyrus content = 50 wt%) at 10 Hz.

sample was relatively good enough without special modification of filler and/or matrix. So the whole failure of the composite occurred both through the interfacial debonding and the particle and/or matrix fracture, which also contributes to the high tensile strength shown in Fig. 4. Further increase of particle content with optimum surface treatment is expected to enhance the mechanical properties of the resulting composites.

Figure 6 shows the temperature dependence of the storage modulus E' of the composite and the PLLA matrix. The E' value of the matrix decreased abruptly around 60°C corresponding to the glass transition of PLLA. As described above, this decrease limits the PLLA applications requiring heat resistance. The re-increase of the E' value above 100°C is due to the crystallization of PLLA. On the contrary, it is evident that the E' value of the composite was higher than that of the PLLA matrix throughout the whole temperature range studied, and this high value was almost maintained up to 120°C: this reveals a relatively high thermal resistance of this composite.

4. CONCLUSIONS

An environmentally friendly composite, made of papyrus-stem milled particles and PLLA resin, was obtained. The papyrus particles were well dispersed in the matrix. This composite possesses superior mechanical and thermal properties compared with PLLA. These mechanical and thermal properties were attained for this composite without any surface modification; which implies high interfacial adhesion between papyrus and PLLA. In addition, papyrus intrinsically provides very high propensity for soil and water purifications and CO_2 absorption. Accordingly, the world famous papyrus can be a good candidate for the reinforcement of the modern environmentally friendly composite.

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