

Nanoindentation of the Interphase Region of a Wood-Reinforced Polypropylene Composite

Joseph E. Jakes, John C. Hermanson, and Donald S. Stone

Abstract

The interphase region of a wood-reinforced polypropylene (PP) composite was investigated with nanoindentation techniques capable of separating intrinsic properties of PP in the interphase region from the effect of elastic discontinuity caused by the nearby wood cell wall. From data collected in this experiment, no differences in hardness or Young's modulus for PP were observed between bulk PP and PP in the interphase. Had the elastic discontinuity not been taken into consideration, the measured Young's modulus would have appeared to increase in the interphase region. Observations were also made about morphology of the composite, and it was noted that filler particles were present in the majority of PP but were absent in PP present in lumens of intact wood cells. Effects of these filler particles on the nanoindentation data were also investigated.

Introduction

In an interphase region of a wood-plastic composite (WPC), a compliant polymer matrix is adhered to a stiff piece of a wood cell wall. Properties in this interphase region transition from those of a wood cell wall to those of the bulk polymer matrix. How large this

interphase is or how properties change through the interphase is not well understood, but overall structural performance of the WPC is believed to be governed by the properties of this interphase. Therefore, a critical step in understanding a WPC is to determine the size and properties of the interphase region.

Nanoindentation is an experimental technique capable of probing volumes of material with micrometer-size dimensions, comparable to what is believed to be the size of the interphase region. But to reveal how these material properties change as a function of position through the interphase region, efforts must be made to separate the intrinsic properties of the interphase material from the effect of the neighboring bulk polymer matrix and wood cell wall. In this paper, a simple nanoindentation method capable of separating the intrinsic material properties of the interphase material is presented.

Previous Work

Only a few published attempts have been made to characterize the mechanical properties of the interphase in a fiber-reinforced polymer composite. A brief review of these attempts makes clear the necessity for an indentation method capable of removing the effects of boundaries during indentation experiments. Hodzic et al. (2000) employed standard nanoindentation techniques to probe the interphase region of polymer-glass composites. The calculated hardness and elastic modulus values for the interphase regions were drastically higher than those of the polymer matrix. The elastic modulus increased by an order of magnitude, and the hardness increased over four times that of the polymer matrix. They concluded that these in-

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creases could not be a result of just the interphase and must be influenced by the close proximity of the glass fiber. Downing et al. (2000) also performed nanoindentation experiments on a glass-reinforced polymer composite and found that the elastic modulus increased as the indent location approached the fiber. Interestingly, though, when the fiber was removed by chemical etching and the same nanoindentation experiments were performed, the apparent elastic modulus decreased as the vacant hole was approached. In other experiments, Gao and Mäder (2002) also recognized that indents performed in close proximity to glass fibers had large increases in apparent material properties. To avoid this problem, Gao and Mäder proposed the use of atomic force microscopy (AFM) nanoindentation techniques in which extremely low load ($0.24 \mu\text{N}$) indents were performed. But even with these low load indents, large increases in elastic modulus were still observed as the glass fiber was approached, from 5 GPa in the matrix to 21 GPa in the interphase. Also, indents performed at such small loads have large uncertainties because of surface roughness, uncertainties in tip geometry, and effects of surface Van der Waals and capillary forces. Indents performed with larger forces would be advantageous, but nanoindentation methods that remove the effects of the glass fiber (or vacant hole) must be used.

The interphase properties of a cellulose-fiber-reinforced polypropylene (PP) composite were recently evaluated by nanoindentation and finite element analysis by Lee et al. (2007). Similar to the previous results, they reported increases in measured properties of the matrix as the cellulose fiber was approached. After conducting a finite element analysis, they concluded that standard nanoindentation techniques could not be used to determine the exact mechanical properties of the interphase because the effect of the cellulose fiber cannot be separated from the property measurement of the interphase. From their finite element analysis, they conclude that indents performed on the fiber within five diameters of the indent from the polymer-fiber boundary will be affected by the presence of the boundary. Indents performed in the polymer within three indent diameters will also be affected. Therefore, to minimize the effect of the polymer-fiber boundary, they recommended minimizing the size of the indent. Our proposed method aims to minimize the artifact of the elastic discontinuity created by the polymer-fiber boundary on the nanoindentation data.

