Gypsum-Cellulose Interactions – a Colloidal Probe Microscopy Study

JUAN C. BASTIDAS¹, JOEL J. PAWLAK¹,², RICHARD A. VENDITTI¹, JOHN A. HEITMAN¹, MARTIN A. HUBBE¹ AND JOHN F. KADLA²

¹Department of Wood and Paper Science, North Carolina State University Raleigh, NC 27695-8005 USA
²Faculty of Forestry, University of British Columbia, Vancouver, British Columbia, Canada
³Corresponding Author: Email: jjpawlak@unity.ncsu.edu, Telephone: 919-513-0511, Fax: 919-515-6302

ABSTRACT

Drywall, which is made primarily of a calcium sulfate dihydrate (gypsum) core with paper on both sides, is one of the most widely used construction materials. Because board failure often occurs at the gypsum core/paper interface, it has become important to know the exact nature of the gypsum/cellulose bond. This study provides data about the nature of this interaction by means of AFM and Colloidal Probe Microscopy. These methods made it possible to distinguish among the different crystal faces and their respective interactions with cellulose. Measured in air, the adhesive forces between the AFM tip and the different faces varied according to f(010) < f(120) < f(111) at 50 % relative humidity. The differences in adhesive force with the different gypsum crystals can be attributed to the differences in surface chemistry. The information obtained will help guide improvements in the crystal production process to obtain better bonding between the crystal and the paper.

INTRODUCTION

One of the cellulose composite materials in widespread use in North America is gypsum wallboard. Also known as drywall, it is used as an interior wall in many building applications and also in limited external applications. This composite material can be described as a flat board comprised of a gypsum core with the external surfaces covered with paperboard. The result is a three-layer composite composed of paper/gypsum/paper. By varying the wallboard thickness and composition, as well as the paper characteristics, a tremendous range of products can be produced. These products are well described in manufacturers’ technical information.

Gypsum mineral (Calcium Sulfate Dihydrate, CaSO₄•2H₂O) and cellulose constitute the primary raw materials for this multi-billion dollar industry in the United States. In 2003, the operating capacity of wallboard plants in the United States was 36 billion square feet per year [1]. Since its development at the end of the 1940’s, wallboard has revolutionized the construction industry and currently is the main industrial consumer of the gypsum mineral. It is also an important fate for recycled paper, consuming 10 % of the recycled paper stream in the United States [2].

Paper, gypsum core and the gypsum core/paper interface impact the quality of the gypsum wallboard. Raw material qualities that enhance and facilitate the production of wallboard are achieved by the addition of chemicals (additives) to the paper and gypsum during manufacturing. The paper fiber furnish, as well as the paper additives, such as alum, size and starch, determine the chemical and physical properties of the paperboard, including strength, bulk, porosity and absorptivity [3]. The gypsum core characteristics, including crystal size and distribution and hydration level profiles, are strongly affected by the presence of gypsum core additives and coupling agents. Properties of the final composite product are dictated by paper/gypsum, paper/additive, and additive/gypsum interactions taking place during wallboard formation [3].

Colloidal Probe Microscopy

Among the several variants of Atomic Force Microscopy, a technique that has been often used is Colloidal Probe Microscopy (CPM). In this technique, a “colloidal” particle is attached to the end of an AFM cantilever and used as a probe. Because the radius of the probe is increased by three orders of magnitude, images obtained with CPM are different from those obtained with regular AFM tips. The study of interactions between the colloidal particle and surfaces of interest has broadened the scope of CPM. The colloidal probe can be a polymer, a cell, a crystal, or another microparticle, making CPM a
versatile technique for studying surface interactions.

The first reported application of CPM was made by Ducker et al. [4] for the study of interaction forces between a colloidal silica particle and a flat silica surface. Since then Colloidal Probe Microscopy has become a valuable technique for the study of surface interactions. Many systems in material science and chemistry deal with interactions among colloidal particles or between the particles and other surfaces. The CPM technique allows single-particle studies for such systems. Its applicability goes from the fields of materials science to pharmaceuticals, including biological and crystal sciences; that is every field where adhesive forces are important. An excellent review about the technique is reported in the literature [5].

Until now, improvements of gypsum wallboard material have been mainly made through the control of variables in the manufacturing process and through the use of additives. The function of the additives is to modify the raw materials and to enhance the quality of the final product. However, the bonding interactions between gypsum and cellulose are not well understood. A basic understanding of the nature of the bond between these materials may lead to the engineering of the bond to perform more robustly in a variety of environments, and/or to improve the wallboard durability. In this study, a colloidal probe microscopy technique was used to measure the adhesive interactions between cellulose colloidal probes and two sets of gypsum crystals (naturally grown and laboratory grown).

