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Modification of the Semitransparent *Prunus serrula* Bark Film: Making Rubber out of Bark

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We report an extensive structural and mechanical characterization of the semitransparent bark of *Prunus serrula*. Variations in the properties were observed. Mechanical properties along the fiber axis of these films are strongly related to the cell dimensions. Several trends can be seen with increasing cell length: tensile strength and Young's modulus increase; ductility decreases. Perpendicular to the fiber axis, similar radial dimensions of the bark cells contributes to similar mechanical properties. Plasticization not only shrinks the dimension of the bulk films along the tangential axis, which is unique, but also dramatically changes the mechanical properties. We have shown, for the first time, that the mechanical properties of the *Prunus serrula* bark can be effectively tailored with different plasticization and modification agents. The plastic bark can be successfully converted to rubberlike material either temporally or permanently, or it can be strengthened by tensile deformation of the plasticized bark.

Introduction

Biomaterials, such as drug and gene delivery biopolymers,[1] bacteria-produced silk proteins,[2,3] and bone replacement materials,[4] have generated intense interest in the biology and materials science communities. Other studies are currently underway in the area of biomineralization to understand how nature works in assembling its raw materials into the "final products".[5,6] For example, calcium carbonate ($CaCO_3$) can be formed as fibers, platelets, or blocks depending upon the structure-directing agent present.

We recently reported on the remarkable properties of the semitransparent bark of *Prunus serrula* or birch-bark cherry.[7] This natural composite plastic film has anisotropic mechanical properties due to its elongated cell structure and high density. The average tensile strength along the fiber axis is 100 MPa with 100% elongation to failure and toughness of 4×10^4 J/kg. These values are comparable to those of commercially important films such as Mylar [poly(ethyleneterephthalate)] or Kapton;[8] therefore, the bark of *P. serrula* is an attractive alternative to commercial synthetic films. The Young's modulus along the fiber axis can be increased to 2.5 GPa, by tensile deformation to a draw ratio of 2.0. The tensile strength across the fiber axis is ∼24 MPa with a strain to failure of 6%.

A large number of techniques have been used to modify or enhance the physical properties of wood composites, such as plasticization, chemical modification, and polymeric impregnation.[9] Steam has been used for many years to plasticize wood, where the combined effects of heat and moisture reduce the stiffness of wood and permit deformation into various shapes. The dimension of the wood cells often expands after chemical treatments. Plasticizers, such as poly(ethylene glycol), have been used to lock in the changes in dimensions.[10,11] Recently, Aksay and co-workers showed that by infiltrating inorganic precursors, such as silica into hollow wood cells, the mechanical properties of wood can be enhanced.[12] All work has so far been conducted on wood, not bark materials. In this report, we performed an extensive characterization of samples

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collected from different parts of the tree as well as chemically modified samples for comparison and show that the properties of the *P. serrula* bark can be effectively tailored with different plasticization and modification agents.

Experimental Section

Materials and Characterization. Three *Prunus serrula* branches were collected at Meerkerk Rhododendron Gardens in Whidbey Island, WA. Bark films were peeled off from the branches immediately before any characterization or modifications. Samples were prepared by slicing the film into thin sections 5 mm wide by 25 mm long. Optical birefringence was examined with a Nikon Microphoto FX optical microscope equipped with cross-polarizers. Surface morphology was examined with a JEOL 6300F scanning electron microscope. Fourier transform infared (FTIR) spectra were recorded on a Mattson Galaxy 3000 spectrometer using conventional KBr wafer techniques. Elemental analyses were obtained from Atlantic Microlaboratory, Inc., and Galbraith Laboratory, Inc. Thermogravimetric analysis (TGA) was performed under dry air on a Perkin-Elmer TGA 7 thermogravimetric analyzer. 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. Tests were performed on samples oriented either parallel or perpendicular to the cell axes. Macroscopically, the long cells are aligned and appear as fibers. The direction parallel to the elongated cells is defined as the fiber axis, conforming with the definition in our previous report.[7] The density of the bark film was measured by the flotation (pycnometer) method in aqueous cesium chloride.

All reactions were carried out in nitrogen atmosphere. Pyridine was dried and distilled over potassium hydroxide and stored under 4A activated molecular sieves (J. T Baker Inc.). Toluene was dried and distilled over calcium hydride. Reagent grade chlorotrimethylsilane (TMSCl), ethylene glycol, and poly(ethylene glycol) ($M_r = 200$ g/mol) were purchased from Aldrich and used without further purification.