Nanoindentation Theory

The nanoindenter itself is an instrument that pushes a carefully shaped diamond indenter into a sample to allow the measurement of the local elastic,

hardness, creep, and other properties of materials (Stone and Yoder 1994, Oliver and Pharr 2004). The vast majority of nanoindentation analyses in the literature rely on the analysis of Oliver and Pharr (1992). The key to this standard method is that the shape of the indenter and machine compliance are first calibrated prior to an experiment. Then the contact area may be determined based on the depth of indentation and the previously calibrated area function. This analysis method will be referred to throughout this paper as the “standard” analysis. From a load-depth trace obtained during a nanoindentation experiment with the machine compliance (C_m) already accounted for, the Meyer's hardness (H) and effective modulus (E_{eff}) may be calculated from:

$$H = \frac{L_{\text{max}}}{A(h_c)} \quad [1]$$

$$E_{\text{eff}} = \frac{S}{\sqrt{A(h_c)}} = \frac{1}{C_p \sqrt{A(h_c)}} \quad [2]$$

In Equation [1],

L_{max} = the maximum load of the unloading portion of the curve and

$A(h_c)$ = the contact area based on contact depth (h_c).

In Equation [2],

S = the initial unloading contact stiffness determined by the slope of the initial portion of the unloading curve.

C_p = the compliance due to local elastic deflections in the specimen and indenter during an indent and is the inverse of S .

Young's modulus of the indented specimen may be calculated from:

$$\frac{1}{E_{\text{eff}}} = \frac{1}{\beta} \left(\frac{1 - \nu_s^2}{E_s} + \frac{1 - \nu_d^2}{E_d} \right) \quad [3]$$

In Equation [3],

E_s = Young's modulus,

ν = Poisson's ratio of specimen, and

E_d and ν_d are for the diamond indenter.

In the standard analysis,

$$\beta = 2/\sqrt{\pi} \approx 1.128.$$

For our “corrected” analysis, which will be capable of separating intrinsic material properties from boundary effects, a useful correlation discovered by Stone et al. (1991) will be used (SYS correlation). One of the keys to the corrected analysis is that any additional compliances associated with the boundary ef-

fects in the indentation experiment are to be independent of the size of the indents. Therefore, they can be combined in an additional term called the structural compliance (C_s) that can be accounted for simultaneously with C_m (Jakes et al. 2007). If the square root of load is multiplied by the total unloading compliance ($C = C_p + (C_m + C_s)$), then Equations [1] and [2] can be used to derive:

$$C\sqrt{L_{\max}} = (C_m + C_s)\sqrt{L_{\max}} + J_0^{1/2} \quad [4]$$

where:

by solving Equation [1] for $A(h_c)$, substituting it into Equation [2], and rearranging. Unlike the standard analysis, this correlation does not require knowledge of the area of the indent, and the combined machine and structural compliance ($C_m + C_s$) can be inferred independently at each indent location. According to Equation [4], a plot of $\sqrt{L_{\max}}$ vs. $\sqrt{L_{\max}}$ forms a straight line when there is no size effect in the properties (i.e., $J_0 = \text{constant}$). The slope of the line gives $(C_m + C_s)$ and the intercept represents the material properties ($J_0 = H/E_{\text{eff}}^2$). What makes this correlation so useful is that the experimenter does not need to know the areas of the indents to construct the correlation. From this SYS correlation and the measured area, values for E , and H may be calculated. The areas in the corrected analysis will be measured directly from AFM images. To calculate E_s using Equation [3], a critically determined value of $\beta = 1.22$ will be used (Jakes et al. 2007).

Experimental Methods

Materials

A WPC composed of a PP matrix and wood flour was used in this work. The PP WPC formulation consisted of 58.9 percent wood flour, 33.8 percent PP, 4.0 percent talc, 2.3 percent AC950P (maleated copolymer) (Honeywell, Morristown, NJ), and 1.0 percent Optipak 100 (Honeywell, Morristown, NJ) by weight. Further details about the formulation are provided by Slaughter (2004). To prepare a suitable surface for nanoindentation, a 10-mm cube was created, and on the surface perpendicular to the extrusion direction, a gently sloping apex was microtomed. Then the specimen was submerged in liquid nitrogen. After cooling, the specimen was secured in a sledge microtome fitted with a custom-built diamond knife holder. Finally with one cut, the tip of the apex was sliced off with a diamond knife, revealing a surface suitable for nanoindentation experiments. The best results were achieved when the clearance angle and cutting angle were both set to approximately 5°.

