

## Nature's High-Strength Semitransparent Film: The Remarkable Mechanical Properties of *Prunus Serrula* Bark

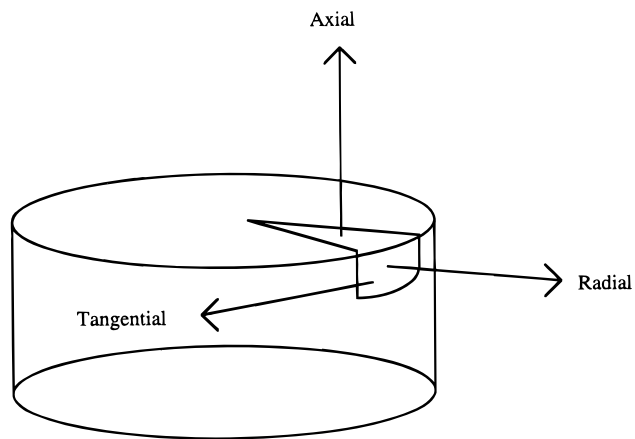
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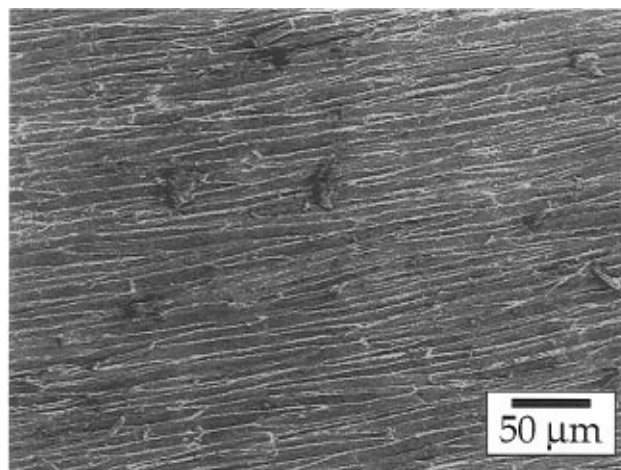
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*Prunus serrula*, commonly called the birch bark cherry,<sup>1</sup> is a member of the rose family (*Rosaceae*). Native to the mountains of northern China, the tree traditionally has ornamental value due to its characteristic shiny, mahogany-brown, exfoliating bark. This bark drew our attention, not only because it is visually attractive but also because it is tough, flexible, and semitransparent. In this report we describe the morphological characteristics and mechanical properties of this strong natural polymer film. Morphological characterization of the biodegradable<sup>2</sup> film was performed by cross-polarized optical microscopy and scanning electron microscopy (SEM), while the mechanical behavior was quantified by tensile tests.

Currently a vast array of naturally occurring materials is widely used due to their excellent materials properties and biodegradability. Almost all natural materials that must bear a load such as wood, bone, and muscle are composites. The structures of many of these materials are cellular or foams which permit an optimization of stiffness and strength for a given weight of material. Wood is a fibrous composite that consists of long, hollow cells packed together like straws. Both the foam component and the cellulose fibrils within the cell secondary walls are aligned parallel to the tree growth axis, giving wood a higher axial modulus and strength. Cork, the bark of *Quercus suber* L., due to its excellent materials properties is used in a variety of applications such as bottle stoppers, acoustic insulators, and shock absorbers. Cork's excellent elastic properties are due to a honeycomb of hollow cylindrical cells, 25  $\mu\text{m}$  wide and 50–100  $\mu\text{m}$  long, arranged radially (Figure 1 defines tangential, axial and radial) outward. Contrary to the rough, spotted countenance of cork, the appearance and texture of the bark of *Prunus serrula* is remarkably like that of a semitransparent yellow synthetic plastic film; e.g., Kapton. The film is ductile, as strong as Mylar<sup>3</sup> and as tough as Kevlar.<sup>4</sup>



**Figure 1.** Schematic of a tree section showing the definition of various directions.



**Figure 2.** SEM plane micrograph showing 5–10  $\mu\text{m}$  wide fibers aligned parallel to the bark wrapping direction.

Bark samples were collected from a *Prunus serrula* tree at Meerkerk Rhododendron Gardens in Whidbey Island, WA. The optical birefringence was examined with a Nikon Microphoto FX optical microscope equipped with cross polarizers. Thin sections were dehydrated in a *tert*-butyl alcohol series and then infiltrated and embedded in paraffin. The samples were then sectioned on a rotary microtome.<sup>5</sup> Surface morphology was examined with JEOL 6300F and Bausch and Lomb Nanolab scanning electron microscopes. Tensile testing was performed on an Instron tensile tester (Model 1123) with a 500 N load cell at an elongation rate of 12.5 mm/min. Samples were prepared by slicing the film into thin sections 5 mm wide by 25 mm long. Tensile tests were performed on samples oriented along and perpendicular to the cell axes. Macroscopically, the long cells are aligned and appear as fibers. The density of the bark film was measured by the floatation (pycnometer) method in aqueous cesium chloride.