Materials
Cellulose micro-spheres were obtained from KOBO Industries (South Plainfield, New Jersey, USA). Prior to being used in this work, the micro-spheres were washed several times with acetone. Then, the acetone was exchanged for deionized water. Finally, the spheres were dried at 40 °C for 48 hours. Silicon nitride AFM contact mode cantilevers (Quesant, model # CSC17, Santa Barbara, CA) were used for imaging of gypsum crystals. These cantilevers were also modified with cellulose micro-spheres. The cantilever spring constant was assumed to be 0.15 N/m, as provided by the manufacturer. The tips were cleaned with acetone and DI water, and dried with nitrogen gas at room temperature.

Two sets of gypsum crystals were used in this work. The first set corresponds to naturally grown gypsum crystals (Rocks-and-More Canton, Michigan USA). The second set of crystals was produced in the laboratory by using a slow diffusion procedure [6, 7], which creates crystals on the order of several millimeters.

Procedures
The cellulose micro-spheres and AFM cantilevers described above were used for the fabrication of the colloidal probes used in this work. The cellulose micro-spheres were attached using a small amount of UV-curing, solvent-free epoxy adhesive (NORLAN® 81), which was placed on the cantilever with a glass microtip mounted on a microscope stage. The same device was used to position the cellulose micro-spheres on the cantilever. A photomicrograph of a tip with a cellulose micro-sphere is shown in Figure 1.

![Cellulose micro-sphere attached to an AFM cantilever](image)

**Fig. 1.** Cellulose micro-sphere attached to an AFM cantilever

An Olympus BH-2 optical microscope, linked to a PC computer and a video camera, was used to capture and process crystal images. Gypsum crystals were characterizing by optical microscopy, in order to determine crystal form, faces and dimensions. Using the optical microscope, crystals with the most regular form – that is, crystallographic form described in the literature - were chosen and their faces were identified by axis length and area. Also, the crystals were analyzed by single crystal X-ray diffraction, and the results confirm the gypsum morphology.
A Q-Scope™ 250 AFM (Quesant Corporation, Santa Barbara CA), equipped with an acoustic/vibration isolation chamber was used to obtain AFM images and to conduct CPM experiments. It uses a scanner with 80 µm XY scan range and 0.1 nm Z resolution. For imaging of the gypsum crystals, intermittent contact tips (Quesant, model # NCS 16) were used, and the instrument settings were adjusted according to the instrument manual.

Infrared characterization was made using a Nexus 670 FTIR spectrometer (Thermo Nicolet Corporation, Minneapolis, MN) equipped with Smart OMNI-Sampler™ Attenuated Total Reflectance (ATR) module. Infrared spectra were taken using the Attenuated Total Reflectance attachment, in air with no nitrogen purge. Two crystals of each set were analyzed, and three spectra were taken on each. Because of the variability in the surface, a total of 64 scans were made for each spectrum. Background and automatic base line correction, as well as automatic smoothing were applied to every spectrum. The final IR spectrum for each sample was obtained by averaging all of the spectra using the software provide with the equipment (Omnic ver 4.1).

In order to image gypsum crystals with AFM and to study the adhesive forces between cellulose colloidal probes and gypsum crystal faces, it was necessary to attach the crystal to glass slides. Several crystals were aligned with different face planes perpendicular to the Z direction of the glass slide. The crystals were attached to the slide using a UV-curing, solvent-free epoxy adhesive (NORLAN® 81). Then, the crystals were imaged with a regular silicon nitride AFM cantilevers for contact mode (model CSC 17) and for intermittent contact mode (model NCS 16). To obtain adhesive forces, the tip or the colloidal probe was brought into contact at five different locations on at least two different crystals, and 10 force curves were obtained at each location, for a total of 50 force curves per face.

AFM images were processed removing the tilt using a parabolic baseline adjustment, and the surface roughness and other dimensions were obtained using the software provided with the instrument. The adhesive force was determined as the difference between the minimum point and the constant force retracting line, as shown in Figure 2. A few curve forces with very irregular shapes and/or characteristics were excluded.

**RESULTS AND DISCUSSION**

The typical crystallographic form for a gypsum crystal is shown in Figure 3. As reported in the literature, gypsum crystals grown in bentonite gels without additives show well-developed (010), (111), (120) faces [7, 8]. The visual identification of faces was used to line-up and attach the crystals to glass slides for AFM imaging and force measurements.

**Fig 3.** Gypsum crystal growth by slow diffusion procedure, with its faces labeled (scale bar: 0.25 mm)

Infrared spectra of several samples of laboratory and naturally grown gypsum crystal were obtained using an ATR technique. For comparison, a standard spectra from a gypsum reagent was acquired. Calcium Sulfate Dihydrate reagent powder (Fisher No. 984-7) was made into a pellet and the IR spectra were obtained. The $\text{SO}_4^{2-}$ ion peaks appeared at 981 and 1104 cm$^{-1}$. Also, in this region, peaks corresponding to the twisting and rocking of the
water molecule appeared at 690 and 834 cm\(^{-1}\). The adsorption bands at 745 and 1074 cm\(^{-1}\) confirm the presence of sulfate. The band at 1632 cm\(^{-1}\) and the broad band at 3100 cm\(^{-1}\) are associated with the presence of water. IR spectra of the gypsum samples are similar to those cited in the literature [9].