Nanoindentation

A Hysitron (Minneapolis, MN) Triboindenter® equipped with a diamond Berkovich tip was employed in this study. Standard methods were used to calculate the machine compliance and area function (based on contact stiffness) using a series of indents in the center of the fused silica standard ranging from 50 to 10,000 μN . Based on this series of indents, the machine compliance was determined to be 2.7 $\mu\text{m}/\text{N}$ for the indenter configuration used in this study. All of the experiments in this study employed multi-load indents in force control. Each partial unload was 75 percent of the previous partial load and the final partial unload was held for 60 s to calculate thermal drift before complete unloading. To calculate Young's modulus using Equation [3], E_d and ν_d for the diamond indenter were taken to be 1,137 GPa and 0.07, respectively, and the Poisson ratio for PP was assumed to be 0.3.

AFM and Area Measurements

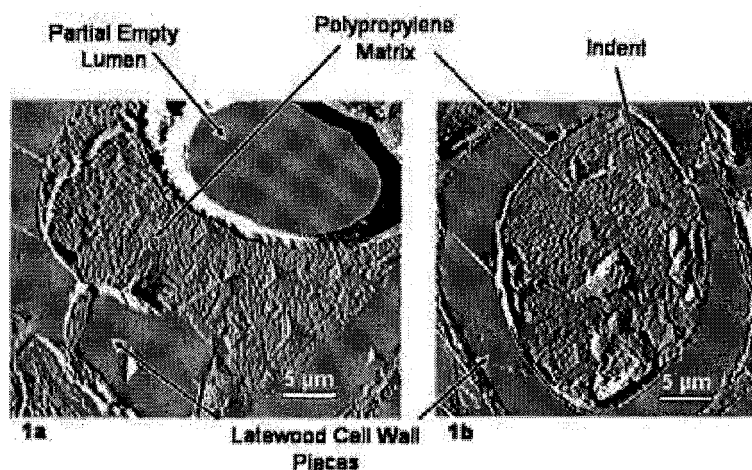
A Quesant (Agoura Hills, CA) AFM attached to the same stage of the nanoindenter was used to image all residual indents. The Quesant AFM, operated in contact mode, was calibrated using an Advanced Surface Microscopy Inc. (www.asmicro.com) calibration standard with a pitch of 292 ± 0.5 nm. Successive 4- μm scans and calibration routines revealed the reproducibility of the AFM calibration was ± 1 percent. Individual images (4 to 12 μm , depending on the size of the indent) were made of each indent and ImageJ (<http://rsb.info.nih.gov/ij/>) image analysis software was used to manually measure the areas. The areas were measured by carefully outlining the edges of contact. Sakai and Nakano (2002) demonstrated for soda lime glass and poly(methyl methacrylate) that in-surface displacements perpendicular to the loading direction that occur during the unloading are negligible. Therefore, residual indent areas will be considered equivalent to contact areas during maximum load.

Results

Observations of WPC Surface

From surveying the prepared surface of the WPC with both a light microscope and AFM, a few general observations were made. Few wood cells are left intact within the PP matrix. The cells that are intact are all thick-walled latewood cells (Fig. 1). Presumably, the thin-walled, weaker earlywood cells were all pulverized into smaller pieces during the milling of the wood flour. Even the thick-walled cells in Figure 1 show extensive cracking. A regular topography present on the PP resembles peaks and valleys with height variations ranging from 10 to 50 nm. The peaks appear to have a regular spacing of ~ 500 nm and are most likely a result

Figure 1. ~ AFM images of thick-walled latewood cells, which are mainly intact. Indents were placed in the PP inside the lumens of the cells.



of the surface preparation technique. Pieces of wood cells are also evident in the PP matrix (Fig. 2). With the exception of the lumen in Figure 1, all other lumens observed on the prepared surface were completely filled with PP. Close examination of the PP inside the lumen (lumen PP) and outside the lumens (matrix PP) reveals that small filler particles are evident in the matrix PP but not the lumen PP (Fig. 3). It is hypothesized that the filler particles are either small pieces of talc or cell wall material and these filler particles are filtered out when the liquid PP enters the lumen during the manufacturing of the WPC. Because of this observation, the indents performed in the PP will be divided into two groups: indents performed in PP inside the lumen (called lumen PP indents) and indents performed in PP outside the lumen (called matrix PP indents).

