# Enhanced Bondability Between Inorganic Particles and a Polysaccharide Substrate by Encapsulation with Regenerated Cellulose

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**ABSTRACT:** Inorganic fillers are widely used in coatings, paints, printing inks, and papermaking. A general problem in such applications is the poor compatibility and weak bondability of the filler with polymeric substrates. Surface modification and encapsulation are common methods adapted to enhance interactions between the filler surface and the substrate. This article presents a bondability improvement between inorganic particles and a polysaccharide substrate by the use of cellulose-coated, inorganic core–shell nanoparticles. The crystallinity of the coated carbohydrate layer is shown to significantly affect the bondability of the core–shell particles. The impact of the coating layer on the light scattering efficiency has also been studied with theoretical Mie scattering calculations. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2830–2836, 2008

**Key words:** coatings; fillers; macroporous polymers; polysaccharides; strength

## INTRODUCTION

Micrometer- and nanometer-sized capsules and core–shell particles have found applications in diverse areas such as drug delivery,[1–3] polymer composites,[4–6] foods and drinks,[7,8] coatings and paint,[9,10] sensors,[11,12] and papermaking.[13,14] Many encapsulation methods such as *in situ* polymerization[15,16] and layer-by-layer assembly[17,18] have been developed with a range of functional or biodegradable encapsulating polymers.[19–21] For example, the bad taste of mineral particles can be reduced by starch being coated onto their surface. This technology has been used for preparing nutrimental drinks and foods. The encapsulation of drugs by biodegradable polymers is the most important technology in drug delivery control. Poly(lactic acid), polyhydroxybutyrate, and poly(ε-caprolactone) are examples of biodegradable polymers used in the encapsulation of drugs or nanosensors. Cellulose is the most abundant natural polymer and is considered an almost inexhaustible source of raw material for environmentally friendly and biocompatible products. Cellulose can form a hydrogel when it absorbs waters and can form hydrogen bonds with many biomaterials and engineering substrates. Therefore, successful encapsulation of nanoparticle or microparticle surfaces with cellulose has great potential for making new functional materials with widespread applications, including bioinert biosensors, microcapsules for drug delivery, food additives, and fillers with strong hydrogen bonding ability. However, pure cellulose has not previously been used as a discrete coating material because of the poor processibility of cellulose in water and most common organic solvents.

Recently, we reported a series of filler modification methods,[1,3–6,9] including starch–gel-coated precipitated calcium carbonate (PCC),[12] starch-coated clay by a drying method, clay–starch composites with $(NH_4)_2SO_4$ as a precipitation agent, and clay–starch composites with a fatty acid as a complexation agent, to improve the paper strength for high-filler-content papers. The concept for improving the paper strength is to coat the filler with polysaccharides so the bonding strength between the filler and fibers can be improved. These methods showed dramatic improvements in tensile, burst, and folding strength without the loss of the optical properties in comparison with unmodified filled papers.

Inorganic fillers such as $TiO_2$, clay, and $CaCO_3$ have traditionally been used to improve end-use properties of paper, such as opacity, brightness, gloss, smoothness, porosity, and printability.[22] The increased substitution of low-cost inorganic fillers, such as clay and $CaCO_3$, for expensive wood fibers in the paper sheet should also lead to a significant

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reduction in the cost of papermaking. In fact, as the price of wood pulp continues to rise (a 75% price increase per ton between 2001 and 2006), there is mounting pressure to increase the filler loading across all paper grades. However, it is well known that increasing filler content decreases paper strength, as the nonbonding filler disrupts and reduces the fiber–fiber bonding within the sheet. To overcome this critical constraint, an active research area has developed to synthesize organic–inorganic composites capable of forming high-strength bonds with wood fibers. The most promising composites to date combine traditional papermaking fillers and renewable carbohydrate materials, such as starch and wood fines, that can form strong hydrogen bonds with fibers.[13,14,22–24] These composites give dramatic improvements in paper strength over comparable unmodified fillers at a constant filler loading. However, the particle size, size distribution, and shape of these composite filler particles cannot be well controlled, and this hinders a fundamental understanding of core–shell functional fillers and their practical industrial applications.

