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Applications of Nanoindentation-Based Mechanical Spectroscopy in Forest Products Research

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ABSTRACT
Broadband nanoindentation creep (BNC) and broadband nanoindentation viscoelasticity (BNV) are recently developed techniques capable of assessing viscoplastic and viscoelastic properties over a wide range of time scales from small volumes of material (less than 1 μm^3). Using BNC and BNV, a nanofibrilated cellulose (NFC) film is characterized after being conditioned at 30% and 67% relative humidity (RH). Hardness and elastic modulus were found to be time- (or rate-) dependent properties that were also sensitive to RH. Hardness and elastic modulus decreased by 60% and 40%, respectively, when the RH was increased from 30% to 67%.

INTRODUCTION
We are developing nanoindentation into a probe for local mechanical spectroscopy capable of probing micron-scale features such as wood cell walls, individual components in composites, and nanofibrilated cellulose thin films. The measurements are local because artifacts arising from nearby structural heterogeneities (e.g., free edges and heterophase interfaces) can be isolated and in most cases removed from the measurement [1-4]. The spectroscopy enters through two types of experimental method. Broadband nanoindentation creep (BNC) measures viscoplastic properties across four to six decades of strain rate [5-7]. Broadband nanoindentation viscoelasticity (BNV) measures viscoelastic properties over more than eight decades of time scale [7-9]. The methods require an instrument with fast response that is also stable against thermal drift. Model materials previously studied with BNC and BNV include poly(methylmethacrylate), polycarbonate, polystyrene, and molybdenum [5, 7-9]. BNC experiments generate hardness vs. strain rate. Using the Tabor–Marsh–Johnson correlation, the hardness vs. strain rate data can be converted to compression flow stress vs. strain rate data; and the converted data agree closely with literature compression data for these model materials [5, 7]. Likewise, BNV data follow the trend of more conventional viscoelasticity measurements made using dynamic mechanical analysis and broadband viscoelastic spectroscopy [5, 7, 9]. Here, we use BNC and BNV to assess how viscoplastic and viscoelastic properties of a nanofibrilated cellulose (NFC) film change with relative humidity (RH). NFC fibers have extremely high aspect ratios (>1000) and form dense, transparent films. Characterization of NFC films is important for their application in multi-layer composites.

MATERIALS AND METHODS
An aqueous suspension of NFC was prepared from eucalyptus dry lap material using the TEMPO catalyst following a previously reported method [10]. The film was cast in a 15.2-mm hand sheet mould by vacuum suction and dried without restraints inside a 90% RH canister at room temperature for 12 days, resulting in a film thickness of about 0.1 mm. A nanoindentation surface was prepared in cross-section using a diamond knife [7-8]. In this orientation, the indentation direction is parallel to the face of the NFC film. A Hysitron (Minneapolis, Minnesota, USA) TriboIndenter equipped with a Berkovich probe was used in the work. Previously reported experimental procedures and data analyses were followed [5, 7-8]. For all indents, a maximum load of 1 mN was used. The film was tested first at 30% RH and then 67% RH. The RH inside the enclosure was controlled by changing the amount of water in a water–glycerin bath inside the TriboIndenter enclosure. The film was allowed to condition for multiple days at each relative humidity prior to testing.

RESULTS AND DISCUSSION

Figure 1a shows hardness over nearly five decades in strain rate from experiments performed at both 30% and 67% RH. Hardness increases by a factor of two over the range of strain rates tested, and the curves are slightly concave up. Hardness data from 67% RH are approximately 60% lower across all the strain rates tested than the 30% RH hardness data. In addition to the hardness data, compression flow stress data derived from the hardness data using the Tabor–Marsh–Johnson correlation are also shown in Figure 1a. Compression flow stress is a more common and better understood metric of plasticity, and in the future we will use these data to better understand the mechanisms controlling viscoplastic properties. In Figure 1b, elastic moduli over 3.5 decades of frequency are plotted. A time-dependent elastic modulus is observed. Over the range of frequencies tested, the elastic modulus drops by about 40% when the RH is increased from 30% to 67%.

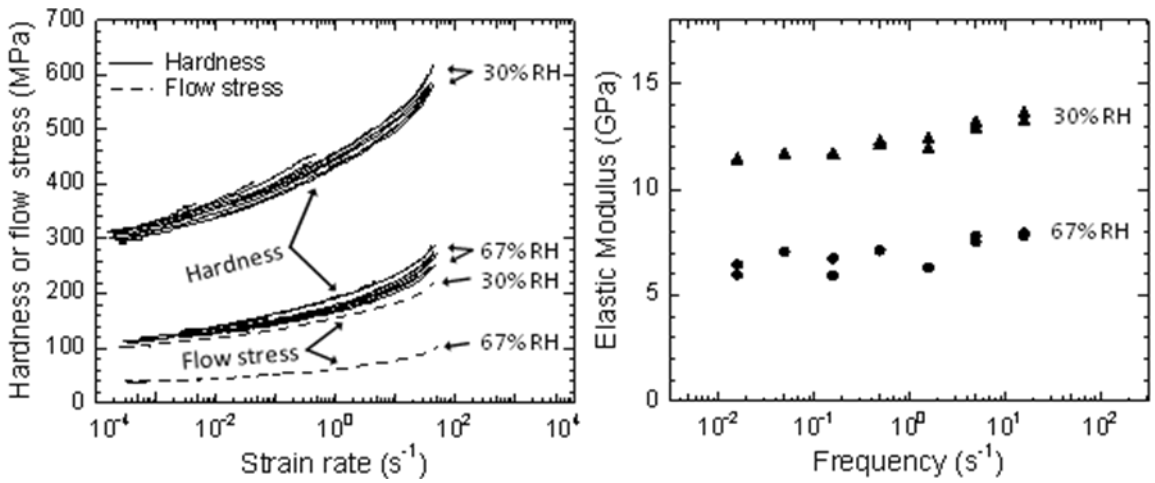

Figure 1. BNC (a) and BNV (b) results from the cross section of a NFC film conditioned at 30% and 67% RH.

CONCLUSIONS

BNC and BNV experiments showed that both hardness and elastic modulus are time-dependent in NFC thin films and increase with strain rate. When RH is raised from 30% to 67%, both hardness and elastic modulus decrease nearly uniformly over all the strain rates tested. Hardness decreases by 60%, and elastic modulus decreases by 40%.

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