Chemical Plasticization and Modification. Plasticization was carried out by mixing 0.2 g of bark with 5 g of ethylene glycol or poly(ethylene glycol) (PEG). After the mixture was stirred at 50−60 °C for 2 days, the bark films were recovered and the excess plasticizing agent was blotted away with a paper tissue and dried in air. Silylation of the cellulose (chemical modification) was performed by immersing 0.146 g of bark in 10 mL of dry toluene in a round-bottom flask equipped with a condenser, to which TMSCl (0.586 g, 5.39 mmol) and pyridine (0.465 g, 5.87 mmol) were added consecutively.[13] After stirring of the mixture at 110 °C for 2 days, the bark was recovered, washed with distilled water, and dried in air.

Bark films with enhanced mechanical properties were obtained from draw-strengthening of the ethylene glycol-treated bark. The plasticized films were prestretched to their maximum strain using a homemade stainless steel stretcher. Ethylene glycol was removed in a vacuum oven at 60 °C for 2 days.

Results and Discussions

Morphological Characterization. Samples from three branches with diameters of 0.60, 0.73, and 1.13 cm, five, six and seven years old on the basis of growth rings analyses of the secondary xylem (wood), were examined. Each bark sample has two layers of phellem in the periderm (bark) and an inner layer consisting of the secondary phloem or the inner bark. The physical appearance of the outer and middle layers is very similar to that of the bark obtained from the main trunk, which is semitransparent, glistening, mahogany brown and can be easily peeled off. The inner layer, however, is a nontransparent yellow film which is closely attached to wood. The outer and middle layers of the three branches are optically anisotropic and show birefringence under a cross-polarized optical microscope. A typical SEM examination of these samples in Figure 1 (taken from ref 7) shows that bark films are composed of interconnected elongated phellem (cork) cells. Although the radial dimension was measured to be about the same throughout the three samples (~8 μm × 0.5 μm), the tangential length of the bark cells increases with increasing circumference of the branch axis, as shown in Table 1. Therefore, the cells in the outer layer of the seven-year-old branch have the longest tangential length of 160 μm among the three branches but are only about 70% of the "trunk bark". Generally with age, cell length increases by ~60% from the middle layer outward. (~20% increase from five- to the seven-year-old branch). The aspect ratio, i.e., the tangential length over the radial dimension, increases as the bark expands during tree growth and is proportional to the circumference of the branch. The inner layers (phloem) of the three branches, however, lack a definite cell structure and birefringence.

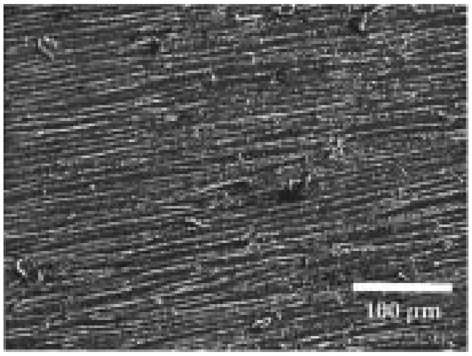

Figure 1. SEM plane micrograph of the outer layer of the seven-year-old branch, showing 5−10 μm wide fibers aligned parallel to the bark wrapping direction.

Table 1. Tangential Cell Length of the outer Two Layers of the Five-, Six-, and Seven-Year-Old *P. serrula* Branches

branch age	branch diameter (cm)	layer	cell length (μm)
5	0.60	outer	160
		middle	98
6	0.73	outer	168
		middle	104
7	1.13	outer	187
		middle	116

Mechanical Properties. All bark films exhibit anisotropic mechanical properties due to the aligned, elongated cell shape. Variations in the properties of bark samples were observed. Several trends can be seen with increasing cell length: tensile strength and Young's modulus increase; ductility and density decrease. The mechanical properties and densities of the three layers of the seven-year-old branch are shown in Table 2. Although the outer layer has the highest tensile strength of 55 MPa, it is only 55% of the "trunk bark" whose cell length is 34% longer. The mechanical properties of the three layers of the five- and six-year-old branch are lower than that of the seven-year-old but follow the same trend with increasing cell length. All three layers