Here we report the preparation of cellulose core/inorganic fillers using a simple method of precipitation from a 4-methylmorpholine N-oxide (NMMO) solution. The process is based on a subtle modification of the Lyocell process, which has been widely used in manufacturing regenerated cellulose (RC) fibers and films from an NMMO monohydrate solvent system.[25,26] The bonding strength between the core–shell particles and different polysaccharide substrates was investigated. Using a well-known computer code based on the Mie theory (BHCOAT), we show that our well-defined, discrete cellulose-coated inorganic fillers can scatter more light within a paper sheet than uncoated fillers under optimized conditions. Thus, the inorganic–cellulose core–shell particles can enhance the physical and optical properties of paper.

## EXPERIMENTAL

### Materials

Cotton pulp (Procter & Gamble Cellulose, Cincinnati, OH), potato starch (Experimental Industrial Starch X100, Grain Processing Corp, Muscatine, IA), mechanical pulp (Augusta Newsprint/Abitibi Consolidated, Augusta, GA), and cationic polyacrylamide (CPAM; retention aid with a medium-charge density and high molecular weight; Ciba Specialty Chemicals Corp, Jarrytown, NY) were used as received. Cellulose powder (medium fibers from cotton linters; Sigma, St. Louis, MO), NMMO (50% w/w aqueous solution; Alfa Aesar), and sulfuric acid (96.5%; Em Science, Gibbstown, NJ) were used without further purification. Water was obtained from a Nanopure ultrapure water system (Applied Science Inc., Chesterland, OH) with a resistivity of about 18 MΩ cm.

### Preparation

To determine the polymer property effect on the bonding improvement, films made from common polysaccharides, including cellulose nanowhiskers, starch, and RC, were used to test their bondability with wood fiber sheets. The experimental details of the testing were given previously[27] and are illustrated in Scheme 1. Typically, for the preparation of pure RC nanospheres, a dilute solution of cellulose dissolved in NMMO (1 wt %) was first prepared by the dispersion of 0.5 g of cellulose powder with 95.5 g of aqueous NMMO (50 wt %). This mixture was then heated in a rotary evaporator *in vacuo* at 60°C for 20 min followed by 95°C for 20 min. During heating, bulk water was removed from the solution, and the cellulose dissolved in NMMO. The solution was then transferred to an oil bath and maintained at 95°C under mechanical stirring. The dissolved cellulose in NMMO was then reprecipitated by the addition of 50 mL of water drop by drop at a rate of 5 mL/min. The resulting solids were isolated by three centrifugation (25,900 RPM for 2.5 min) and water-washing cycles and then freeze-dried.

Cellulose nanowhiskers were prepared as outlined previously.[17] Cotton fiber was hydrolyzed with 64 wt % sulfuric acid at 45°C for 45 min. Before hydrolysis, the dry cotton fiber sheets were torn into small pieces and fed through a Wiley mill (Arthur H. Thomas Co., Philadelphia, PA) to pass through a 1-mm mesh. Typically, 40 g of ground cotton was treated with 700 mL of a sulfuric acid solution. Immediately after hydrolysis, the unhydrolyzed cellulose whiskers were diluted 10-fold with water. The solids were allowed to settle overnight and then were
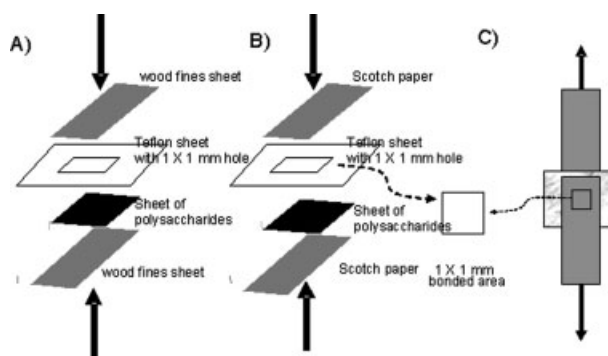