Multi-load Indents

A resulting load-depth trace of a multi-load indent in the PP matrix is shown in Figure 4. A small viscoelastic rebound, which causes hysteresis loops to appear in the unloading–reloading data, is evident in the curve. The viscoelastic rebound dies away after 5 to 10

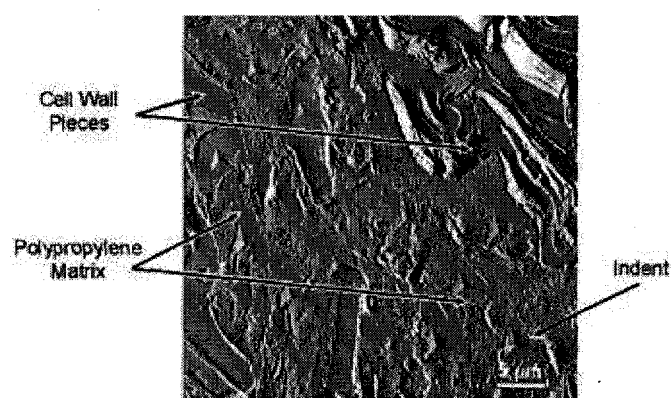
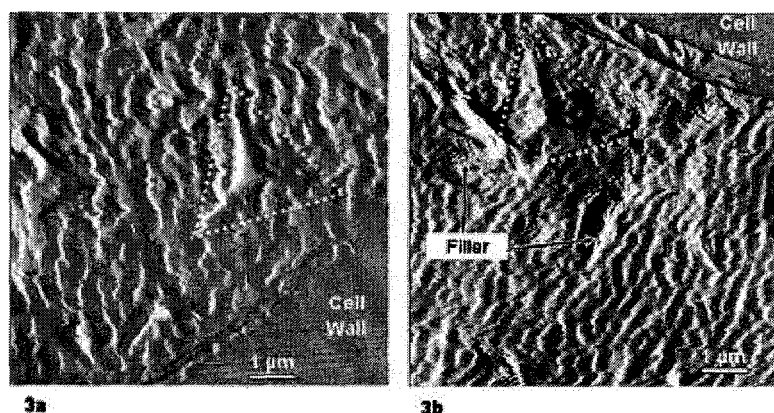


Figure 2. ~ AFM image of pieces of cell wall embedded in PP with indents placed in the PP.

s, so when calculating the thermal drift from the 60-s hold period, these first 10 s were omitted. A small amount of adhesion between the tip and PP is evident from the dip below 0 μN during the final unloading. From these multi-load indents, each of the seven unloading slopes was analyzed and SYS correlations (Equation [4]) were created for each multi-load indent. Then using these correlations and the measured ar-

Figure 3. ~ AFM images comparing the morphology of (a) lumen PP and (b) matrix PP. In both images, the close proximity of a cell wall is observed, but in the matrix PP, small pieces of particle filler are observed.



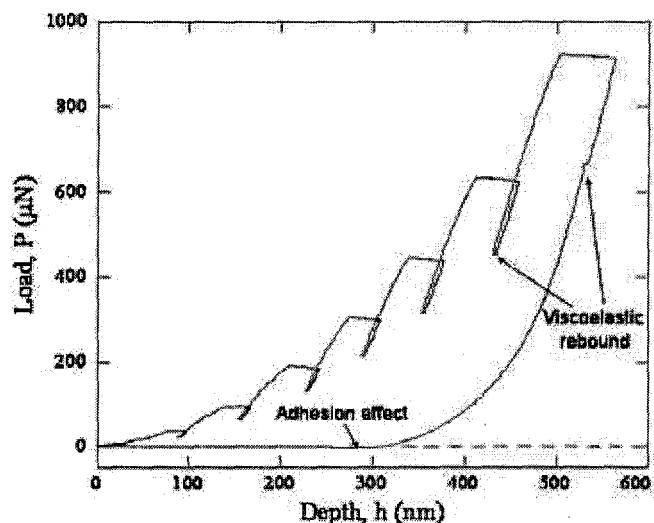


Figure 4. ~ Typical load-displacement curve for a multi-load indent performed in the PP matrix. The standard analysis was also performed on the last unloading slope.

ease, H and E_s were calculated. For comparison, H_{std} and E_{std} were also calculated using the standard analysis for the final unloading slope following the hold at maximum load.

