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Papyrus Reinforced Poly(L-lactic acid) Composite

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Running Head; Papyrus/ PLLA Composite

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ABSTRACT

Mechanical reinforcement of 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 70μm) 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.

Key Words; 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 because of ecological and economical reasons, but also because of their high mechanical and thermal performance. 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 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. 4000BC, 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, the 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". Papyrus, with its Latin name, *Cyperus Papyrus* L., is a plant with its height grown to 4 m at maximum. During growth, papyrus absorbs nitrogen and phosphorus included from the soil / water [5,6]. It also accumulates carbon dioxide at a significantly high rate [7]. Thus papyrus should be a good candidate as 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 their lifetime during the use and storage, but degrade microbially and/or environmentally after disposal. PLLA possesses relatively high melting point (usually around 160℃) [8] and high mechanical performance [9,10] compared with other polymer. However, relatively low glass transition temperature restricts the thermal resistance as shown below in Figure 6.

In this study, papyrus/PLLA composite was prepared, and the mechanical properties of the composites were investigated.

2. EXPERIMENTAL

2.1. Materials and Sample Preparation

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

Figure 1 shows the photographs of a) whole stem, b) cross-section of papyrus stem, and c) scanning electron micrograph of the pith/bast interface of 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 others (ash, pectin etc.) [11]. 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 mesh (No.100).

Figure 2 shows the scanning electron micrograph of the particles from the papyrus stem used in this study. The average size of the particle was 70μ m. 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 compared with that of the bast.

PLLA (Mitsui Chemicals Inc., LACEA, the viscosity average molecular weight $Mv = 3.9 \times 10^4$) was used as matrix.

Both papyrus particles and PLLA were dried at 70℃ in advance, then kneeded using a brabender batch-type mixer (Labo Plastomil, Toyoseiki, Ltd.) at 180℃, 8min with the rotating speed of 60 rpm. The papyrus content of the composite could be changed from 0～50 wt%; determined from the weight loss on the thermogravimetric trace.

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

2.2 Measurements

Stress-strain curve for the composite was measured by a tensile tester (Shimadzu, Autograph AGS-1kND) at room temperature. The initial length of the specimen was 20mm and the extension rate was 2mm/min.

The dynamic storage modulus was measured using a dynamic mechanical analyser (DVA-220S (ITK Ltd.)) from 20 to 130 ℃. A heating rate of 6 ℃/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 monotonously with increasing papyrus content, and it reached 4.2 GPa at 50 wt% papyrus content: i.e. twice the modulus of 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: $E = E_o(1+2.5\ V_f)$, 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 [12]. This suggests that the reinforcement is mainly due to the volumetric effect in this study.

Figure 4 shows the effect of the papyrus content on the tensile strength of the papyrus/PLLA composite. The tensile strength often tends to decrease by the incorporation of the filler for the conventional particulate filled composite [13,14]. However, the tensile strength of this composite was almost constant at around 48 MPa (or even higher) up to the papyrus content of 50 wt%.

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 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 [15]. The papyrus pith contains large amount (2.1 wt%) of pectin compared with hard wood (0.1wt%), which may account for the high dispersibility of papyrus particles in PLLA. From Fig.5, 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 sample was relatively good enough, so the whole failure of the composite occurred both through the interfacial debonding and the particle and/or matrix fracture. Further increase of particles 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℃ corresponding to the glass transition of PLLA. The re-increase of the *E'* value above 100℃ 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℃: 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 without surface modification. This composite possesses superior mechanical and thermal properties compared with PLLA. In addition, papyrus provides very high abilities of the soil/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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Figure Captions

Fig.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.

Fig.2 Scanning electron micrograph of the particles from the papyrus stem. (Average size is 70μm)