**Scheme 1** Illustration of the assembly of laminates for the measurement of the fiber/polysaccharide material shear bond strength. The laminate is (A) assembled and wet-pressed at 20 psi and 105°C for 5 min, (B) reinforced with Scotch tape and pressed for 1 min at 20 psi and 105°C, and (C) delaminated under tensile stress.

collected with minimal amounts of solution. Excess acid was removed by three washing and centrifugation (25,900 RCF for 30 min) cycles followed by dialysis (Spectra/Por membrane, Spectrum Laboratories, Inc., Rancho Dominguez, CA); molecular weight cutoff = 50,000) against water for several days until the water achieved a neutral pH. The cellulose whisker suspension was then sonicated with a Heat Systems Ultrasonics W-385 probe sonicator for 35 min while it cooled in an ice bath. The resulting suspension was allowed to stand over a mixed bed resin (TMD-8; Sigma) for 48 h and then was filtered through hardened ashless filter paper (541; Whatman, Maidstone, Kent, England) and concentrated to 8.27% with a rotary evaporator *in vacuo*.

Wood fines were prepared by the refining of mechanical pulp for 1 h at 25% consistency in a Valley beater (Deja Vu Lab and Test Equipment Inc., Nova Scotia, Canada). Fines were collected from the fiber suspension with a Britt jar (Paper Research Materials Inc., Seattle, WA) with a 200-mesh screen, and this yielded a stable suspension. To concentrate the suspension, CPAM (1 ppm) was added to flocculate and settle the fines, and a majority of the supernatant was removed.

The bonding strength between the polysaccharide coating material and fiber was measured for laminates prepared with the method illustrated in Scheme 1. Wood fines were used as the model fiber because their size and conformability allowed them to be pressed into strong, smooth sheets. These sheets were prepared by vacuum filtration of the concentrated suspension of fines onto qualitative filter paper (Whatman). With a razor blade, the damp pad was cut into individual strips, approximately 1 cm × 3.5 cm in size, and the filter paper backing was removed. Several different methods were required to obtain a compressed and uniform 1 cm × 1 cm polysaccharide material sheet, depending on the type of material. The freeze-dried cellulose nanospheres were dampened and pressed at 90 psi and 120°C for 10 min with an automated pressing apparatus (P. Bonk & Co., Highland, England). Starch powder was dampened and pressed at 50 psi and 120°C for 10 min. Cellulose nanowhiskers were cast as a film from a concentrated solution and dried at room temperature. The fines filler sheet was prepared as previously described.