**AFM images of gypsum crystals**

Typical AFM images of gypsum crystal faces in air are shown in Figure 4. The AFM images show that face (010) is flatter than the other two faces, as indicated by the Z-scale values. Also, it can be seen that the faces (120) and (111) have a bulky structure on the surface. Although the bulky structures were not abundant, they may be attributed to bentonite residues on the surface.

![AFM images of gypsum crystals](image)

**Fig 4.** AFM images (contact mode) of the gypsum crystal faces and their correspondent error images (a) and (b) face (010), (c) and (d) face (120), (e) and (f) face (111). The Z scales are 150, 600 and 500 nm respectively.
Another important feature is that the surface texture itself is distinct among the different faces as revealed by the error images. This is a consequence of the different composition of the faces. Different faces of gypsum show different chemical “composition”, meaning that the atoms or atom groups exposed at the surface are different. For the (010) face, water molecules are the surface entities; for the (120) face, sulfate groups make up the surface layer; and for the (111) face, both calcium and sulfate ions are exposed to the surface [10]. This heterogeneity should be reflected in the adhesive force between the cellulose micro-sphere and the different gypsum faces.

For the laboratory grown crystals, the surfaces were not as flat as reported in dissolution studies for naturally grown crystals [11, 12]. It is well known that gypsum can be easily cleaved along the (010) face; AFM imaging studies had shown that gypsum surfaces are “atomically flat” and because of this had been suggested as a substrate for the preparation of smooth gold surfaces for AFM studies [13].

Adhesive forces between gypsum crystals and AFM tips

Random Landing
Initially, the silicon nitride tip and the cellulose micro-sphere were brought into contact (landed) with the naturally grown crystals, and adhesive forces were measured. This approach is called “random landing”, because it is not possible to define the face(s) where the probe is contacting the surface. The results will be discussed in two parts: the adhesive forces between silicon nitride tip – gypsum crystals, and cellulose bead – gypsum crystal.

Tip/Gypsum: The frequency of adhesive force data obtained for the interaction between the silicon nitride tip and the gypsum crystal is shown in Figure 5a. There are three regions around which the adhesive forces are distributed, corresponding to the mean values of 11, 30 and 76 nN. This behavior may be due to the tip landing over different faces of the gypsum crystal. This phenomenon has been reported in the literature by Finot et al [10, 14]. It was found that for the 50-60% relative humidity range two sets of adhesive forces were distinguishable, one for the (010) face and another for the (120) and (101) faces, with mean values of 78 and 47 nN. It is important to note that the comparison of AFM force values from different experimental set-ups should be done carefully, because force values depend on several factors such as the contact area (tip radius), which is different for each probe, and on the particular settings of the experiment such as the retraction-advancing scan speed, maximum contact force, etc. However, it is worth noting that the adhesive force measurements of 78 and 47 nN are quite similar to the 76 and 30 nN found in the current set of experiments.

![Figure 5](image-url)

**Fig 5.** Adhesive force distribution histograms in random landing (a) AFM probe on gypsum crystal in air (b) cellulose micro-sphere probe on gypsum crystal in air.
Cellulose/Gypsum: A multimodal distribution of adhesive forces was found for the cellulose/gypsum interaction, as shown in Figure 5b. Two differences are found when compared with the tip/gypsum interactions (i.e. Figure 5a). First, the regions for the forces were not as clearly defined as in the former case, and second the magnitude of the adhesive force is increased by one order of magnitude. These differences may be attributed to several factors. First, the contact area between the cellulose micro-sphere and gypsum crystals is larger, which leads to an increased magnitude in force. Second, the interaction occurs between different materials (contributing to differences in magnitude of adhesion levels). Third, the larger radius of the cellulose micro-sphere \(15 \mu m\) is likely to interact with more than one type of crystal face during an individual test, when compared to the smaller silicon nitride tip \(20 \text{ nm}\).

The measurement of adhesive forces with AFM in air is influenced by Van der Waals (VdW) forces, hydrogen bonding and capillary forces [15]. The VdW component, which is always present and dependent on the type of materials interacting, is assumed constant and independent of the relative humidity. Capillary effects are also present due to the wetting of the surfaces by a thin layer of water and the formation of a water meniscus between the probe and the sample. These effects are dependent on the surface chemistry of the material and the geometry of the contact. Hydrogen bonding is also important when the surface chemistry is of the proper type (i.e. hydrogen present and accompanying electronegative atoms). Hydrogen bonding may be important for certain faces of the gypsum crystal when contacted by the proper material, such as the (010) and (120), which expose water molecules and sulfate groups respectively.