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Table 2. Mechanical Properties of the Three Layers of the Seven-Year-Old Branch, Showing a Strong Dependence on the Cell Length

sample[a]	cell length (μm)	σ_{TS}[b] (MPa)	ϵ (%)[b]	*E* (GPa)[b]	*d* (g/cm^3)
outer layer	187	56 ± 5	35 ± 5	0.72 ± 0.15	1.113
middle layer	116	37 ± 4	66 ± 8	0.52 ± 0.10	1.239
inner layer		26 ± 2	102 ± 10	0.33 ± 0.06	1.306

[a] Six samples of each were tested. [b] *E*, Young's modulus; σ_{TS}, tensile strength; ϵ, strain.

of *Prunus serrula* are denser than most of the bark species;[14] however, the mechanical properties of the three layers decrease as their corresponding density increases. It is concluded that although the high density may contribute to the overall high mechanical properties of the *P. serrula* bark, it is less important than cell length. Perpendicular to the fiber axis, similar radial dimensions of the bark cells contribute to similar mechanical properties. All three bark layers have a tensile strength of 24 MPa, Young's modulus of 0.7 GPa, and elongation to break of 6%. These values are comparable to that of the "trunk bark" as well as the three layers of both the five- and six-year-old branches. Due to the similar properties between the seven-year-old branch and the five- and six-year-old branch, further characterization was all based on the seven-year-old branch.

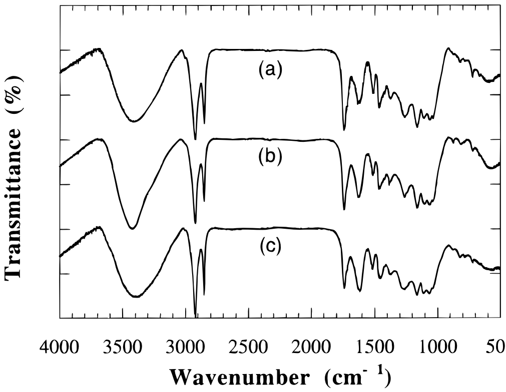

Figure 2. Fourier transform infrared spectrum (FTIR) of the three layers of the seven-year-old branch: (a) inner layer; (b) middle layer; (c) outer layer.

Table 3. Elemental Analyses of Cork, the "Trunk Bark", and the Three Layers of the Seven-Year-Old Branch of *P. serrula*

sample	C (%)	H (%)	N (%)
cork[a]	62.38	8.00	0.63
"trunk bark"[b]	59.51	7.91	<0.5
outer layer[a]	58.94	7.52	0.25
middle layer[a]	58.64	7.71	0.26
inner layer[a]	58.48	7.55	0.34

[a] Results obtained from Atlantic Microlaboratory, Inc. [b] Results obtained from Galbraith Laboratory, Inc.

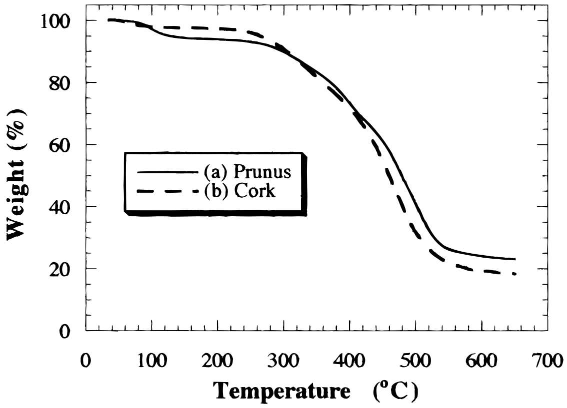

Figure 3. Thermogravimetric analysis (TGA) under air with heating rate of 10 °C/min: (a) outer layer of the seven-year-old *Prunus serrula* branch; (b) cork, the bark of *Quercus suber* L.