In the bonding strength tests, a polysaccharide sheet was placed on a wet wood fines sheet, and this was followed by a thin Teflon film with a 2 mm × 2 mm hole in the center and then another wet fines sheet. The bonding area between the filler and fiber was fixed by the hole in the Teflon film. This composite was then pressed at 20 psi and 105°C for 5 min to form a laminate. To ensure the integrity of
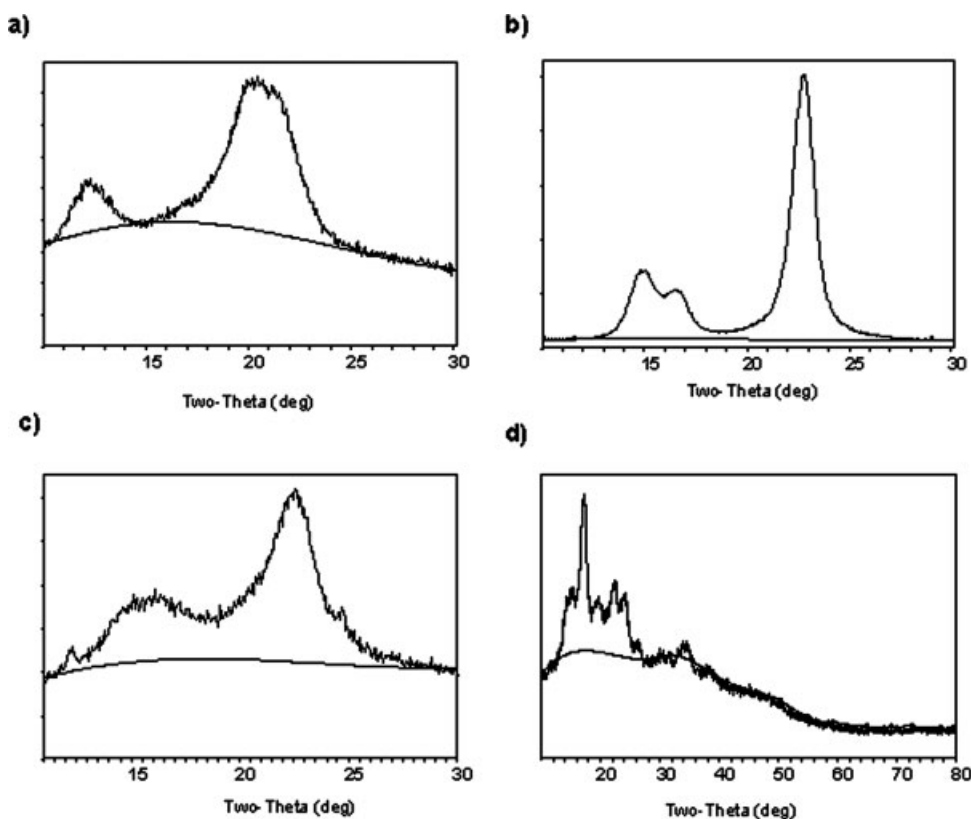


**Figure 1** XRD spectra and corresponding background estimates for the determination of crystallinity for (a) RC nanospheres, (b) cellulose whiskers, (c) wood fines, and (d) starch.
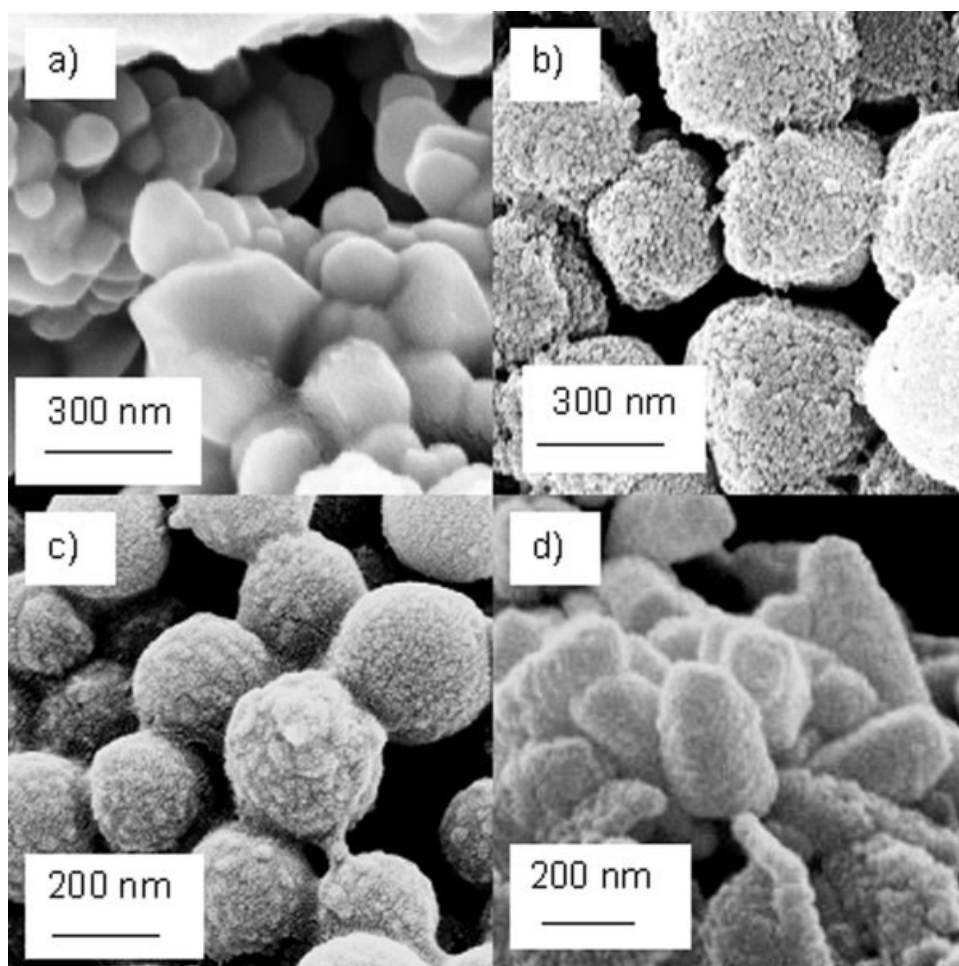
**Figure 2** Scanning electron microscopy images of (a) uncoated rutile particles, (b) RC-coated rutile, (c) RC-coated silica, and (d) RC-coated PCC.