Lumen PP Indents

Examples of indents performed in the PP inside lumens are shown in **Figure 1**. In agreement with previously mentioned observations, no pieces of filler material were noted in the imaging of the indents (**Fig. 3a**). The large blemishes in the lumens of **Figure 1** were determined to be topographic and not filler material. Multi-load indents were performed in loads ranging from 300 to 1,000 μN at various distances from the cell wall. The corresponding SYS correlations for each multi-load indent are shown in **Figure 5**. The values of the slopes correspond to $(C_m + C_s)$ and range from -75 to $34 \mu\text{m}/\text{N}$, with the negative slopes corresponding to indents in close proximity of the cell wall and the positive values corresponding to indents near cracks or holes. The average intercept, representing J_0 (H/E_{eff}^2), was $3.6 \pm 0.1 \mu\text{m}/\text{N}^{1/2}$. Using the measured areas and data from the SYS correlations, the corrected values of E , and H were calculated and plotted with respect to measured distance to the nearest cell wall (**Fig. 6**). The average calculated values for E , and H in the corrected analysis were $2.7 \pm 0.2 \text{ GPa}$ and $170 \pm 30 \text{ MPa}$, respectively. Also included in the plot are values calculated from the standard analysis. Data for the two analysis methods are in agreement for indents placed greater than $1.5 \mu\text{m}$ from the cell wall, but a sharp increase in modulus is observed for the indents in closest proximity to the cell wall for the standard analysis. In

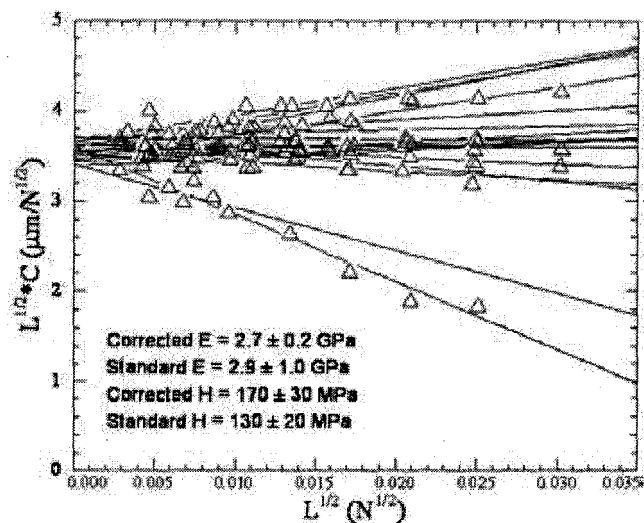


Figure 5. ~ SYS correlations for lumen PP indents.

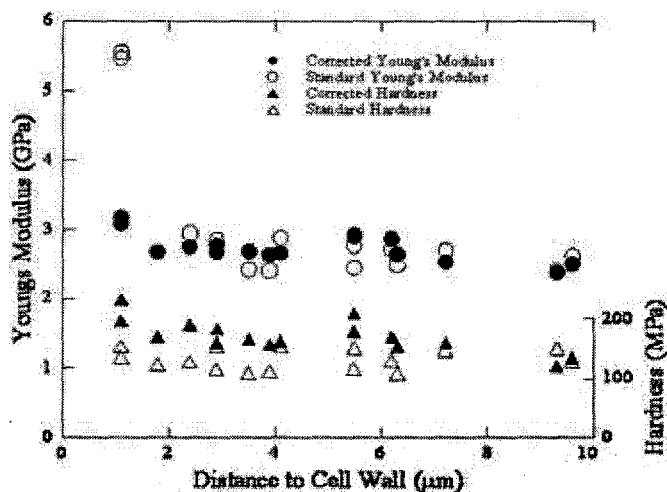


Figure 6. ~ Comparison of values obtained from standard and corrected nanoindentation data analysis methods plotted against measured distance from the cell wall for lumen PP indents.

the corrected analysis, however, only a very modest increase is evident. Imaging of the two indents closest to the cell wall showed that a very small portion of the residual indent actually contained portions of the cell wall. This likely caused the modest increases observed in **Figure 6**.