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

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

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

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

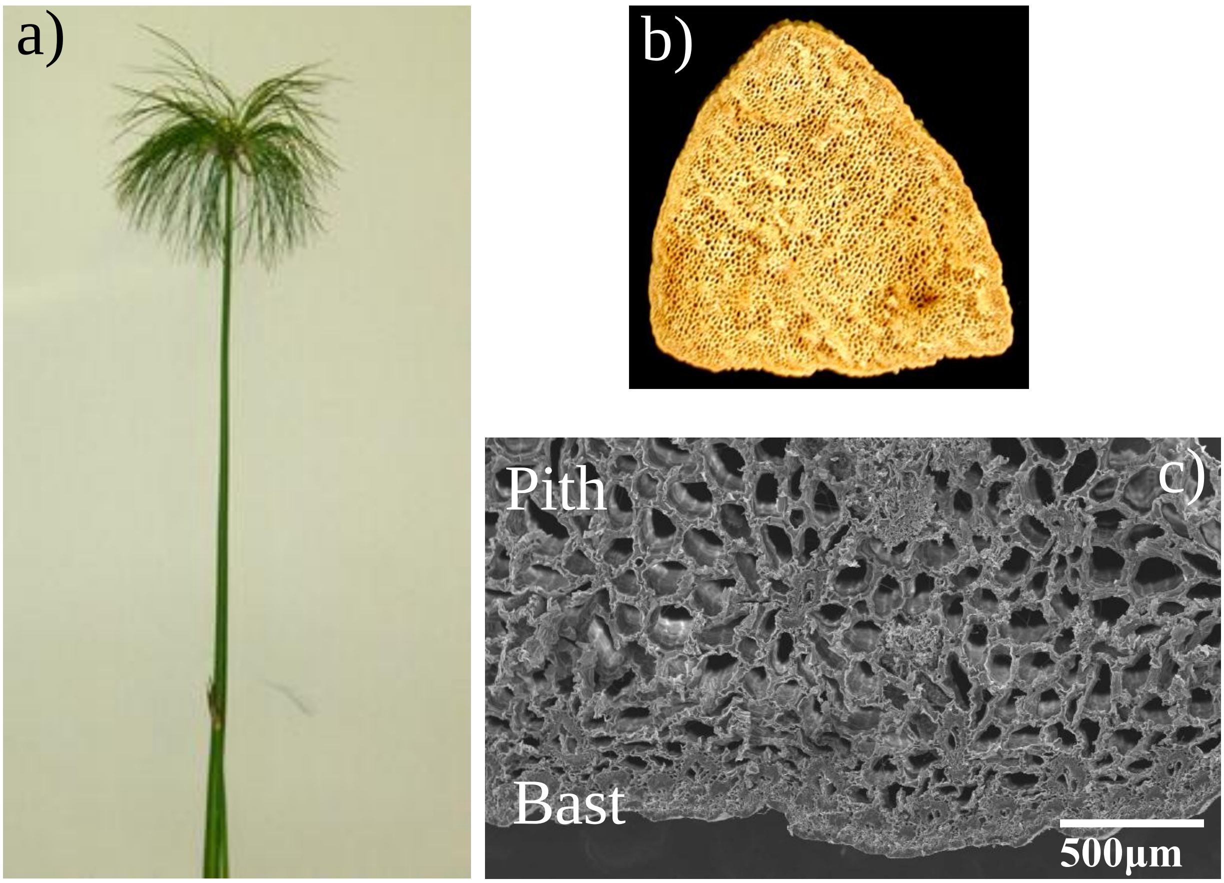

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Fig.1 Nishino@kobe-U.