Landing on Faces
Using the laboratory grown crystals, the adhesive forces between bare tip/gypsum crystal and cellulose micro-spheres/gypsum crystal were measured on the different faces. The results are summarized in the following sections:

Tip/Gypsum: The frequency of adhesive force data obtained for the interaction between the silicon nitride tip and the gypsum crystal for the faces \((010), (111)\) and \((120)\) respectively are shown in Figure 6. Table 1 shows the averages and standard deviations for the measurements. For the faces in which the forces seem normally distributed, that is \((010)\) and \((120)\) the mean values for the corresponding forces are 5 and 40 nN respectively. For the face \((111)\), the force distribution seems bimodal, with centers around 10 and 60 nN. This phenomenon was not observed previously in the random landing of the tip. Also, the values are somewhat different from those previously obtained, which correspond to mean values of 11, 30 and 76 nN.

Cellulose/Gypsum: The adhesive force values and standard deviation data obtained for the interaction between the cellulose micro-sphere (colloidal probe) tip and the gypsum crystal for the faces \((010), (111)\) and \((120)\) respectively are shown in Table 1.

One observes that the forces obtained with the colloidal cellulose tip are higher than the forces obtain with the silicon nitride tip, cf. Table 1. The same reasons discussed in the force analysis of naturally grown crystals can explain the differences in magnitude for the forces.

![Figure 6](image.png)

**Figure 6.** Adhesive force distribution histograms for AFM probe on gypsum crystal faces, in air (a) face \((010)\), (b) face \((111)\), (c) face \((120)\).
Table 1. Adhesive forces on gypsum crystal faces, n = 50 force values. (* indicates bimodal distribution)

<table>
<thead>
<tr>
<th>Face</th>
<th>AFM Tip: Adhesive force (nN)</th>
<th>Cellulose Micro-sphere: Adhesive force (nN)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Standard deviation</td>
</tr>
<tr>
<td>(010)</td>
<td>4.9</td>
<td>1.2</td>
</tr>
<tr>
<td>(111)</td>
<td>10, 60*</td>
<td>*</td>
</tr>
<tr>
<td>(120)</td>
<td>31.7</td>
<td>21.8</td>
</tr>
</tbody>
</table>

Crystal growth occurs in such manner that the surface energy is minimized. Therefore, one would expect that the largest surface area has the lowest surface energy (ie. (010) face followed by the next two faces in some order. Furthermore, one would expect a dramatic difference in the surface energy between the (010) face and the other two faces due to the much larger surface area. The Johnson, Kendall, and Roberts (JKR) [16] theory of elastic contact predicts that the adhesive force can be modeled using the following equation:

\[ P = -\frac{3}{2} \frac{\gamma \pi R}{2} \]  \[ [1] \]

where \( P \) is the adhesive force, \( \gamma \) is the surface energy per unit contact area, and \( R \) is the radius of curvature of the contacting probe. This model has been commonly used to analyze adhesive force data gathered with AFM [17]. Therefore, one would anticipate that adhesive force measured on the (010) face should be significantly smaller than the other two faces. This is indeed found for both the tip/gypsum interaction and cellulose/gypsum interaction (cf. Tables 1).

In the JKR theory, the pull-off force is a function of the surface energy of the surfaces in contact and the probe radius of curvature, without any dependence of the elastic properties of the materials. Previous work predicts the pull off force for cellulose micro-sphere/cellulose surface to be on the order of 10 µN [17]. However, the actual force values measured between cellulose surfaces in that study were four orders of magnitude lower than the predicted value from theory [17]. In a similar fashion, the forces observed in this work, for cellulose micro-spheres and gypsum crystals, were found to be 2-3 orders of magnitude less than 10 µN. The discrepancy suggests a more complex adhesion phenomenon between cellulose and gypsum. The discrepancies may be attributed to the rough surface of the cellulose micro-sphere and gypsum surface, which may dramatically reduce the real contact area between the micro-sphere and the surface, and/or plastic deformation of the surface or probe, which is not accounted for in the JKR theory.

CONCLUSION

Atomic Force Microscopy and colloidal probe microscopy were used to obtain information about the adhesion magnitude between cellulose and gypsum, the primary materials of drywall. The results show a face-dependence of the adhesive forces between gypsum crystals and cellulose. Also, it was found that the magnitude of adhesive forces between cellulose micro-spheres and gypsum crystal faces was much smaller than a theoretical prediction for smooth surfaces.

ACKNOWLEDGEMENTS

The financial support of National Gypsum Corporation is greatly appreciated. The discussions of this work with Dr. Stefan Zauscher of Duke University were valuable in completing this work and are greatly appreciated.

REFERENCES