Chemical Composition. The FTIR spectra demonstrated that the chemical composition of the "trunk bark" of *P. serrula* is very similar to that of cork, the bark of *Quercus suber* L.[7] Both have a broad OH stretching vibration at ~3440 cm^{-1}, two sharp CH stretching bands at 2929 and 2851 cm^{-1}, and a strong carbonyl stretching vibration at 1740 cm^{-1}. The *Prunus* "trunk" bark has a stronger C=C stretching band at 1627 cm^{-1}. The major IR stretching vibrations of cork were assigned to its various chemical constituents.[15] (Cork is composed of 40% suberin, 22% lignin, 20% polysaccharides, 15% waxes, and other extractives.[16]) Compared to the "trunk bark", the middle layer of the seven-year-old branch has the same FTIR spectral characteristics. The outer and inner layers, however, have slightly different IR spectra shown in Figure 2, which suggest a slightly different chemical composition. The intensity of the carbonyl stretching vibration decreases from the inner layer outward. This is due to the lack of extractives (tannins and fats) in the outer layer, which is common in most bark species.[17] This was further confirmed by the FTIR spectrum of an extractive free middle layer, whose carbonyl stretching vibration intensity decreases significantly. Similar elemental analyses for carbon, hydrogen, and nitrogen of cork, "trunk bark", and the three bark layers of the seven-year-old branch of the *P. serrula* bark, shown in Table 3, also suggest that cork and *Prunus serrula* bark have similar chemical compositions. In addition to organic components, *Prunus* bark contains some inorganic substances including 0.3 wt % silicon, 0.15 wt % calcium, 0.11 wt % sodium, and 0.04 wt % potassium.

Thermal Stability. Information on water content and identification of the temperatures at which chemical processes occur is provided by thermogravimetric analysis (TGA). The thermal analysis results of *Prunus* bark and cork, in Figure 3, show that the *Prunus* bark is as thermally stable in nitrogen as cork. This is expected due to their similar chemical compositions. At 50−80 °C there is a ~5% weight drop due to loss of water. This is confirmed by FTIR analysis, where the spectrum of the 80 °C vacuum-oven-dried *Prunus* powder remained unchanged, except for a lower intensity of the OH stretching vibration. The bark did not decompose until 280 °C, where there was a major weight loss of ~70%. In addition, the TGA data are similar to those of cork,[18]

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Table 4. Dimensional Changes of the Outer and Middle Layers of the Seven-Year-Old Branch of *P. serrula* after Plasticization

plasticizing agents	sample	axial[a]	radial[a]	tangential[a]
ethylene glycol	outer layer	3.3	113	−23
	middle layer	1.2	53	−3
PEG 200	outer layer	12	235	−32
	middle layer	0.6	101	−3.6

[a] Expansion (%) of air-dry measurements: +, increase; −, decrease.

where there is a 3% water loss at ~100 °C and a weight loss of ~80% at approximately 260 °C. Upon heating, the content of extractives in cork decreases rapidly. Polysaccharides, however, are more heat sensitive than the rest of the main components, such as suberin and lignin. They start to degrade in cork at 200 °C. Suberin is more resistant and starts to degrade at approximately 250 °C. As temperature increases, the condensation reaction of the lignin side chains starts to increase. At 550 °C, only 20% of cork ash remains.

Modification of Mechanical Properties. *Plasticization.* Plasticizing agents have a strong influence on the mechanical and structural properties of the *Prunus* bark. Cellulose in *P. serrula* bark was found to be mostly amorphous.[19] However, it uniquely contains two cellulose polymorphs of crystal structure of cellulose I and II, where the cellulose fibers are strongly connected to each other with intra- and intermolecular hydrogen bonding.[19] Cellulose is known to swell in hydrogen-bonding solvents such as water, and the dimensional changes on the bulk materials are well documented.[9] The swelling is restricted only to the less dense amorphous regions. The crystalline regions, however, can be disrupted or modified only when sufficient energy is available to rupture the intermolecular hydrogen bonds, e.g., in the presence of strong alkaline agents.[9,20]

Dimensional changes induced by ethylene glycol and PEG 200 in the outer and middle layers of the seven-year-old branch are shown in Table 4. Elevated temperature was used to reduce the viscosity and to increase the flow and penetration rate of the plasticizing agents. The bulk film of the plasticized outer bark layer shrinks up to one-third of its original film length along the tangential axis, expands by a few percent in film width along the axial axis, and increases up to three and a half times its original film thickness along the radial axis. The bulk film of the plasticized middle layer shrinks ~90% less tangentially and expands ~50% less axially and radially compared to that of the outer layer.