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

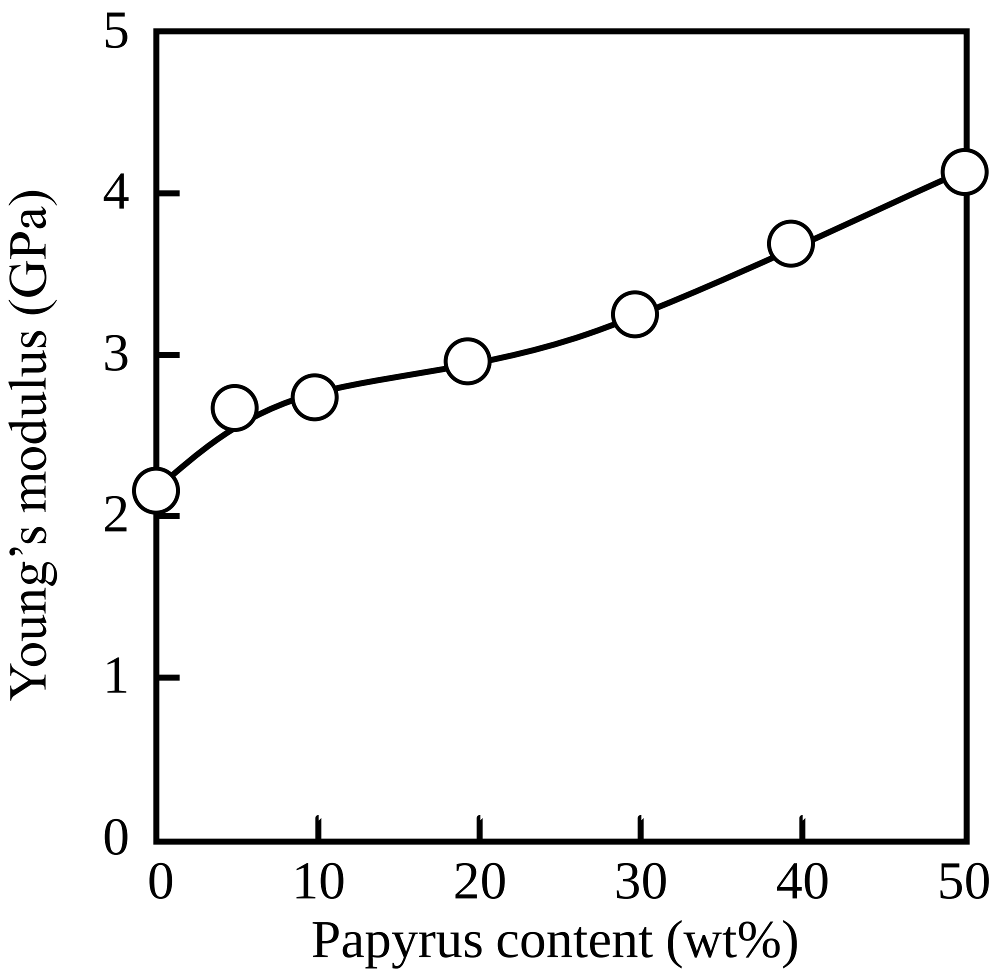

Fig.3 Relationship between Young's modulus and the papyrus particle content of the papyrus / PLLA composite.

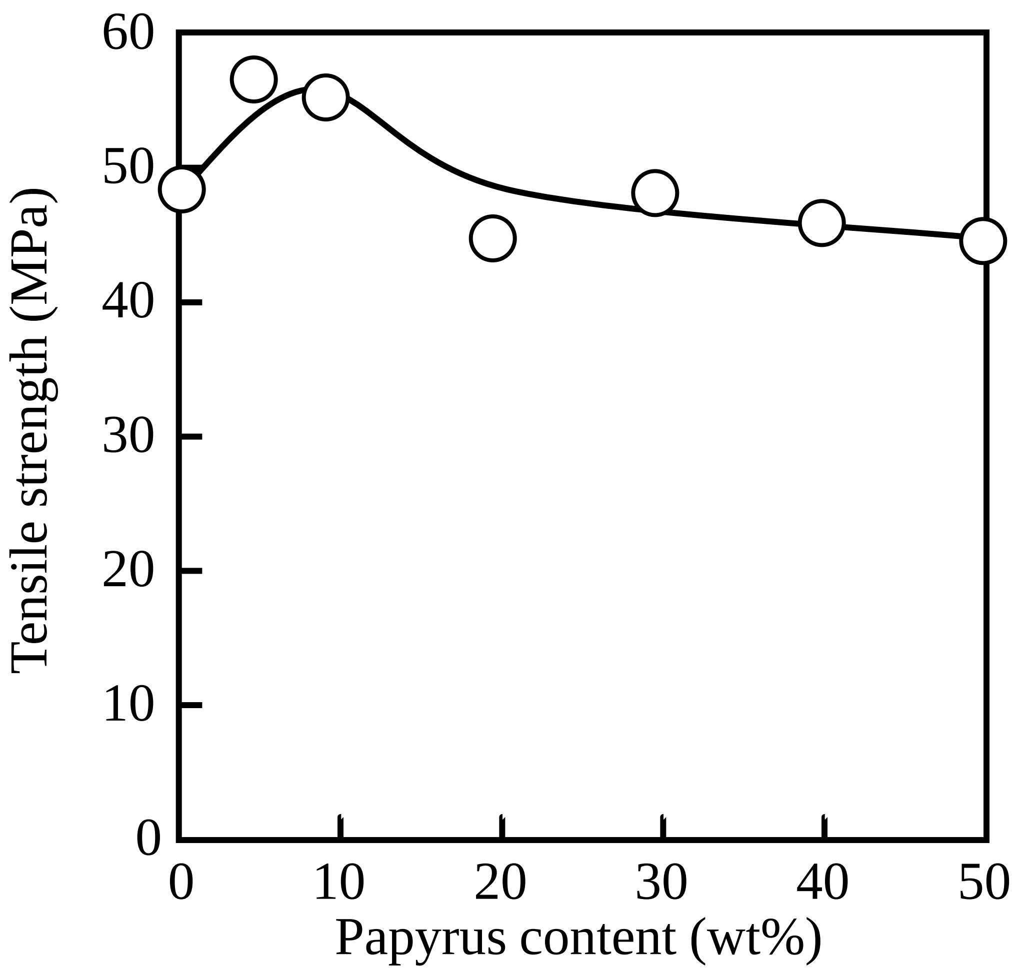

Fig.4 Relationship between the tensile strength and the papyrus particle content of the papyrus / PLLA composite.