The *Prunus serrula* bark is an anisotropic film that unwraps itself horizontally around the tree. Birefringence is exhibited under a cross-polarized optical microscope, suggesting that the film's components are oriented uniaxially. This was confirmed with a plane view SEM, shown in Figure 2, where 5–10  $\mu\text{m}$  wide fibers can be seen aligned parallel to the tangential axis (circumferential direction) of the tree (Figure 1). Figure 3 is a plane view of a thin section of the bark

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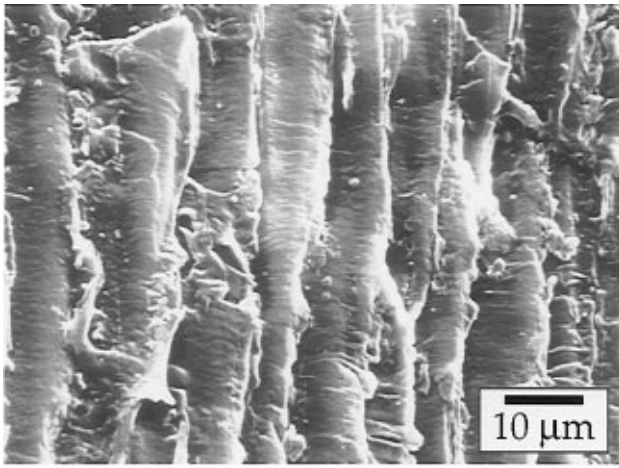
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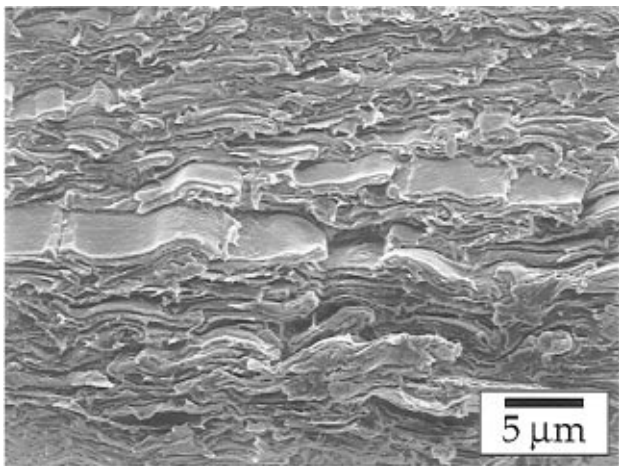
<sup>||</sup> Santa Barbara Botanic Garden.

(1) Brenzel, K. N. *Sunset Western Garden Book*; Sunset Publishing Corp: Menlo Park, CA, 1995.

(2) Samples gathered from the ground were infested with earwigs and had ca. 5 mm holes which were absent in the fresh-picked samples.

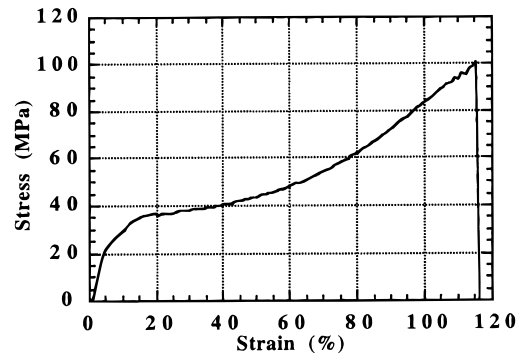


**Figure 3.** SEM plane micrograph of a thin section showing elongated cells with tapering ends and interconnected without intercellular spaces.



**Figure 4.** SEM micrograph of a cross-sectional view showing a layer structure formed by corrugated  $0.5 \mu\text{m}$  thick rectangular cells.