Dimensional changes have been well documented for chemically plasticized wood[10] and certain bark species.[14] Unlike the *Prunus* bark, all three dimensions expand after treatment with chemicals. For example, after treatment with different alcohols and water, red pine expands on an average by 10% along the axial axis, 6% along the tangential axis, and 3% along the radial axis. After treatment with ethylene glycol, wood has an axial expansion of 15%, tangential expansion of 10%, and radial expansion of 5%. After plasticizing with water, 10 species of bark expanded on average by 3% axially, 6% tangentially, and 8% radially. Yet, the *P. serrula* bark shrinks along the tangential axis after plasticization. This is due to the relaxation of the originally strained cell with large aspect ratio. We have shown earlier that the cell length increases with branch circumference during tree growth and the outer layer is strained more in the tangential direction than the middle layer. The plasticizing agents help to relax the stretched and aligned cell walls caused by tree growth; therefore, entropy increases. PEG has a larger effect on the dimensional changes than ethylene glycol.

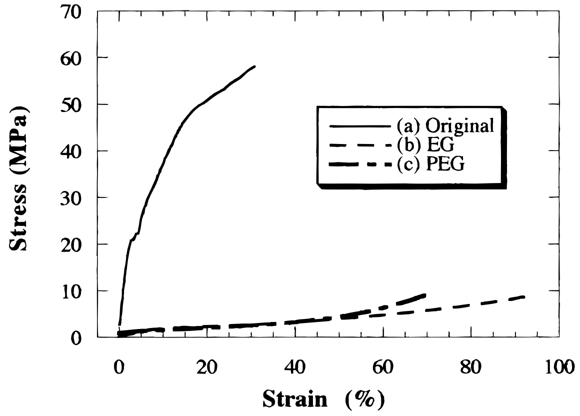

Figure 4. Stress−strain behavior of the outer layer of the seven-year-old branch: (a) original film; (b) ethylene glycol-plasticized film; (c) poly(ethylene glycol)-treated film.

Table 5. Mechanical Properties along the Fiber Axis of the Original, Plasticized, and Strengthened (by Tensile Deformation) Bark Films of the Outer Layer of the Seven-Year-Old Branch of *P. serrula*

plasticizing agents	σ_{TS} (MPa)	ϵ (%)	E (GPa)
original	56 ± 5	35 ± 5	0.72 ± 0.15
ethylene glycol	9.1 ± 0.5	90 ± 10	0.03 ± 0.005
PEG 200	9.4 ± 0.4	104 ± 10	0.01 ± 0.003
(TMS)Cl/py	9.0 ± 0.4	120 ± 11	0.02 ± 0.004
enhanced[a]	87 ± 5	18 ± 3	1.42 ± 0.20

[a] Enhanced bark films of the ethylene glycol-treated sample.

The mechanical properties of the *Prunus* bark are dramatically affected by the plasticization. Plasticizing agents reduce the stiffness and increase the pliability of the films. The original plastic bark is converted into an elastomer whose typical stress−strain curve is shown in Figure 4. *The rubberlike films demonstrated macroscopic reversible extensions up to 100% and a decreased tensile strength and Young's modulus to 10% of its original value.* The mechanical properties of the ethylene glycol- and PEG-treated samples (the outer layer of the seven-year-old branch) are listed in Table 5. The obliterated preferred orientation of the cellulose I in the ethylene glycol-treated samples indicates that hydrogen bonding has been disrupted.[19] Lignin, a 3-D cross-linked macromolecule, may act as a β-cross-linking element in the elastomer. Plasticizing agents also shrink the originally stretched cell walls, thus destroying the alignment in the original bark. Due to the loss of both crystal structure and alignment of the cell walls, the plastic bark is converted into a rubberlike material. The elasticity of the PEG-treated bark films lasts for 6 months, 4 months longer than that of the ethylene glycol-treated bark.