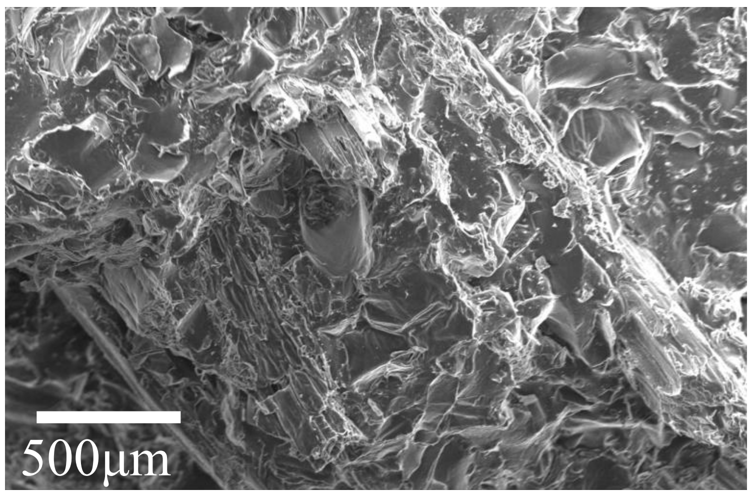

Fig.5 Scanning electron micrograph of the fractured surface of the papyrus / PLLA composite (Papyrus content = 20 wt%).

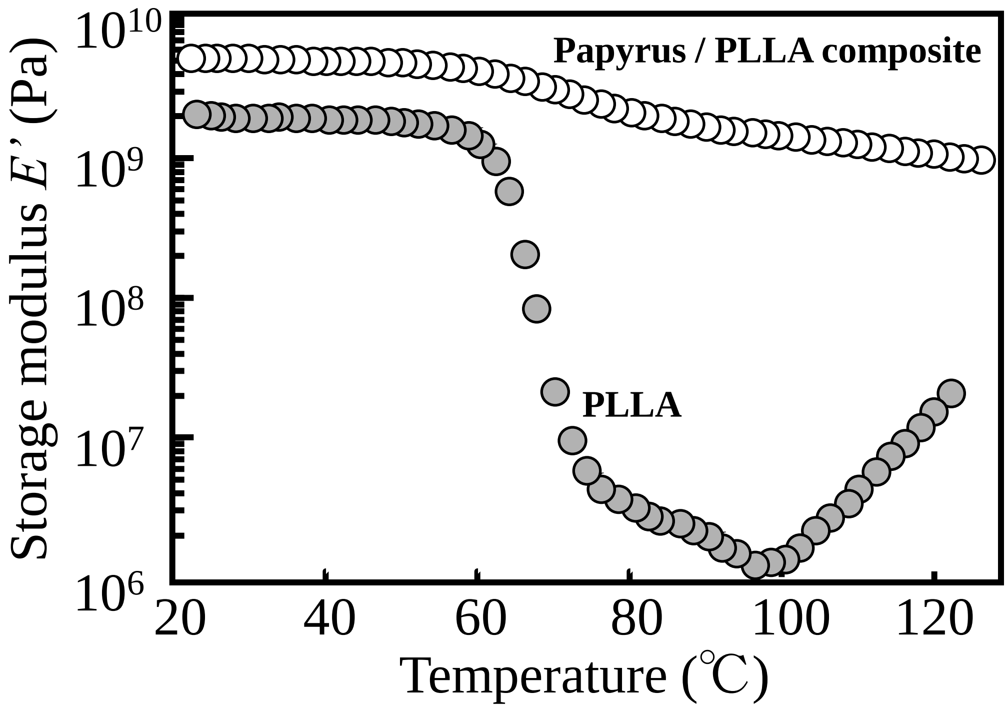

Fig.6 Temperature dependence of the storage modulus *E'* for PLLA and the papyrus / PLLA composite (Papyrus content = 50 wt%) at 10Hz.

Fig.6 Nishino@kobe-U.