the fines sheets during tensile testing, both sheets were reinforced by the application of Scotch tape to the backside followed by pressing at 20 psi and 105°C for 2 min. The laminated sheets were then conditioned at 20°C and 60% relative humidity for at least 3 h. The specific bonding shear strength of the laminates was then measured with an Instron tensile tester (Norwood, MA).

**Characterization**

X-ray diffraction (XRD) was carried out with an X'Pert Pro Alpha-1 diffractometer (GBC Scientific Equipment Pty. Ltd., Dandenong: Melbourne, Australia) with an incident beam monochromator allowing only the $K\alpha_1$ component of Cu radiation. XRD spectra were analyzed with JADE 7 software from Materials Data (Livermore, CA). The crystallinity ($X_c$) was estimated with the following equation:

$$X_c = \frac{A_{cr}}{A_{\text{total}}}$$

where $A_{cr}$ is the area above the background and $A_{\text{total}}$ is the total area (the background plus the area above the background). Figure 1 shows the typical XRD spectra and corresponding backgrounds for the four polysaccharide materials studied.

**RESULTS AND DISCUSSION**

The RC-coated inorganic core–shell nanoparticles are shown in Figure 2. Generally, when dissolved in an NMMO solution containing dispersed inorganic colloids, cellulose forms nanosized aggregates in the hydrogel layer surrounding the inorganic particles. The dissolved aggregates form nanosized, spherical precipitates upon contact with the hydrogel layer, which completely encapsulate the inorganic particle surface. The thickness of the cellulose shell is approximately 30 nm. As shown in Figure 3, the spherical precipitates composing the shell can be isolated as individual RC nanospheres. Generally, the particles are synthesized by the addition of water at a fixed rate to a dilute solution of cellulose dissolved in NMMO under stirring. The crystallinity, size, and shape of the solid RC nanospheres are influenced by
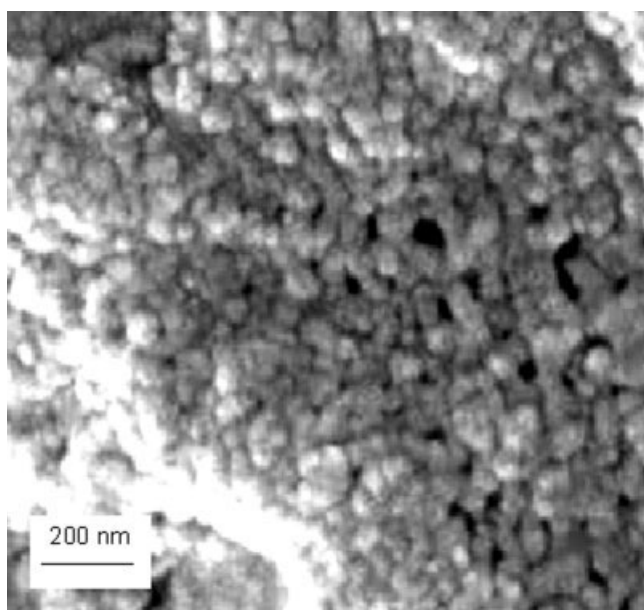
**Figure 3** Scanning electron microscopy image of individual RC nanospheres.