which shows that it is composed of interconnected, elongated cells (ca.  $8 \mu\text{m} \times 200\text{--}250 \mu\text{m}$ ) without intercellular spaces and tapered at the ends. Younger bark cells had tangential dimensions of about  $80 \mu\text{m}$ . The radial dimension of the young and older bark cells is about the same. The bark cells (technically phellem cells) do indeed stretch in a tangential direction with increasing circumference of the twig's axis. No rhytidome is present at the stage studied (i.e., the bark is composed only of phellem at the stages observed—both young and old; the old twig was 5–6 years old based on growth rings in the wood). An interesting observation is the amount of tangential expansion of the phellem cells. While tangential expansion is common, the amount is not well documented in the literature for most plant species. It appears that the cells have expanded tangentially 2–3 times over the period of a couple of years. An edge-on view of the cell walls gives them an appearance of long fibers (Figure 2), whereas a cross-sectional view (Figure 4) shows that the film consists of layers formed by corrugated  $10 \mu\text{m}$  wide and  $0.5 \mu\text{m}$  thick rectangular cells. The direction parallel to the elongated cells is defined here as the fiber axis, conforming with the convention used in the fiber and lamella composite literature. Surprisingly, unlike many bark structures where the individual cork cells have a



**Figure 5.** Stress–strain behavior of the bark of *Prunus serrula* parallel to the fiber axis.

**Table 1. Mechanical Properties of the Bark of *Prunus Serrula***

	parallel to the fiber axis <sup>a</sup>	perpendicular to the fiber axis <sup>b</sup>
tensile strength (GPa)	$0.1 \pm 0.02$	$0.024 \pm 0.02$
ductility (%)	$100 \pm 30$	$6 \pm 1$
Young's modulus (GPa)	$0.94 \pm 0.33$	$0.67 \pm 0.03$
toughness ( $10^4 \text{ J/kg}$ )	$4.2 \pm 1.5$	$0.062 \pm 0.024$

<sup>a</sup> Seven samples were tested. <sup>b</sup> Four samples were tested.

cuboidal or slightly expanded tangentially axis, the cork cells of *Prunus serrula* exhibit a tangential enlargement many times the radial dimension; i.e., they have a **large aspect ratio**.

A typical stress–strain behavior of the bark along the fiber axis is shown in Figure 5 and the mechanical properties of the bark are summarized in Table 1. The average axial Young's modulus was  $0.94 \text{ GPa}$  with a tensile strength of  $\sim 100 \text{ MPa}$ . The bark also displayed high axial strain to failure (100%) and a toughness of  $4 \times 10^4 \text{ J/kg}$ . The average axial tensile strength of the bark is about two-thirds that of Mylar ( $172 \text{ MPa}$ )<sup>3</sup> and much higher than that of cork ( $1 \text{ MPa}$ ).<sup>6</sup> The high values of Young's modulus and ductility are unprecedented for tree bark, especially high toughness values.<sup>4</sup> At low strains, the bark shows elastic deformation due to straightening and aligning of the cells along the direction of tension. Upon further deformation, a plateau region exists where the cell walls stretch until finally the stress–strain curve steeply rises to failure. Figure 6 shows that with a draw ratio of 2, the Young's modulus can be increased to  $2.6 \text{ GPa}$ , which is 360% higher than the undrawn film ( $0.72 \text{ GPa}$ ). This is similar to a process known as draw-strengthening used in the polymer industry to produce high strength fibers and films. Figure 7 shows that perpendicular to the fiber axis the tensile strength is only one-fourth of the axial tensile strength ( $0.24 \text{ GPa}$ ) with a much lower strain to failure of ca. 6%. The anisotropic mechanical properties of the bark are due to the elongated cell shape and aligned cell wall fibers. Anisotropic properties are also commonly seen in woods which typically have tensile strengths of  $35\text{--}55 \text{ MPa}$  along the growth axis of the tree, 3 times higher than across the axis.<sup>7</sup> Note

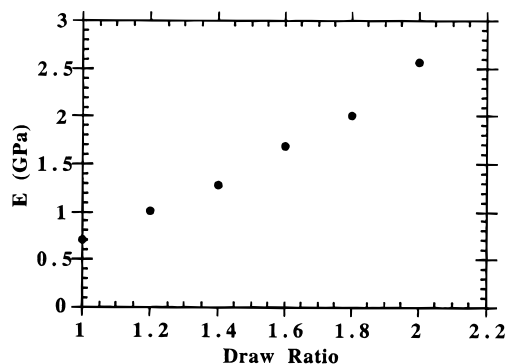
(3) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; John Wiley & Sons: New York, 1989.

(4) Tirrell, D. A. *Science* **1996**, *271*, 39.

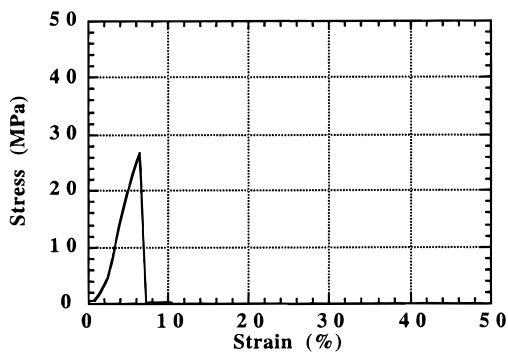
(5) Johansen, D. A. *Plant Microtechnique*; McGraw-Hill: New York, 1940.