When the individual SYS correlations of the two closest indents were being constructed, the effect of the indenter touching the cell wall at the higher loads of the multi-load indents was evident. Data points in the SYS correlation corresponding to the indenter touching of the cell wall had a sharp decrease in $CL^{1/2}$ values. These points were not linear with respect to previous points in the correlation for the smaller loads,

when the indenter was not touching the cell walls. Therefore, these points were excluded when fitting the SYS correlations in **Figure 5**, and the resulting J_0 parameter is independent of the indenter touching the cell wall and accurately represents the material properties of the PP at the given distance from the cell wall. Assuming both H and E_{eff} are not changing simultaneously in such a way that J_0 remains a constant, differences in material properties would be detectable in a plot of J_0 with respect to distance from the cell wall (**Fig. 7**). In this plot, no changes in J_0 were observed with respect to differences in distance to the cell wall. This work gave no evidence of material properties changing in the interphase region of this WPC.

Matrix PP Indents

Numerous multi-load indents ranging from 1,000 to 3,000 μN were performed in regions of the matrix PP. The resulting SYS correlations are plotted in Figure 8. The SYS correlations of the matrix PP indents showed more scatter than did those of the lumen PP indents (Fig. 5). The average value (with standard deviation) for J_0 in Figure 8 is $3.3 \pm 0.7 \mu\text{m}/\text{N}^{1/2}$. The wider range of J_0 signifies larger scatter in the material properties measured by indents in the matrix PP. The average values of E_s and H for the corrected analysis for the matrix PP indents were $3.0 \pm 1.2 \text{ GPa}$ and $160 \pm 60 \text{ MPa}$, respectively. For the standard analysis, the values were $3.0 \pm 0.9 \text{ GPa}$ and $130 \pm 60 \text{ MPa}$.

Discussion

Comparison of Lumen PP and Matrix PP Indents

The most visible difference between the lumen PP and matrix PP indents is the larger amount of scatter in the data of the matrix PP indents. This is attributed to the dispersion of filler material present in the matrix PP but not the lumen PP (Fig. 3). When a portion of an indent contacts a filler particle, the properties from the indent would be expected to increase. For example, the matrix PP indent shown in Figure 9 contacted an embedded filler particle and had a measured E_s of 4.9 GPa, which is above the average E_s of $3.0 \pm 1.2 \text{ GPa}$. The corrected E_s for the matrix PP ($3.0 \pm 1.2 \text{ GPa}$) was slightly higher than the corrected E_s for the lumen PP indents ($2.7 \pm 0.2 \text{ GPa}$). This increase is likely because of the presence of filler particles. Values of corrected H for the matrix PP and lumen PP indents were very similar, 160 ± 60 and $170 \pm 30 \text{ MPa}$, respectively. These values are in good agreement with nanoindentation values ($E_s = 3.0 \text{ GPa}$ and $H = 110 \text{ MPa}$) obtained by Lee et al. (2007) in the matrix of a cellulose-fiber-reinforced PP composite.

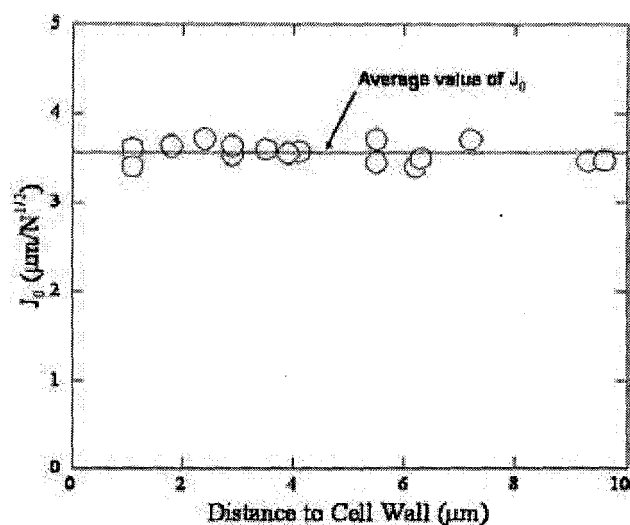


Figure 7. ~ Plot showing the lack of dependence of J_0 (H/E_{eff}^2) on proximity of the cell wall.