Chemical Modification. Covalent modification reagents can be used to modify the intrinsic molecular

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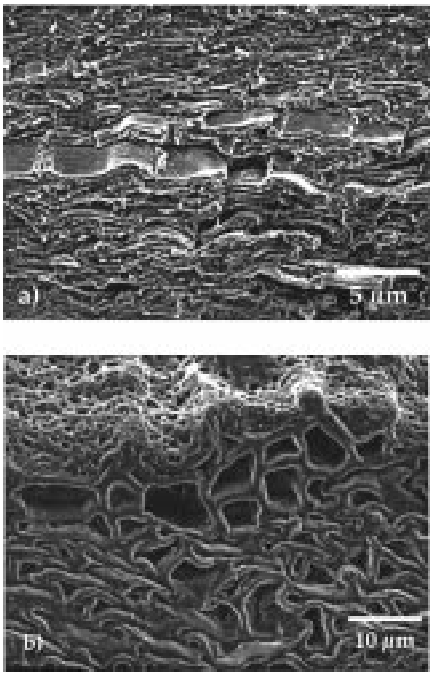

Figure 5. SEM micrograph of a cross sectional view showing the radial dimension of (a) the original *Prunus* bark (from ref 7) and (b) the chemically modified *Prunus* bark film.

structure of bark and therefore to change the mechanical properties. Chlorotrimethylsilane was used to convert the hydroxyl groups in cellulose to silyl groups and, thus, to permanently break the hydrogen bonds. Similar to ethylene glycol- and PEG-treated bark films, this modified bark shrinks tangentially and expands axially and radially. A cross-section view of the modified film in Figure 5 (Figure 5a, from ref 7) reveals that both the cell walls and the cell lumen have been expanded. The original 0.5 μm thick rectangular cells are increased to 3.9 μm. *The elastomeric behavior of these rubberlike films was confirmed by repeated loading and unloading, shown in Figure 6*, where the macroscopic elastic strain is recovered up to 100% after three loading cycles. As in the case of the other plasticized bark samples, the silylized bark exhibits a significant decrease in tensile strength and an increase in ductility as listed in Table 5. *The elastomeric behavior is still evident after 9 months of storage at room temperature in the atmosphere.* Elemental analysis of the silylized bark shows a 0.14% increase in silicon.

Enhancement of Mechanical Properties. Young's modulus of the bark films was previously reported to be increased by 260% by tensile deformation.[7] In this report, the ductility of the bark sample has been shown to increase by plasticization. Ethylene glycol-treated bark samples can increase their elongation to break by 200%. The plasticized films were stretched to an elongation of 100% to introduce the highest possible alignment of the cell walls. Ethylene glycol was then removed in a vacuum oven. Mechanical properties of the materials treated in this way, the outer layer of the seven-year-old branch, are listed in Table 5. Along the fiber axis, tensile strength increases 55% and Young's modulus increases 100% compared to the original sample. This process does not increase the Young's modulus as much as tensile deformation (260%) of the original sample.[7] This is due to loss of the original cell orientation and a decrease in the tangential length of the films after plasticization, which both minimize the overall net increase in orientation introduced by drawing.

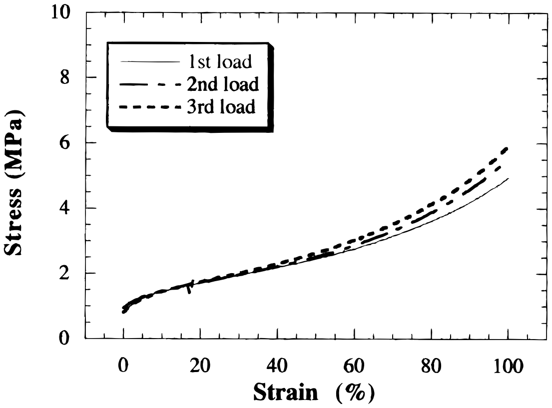

Figure 6. Stress–strain behavior of a (TMS)Cl-treated sample upon cyclic loading (the outer layer of the seven-year-old *Prunus* branch): (a) first loading; (b) second loading, (c) third loading.

Conclusion

From thorough characterization of the *Prunus serrula* bark films, we found that the mechanical properties are closely related to both cell structure and sample origin. Plasticization not only changes the dimensions of the bark cells and bulk films but also dramatically changes the mechanical properties. Although dimensional expansions have been well documented for wood and certain bark species, this *Prunus* bark shrinks uniquely in the tangential direction after plasticization. This behavior is closely related to the strained cells with large aspect ratio in the original film. The plasticizing agents help to relax the stretched and aligned cell walls caused by tree growth. We can successfully convert the plastic bark into a rubberlike material either temporally or permanently, or we can strengthen the material by tensile deformation of the plasticized bark. Other methods to enhance the mechanical properties of these films, such as polymer impregnation, will be further developed.

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