the rate of addition of the nonsolvent during precipitation. The spherical particles shown in Figure 3 were synthesized at a rate of 5 mL/min and had an average diameter of approximately 30 nm and a crystallinity of 25.0%.

The bondability of the inorganic–cellulose core–shell particles with wood fiber was studied through the measurement of the bonding strength of a wood fiber surface wet-pressed against a film composed of the individual RC spherical nanospheres. For comparison, the bonding strength between wood fiber and other polysaccharide materials including cellulose nanowhiskers, starch, and wood fiber itself was also measured. These polysaccharides have either previously been used as the fiber-bonding component of inorganic composite fillers or could be used. Unlike unmodified inorganic fillers that do not form
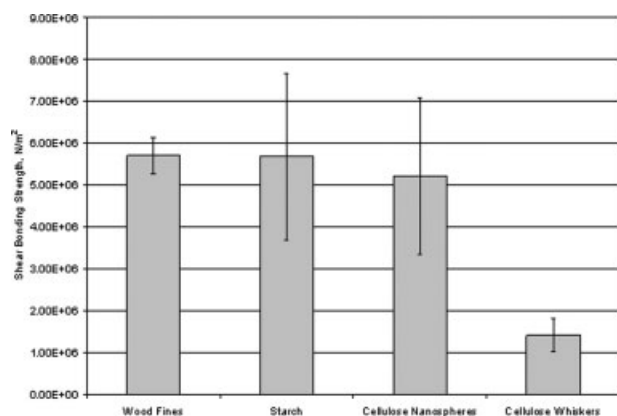
**TABLE I**
**Crystallinity of the Polysaccharide Materials Under Investigation**

|                        | Crystallinity (%) |
| ---------------------- | ----------------- |
| Potato starch          | 15                |
| Cellulose nanospheres  | 25.0              |
| Wood fines             | 31.5              |
| Cellulose whiskers     | 77.6              |