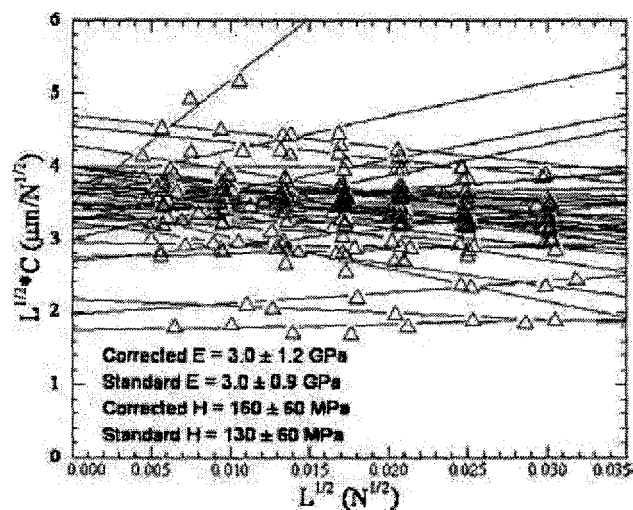


Figure 8. ~ SYS correlation for matrix PP indents. Note the higher amount of variability than in the lumen PP indents displayed in Figure 5.

Properties of Interphase Region and Future Work

The motivation for this work was to measure H and E_s of the interphase region between the PP and the wood cell wall. The results obtained using the standard analysis agreed with those of other researchers (cited previously) who observed a drastic increase in E_s as the fiber was approached. When the corrected analysis was utilized, however, only a modest increase was observed, which was attributed to the indenter coming into contact with the wood cell wall during these indents. Data from the SYS correlations of the indents were fit such that the influence of the indenter

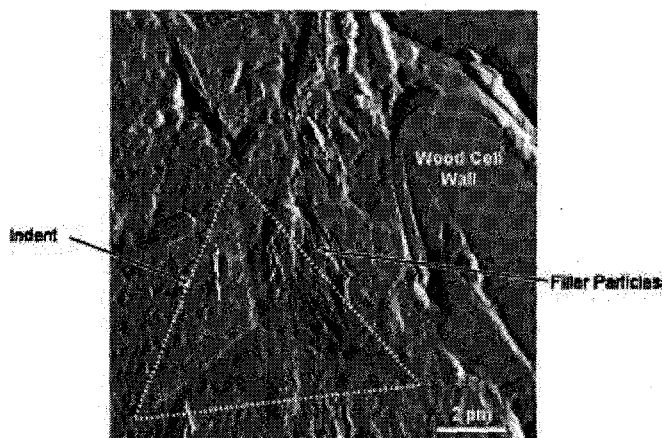


Figure 9. ~ AFM image of a matrix PP indent demonstrating the presence of filler particles within the contact area of the indent.

coming into contact with the wood was removed. Therefore, the J_0 values calculated for all of the lumen PP indents are independent of proximity of the cell wall, and the results in **Figure 7** lead us to believe that the modest increase of properties observed in the corrected analysis of **Figure 6** is truly a result of the indenter coming into contact with the cell wall and not changing properties in the interphase.

The corrected data analysis method presented in this paper would be capable of detecting material property changes in the interphase region of the composite if these changes exist. Our work suggests differences do not exist, but further study should be completed to confirm this. One area of improvement for this type of work would be an improved surface preparation technique, such as mechanical polishing techniques. In addition, employing phase imaging AFM techniques to distinguish the interphase region would be very beneficial, such as Gao and Mader (2002) demonstrated in a glass fiber reinforced PP composite.

Conclusion

It has been recognized in the literature that standard methods of nanoindentation data analysis are not capable of separating intrinsic properties of a material in the interphase regions of a composite from the effects of the nearby fiber. This paper presented an experimental technique capable of achieving this separation and thereby accurately determining H and E , of

PP in close proximity to a wood cell wall. No differences in E_s or H were detected in this experiment for the interphase region. Comparing matrix PP and lumen PP indents, a significant increase in the amount of scatter and a slight increase in the matrix PP indents were observed, both attributed to filler particles present in the matrix PP but not in the lumen PP.

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