(6) Rosa, M. E.; Fortes, M. A. *J. Mater. Sci.* **1991**, *26*, 341.

(7) Ashby, M. F.; Jones, D. R. H. *Engineering Materials*; Robert Maxwell, M.C.: 1980; Vol. 34.



**Figure 6.** Increasing Young's modulus of *Prunus serrula* bark with increasing draw ratio along the long axis of the sample, corresponding to the cells' long axes.



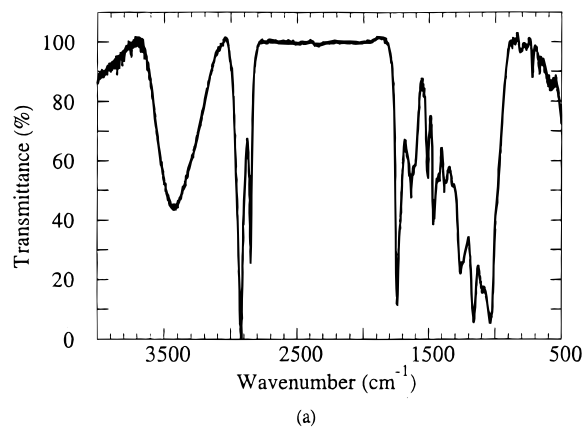
**Figure 7.** Stress-strain behavior of a *Prunus serrula* bark sample measured perpendicular to the long axis of the sample.

that contrary to wood and most known tree barks, in the *Prunus serrula* bark, the tree growth axis is one of the perpendiculars to the bark's fiber axis. As we have documented, through a comparison of different developmental stages, this pattern results from tangential (or circumferential) stretching of the phellem. For cork, the relatively isotropic cells are aligned in a radial direction (Figure 1), giving rise to relatively isotropic mechanical properties.

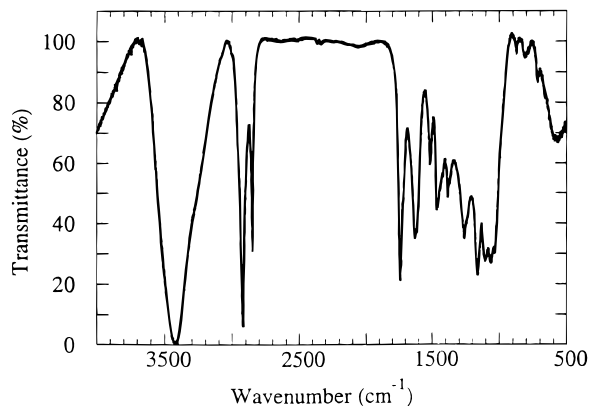
The rather high value of the density of the *Prunus serrula* bark ( $1.239 \text{ g/cm}^3$ ) also contributes to its mechanical properties. It is denser than most of the barks reported in the literature.<sup>8</sup> Although the chemical composition of all barks is almost the same, containing cellulose, hemicellulose, lignin, polyphenols, suberin and some extractives<sup>9</sup> (see Figure 8 for comparative infrared spectroscopy) the mechanical properties vary drastically depending on density. The density of cork reported by Rosa<sup>6</sup> is  $0.155 \text{ g/cm}^3$ ; other species were reported by Martin.<sup>8</sup> Most bark densities are less than  $1 \text{ g/cm}^3$ , except for the yellow poplar, *Liriodendron tulipifera* L,

(8) Martin, R. E.; Crist, J. B. *Forest Prod. J.* **1968**, *18*, 54.

(9) Fengel, D.; Wegener, G. *Wood, chemistry, Ultrastructure, Reactions*; Walter de Gruyter & Co.: Berlin, 1984.



(a)



(b)

**Figure 8.** (A) Fourier transform infrared spectrum (FTIR) of *Quercus suber* bark (common cork). (B) FTIR of *Prunus serrula* bark.

whose density ranges from  $0.986$  to  $1.291 \text{ g/cm}^3$ . Even though the density of the *Prunus* bark is comparable to that of yellow poplar, it is 10 times stronger and 200 times tougher. A general trend directly relating wood tensile strength to density was established before.<sup>8</sup>

In summary, we have shown that the birch bark cherry produces, as its outer layer, a thin, semitransparent film with clear legibility through it when placed directly on any written surface. The mechanical and physical properties described in this preliminary report demand a more thorough exploration of this unusual biomaterial, from a fundamental as well as an applied standpoint.

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