hydrogen bonds or other strong bonds with cellulose fiber, the free glucose hydroxyls of these polysaccharide materials can participate in hydrogen bonding with cellulose molecules on the fiber surface and supplement the number of hydrogen bonds that naturally occur in the bonded area between two fibers.[28] Although dissolved starch has traditionally been used in papermaking to increase paper strength, the starch molecules adsorb onto the surface of fillers in a nondeformable layer of molecular-level thickness. For the polysaccharide–inorganic composites reported previously, including our RC-encapsulated particles, substantial amounts of swollen, deformable polysaccharide material are available for bonding and lead to superior bondability. Zhao et al.[22] found a nearly 20% increase in hand-sheet tensile strength for a starch–gel-coated precipitated calcium carbonate filler over the conventional wet-end starch addition method. To study the effects of different polysaccharides on the bondability with wood fibers, the bond strength of different polysaccharide films against a sheet of wood fines was measured, and the results are shown in Figure 4. The RC nanospheres form a strong bond with the wood fiber sheet that is of an order similar to that of starch–fiber bonds or fiber–fiber bonds. However, the cellulose nanowhiskers have almost 5 times less bonding strength than other polysaccharide materi-
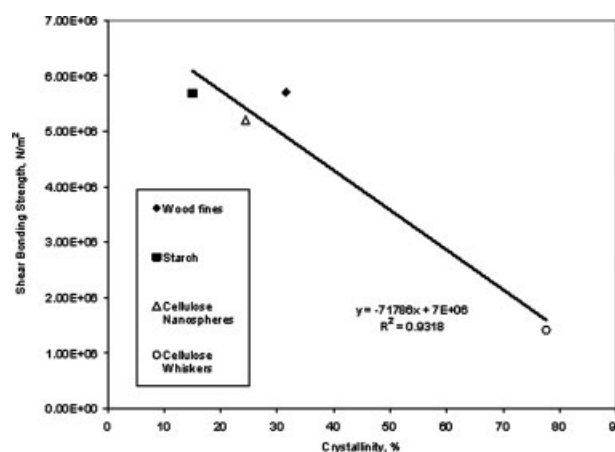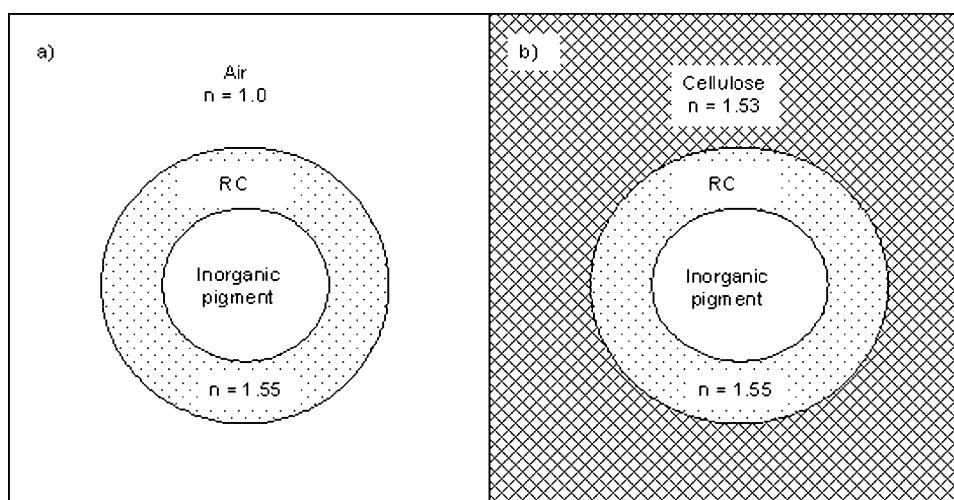


**Figure 4** Shear bonding strength between wood fines and the polysaccharide materials under investigation.



**Figure 5** Dependence of the fiber/polysaccharide bonding strength on the crystallinity of the polysaccharide material.

**Scheme 2** Illustration of the RC-encapsulated inorganic pigments embedded in (a) pure air and (b) pure cellulose.

als. Because all of the polysaccharides studied have similar functional groups, the hydrogen bonding ability is obviously impacted by another factor. It is expected that highly crystallized polysaccharides will have less bonding ability with wood fibers in a paper sheet than amorphous polysaccharides because of a decrease in deformability. Only the amorphous regions of carbohydrate materials can swell in the presence of water. This swelling makes the materials more pliable to conform around fibers, and this increases the bonding surface area and therefore bond strength. Table I shows that the cellulose whiskers have crystallinity 5 times higher than that of starch, the least crystalline and highest bonding material. Thus, the highly amorphous RC nanospheres, wood fines, and starch (with crystallinities of 25.0, 31.5, and 15%, respectively) should have much higher swellability than cellulosic nanowhiskers (with a crystallinity of 77.6%) and therefore bondability. Figure 5 shows that there is a direct relationship between polysaccharide crystallinity and bonding strength with fibers. As crystallinity increases, bonding strength decreases. Notably, the wood fines have a higher bonding strength than anticipated by the trend line. This may be due to the presence of CPAM in the wood fines (CPAM was used to concentrate fines in the fines collection process). Studies have shown that the treatment of both fiber plies with a dry strength agent gives delamination strength improvement over a single-ply treatment.[29] This work suggests that the most affective polysaccharide for paper-strength-enhancing inorganic composites is one with the least degree of crystallinity.

It has been shown in this study that the bonding strength of filler to wood fibers can be improved by the coating of RC on the filler surface. However, the optical property of the filler is another important factor that must be considered. In this study, light scattering efficiencies for the RC-coated and uncoated rutile and silica particles irradiated by light at 572 nm were determined with the well-known computer code BHCOAT, which was developed by Bohren and Huffman[30] and is widely used by others.[31,32] This code is based on the Mie theory and provides solutions for the light scattering of a single isotropic, concentric sphere embedded in a homogeneous medium. The code is publicly available at http://atol.ucsd.edu/scatlib/. The light scattering efficiency was calculated with BHCOAT for the aforementioned particles in air and in a pure cellulose matrix, as illustrated in Scheme 2. The particle size and refractive index data required as input to the program are listed in Table II. The refractive index of rutile, 2.73, was determined with the average index approximation, which accounts for the difference in the refractive index depending on the polarization state of the incident light.[33,34] All other refractive indices were obtained from the literature, and the particle sizes were obtained experimentally.[35] As shown in Table III, for pigments with a low refractive index such as silica, the calculations indicated that RC-coated pigments have higher scattering efficiency than the

**TABLE II**
**Required Input Data for the Light Scattering Program (BHCOAT)**

| | Refractive index at 572 nm |
|---|---|
| Rutile | 2.73 |
| Precipitated silica | 1.45 |
| Cellulose (fiber, cellulose I phase) | 1.53 |
| RC (cellulose II phase) | 1.55 |
| | Core radius (nm) |
| Rutile | 128 |
| Silica | 136 |

**TABLE III**
**Light Scattering Efficiency ($Q_{SCA}$) of Uncoated and RC-Coated Silica and Rutile**
**Nanoparticles at $\lambda = 572$ nm**

| Surrounding medium | Silica pigment | | | Rutile pigment | | |
|---|---|---|---|---|---|---|
| | Uncoated | Coated | $\Delta Q_{SCA}$ | Uncoated | Coated | $\Delta Q_{SCA}$ |
| Air | 0.60 | 1.33 | +0.73 | 4.32 | 3.29 | −1.03 |
| Cellulose | 0.0065 | 0.0035 | −0.003 | 1.66 | 1.12 | −0.54 |

corresponding uncoated pigments, except when surrounded entirely by cellulose, where the scattering efficiencies are the same. Therefore, these coated pigments can impart more opacity than corresponding uncoated particles when surrounded by air, and this is a likely occurrence for porous, bulky sheets. Although the RC-coated pigments (e.g., silica) have higher scattering efficiency than the corresponding uncoated pigments, as also shown in Table III, the RC-coated pigments have lower scattering efficiency than the corresponding uncoated pigments with a high refractive index like rutile.

## CONCLUSIONS

The bondability with cellulosic substrates of discrete, uniformly coated, inorganic–RC nanoparticles was investigated. The RC nanospheres, composing the composite's shell, form bonds with wood fibers on the order of starch–fiber and fiber–fiber bonds. The bonding strength was shown to depend on the crystallinity and therefore swellability and conformability of the polysaccharide material, with starch (crystallinity = 15%) giving about 5 times greater bonding strength than cellulose whiskers (crystallinity = 77.6%). Finally, calculations of light scattering based on the Mie theory indicate that the light scattering of cellulose-encapsulated pigments of a low index of refraction, such as silica, will be equal to or greater than the scattering of the uncoated pigments, depending on the porous structure of the paper sheet.

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