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Surface Modification of Bricks by Chitosan Coatings

Siripan NILPAIRACH and Stephan T. DUBAS*

Metallurgy and Materials Science Research Institute,
Chulalongkorn University, Bangkok, Thailand

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Abstract

Bricks were successfully modified by application of a chitosan coating in order to provide their surface with a water repellant character. The chitosan coating was prepared by depositing solutions of variable chitosan concentration (1% or 2.5% w/w) onto the brick surface and let to dry under ambient condition. In order to improve the water repellant property, the films were cross-linked with a 1% solution of sodium citrate, sodium sulfate or sodium tri–polyphosphate. The effect of the chitosan concentration on the morphology of the coating at the brick surface was observed by scanning electron microscope (SEM). It was found that the brick surface porosity can be completely covered by the 2.5% chitosan solution leading to the formation of a very smooth surface. The effect of the different cross-linking agents was evaluated by measuring the time needed for a 100 μL drop of water to penetrate through the chitosan coating into the bricks. Using this technique, it was shown that the citrate cross-linked films provide the best water resistance to the brick surface. This type of coating could be used in application where water resistant bricks are needed such as freeze/thaw cycles or in roof tile applications.

Key words : Hydrophobic, Coating, Chitosan

Introduction

Bricks and other clay materials, although having been used since ancient time, still suffer from their major characteristic which is porosity. Although their light weight and high porosity provide most of their insulation properties, it is the same porosity which renders them sensitive to water adsorption. The intricate network of micro-channels in bricks allows water adsorption providing a favorable ground for fungi growth and in some instance destructive effect of freeze/thaw cycles. Fractures from freezing water entrapped in micro-cavity can induce the propagation of cracks leading to mechanical failure of the material. The most recent approach to prevent water adsorption in bricks is the formation of a hydrophobic film at the surface of the brick to provide the water repellent properties. Different classes of synthetic organic coatings have been used or tried for this purpose and in particular acrylic and siloxane polymers, perfluoroethers as well as fluorinated polyolefins.(1-4) These coatings are very efficient to repel water and provide a very hydrophobic surface but are expensive and require complex application conditions.

Chitosan [poly(β-(1→4)-2-amino-2-deoxy--glucose)] is a natural cationic polysaccharide derived from chitin which is a copolymer of glucosamine and an N-acetyl glucosamine units, combined together.(5) Chitosan has been extensively studied as carrier for drugs(6) protein carrier and gels for the entrapment of cells or antigens(7) in the pharmaceutical industry. Chitosan has been used in the fabrication of permeable membranes because it possesses strong film formation properties which can be further improved by cross linking with EDTA, sodium citrate, sodium sulfate or sodium tri–polyphosphate.(8,9) Chitosan also presents the advantage that it can be produced inexpensively from waste of the shrimp industry.

Because bricks are a very inexpensive construction material, a commercially successful hydrophobic coating needs to be simple to apply, inexpensive and environmentally friendly. The current siloxane(1-4) based technology used in some advanced applications does not seem to be the appropriate approach due to its high cost and difficulty of preparation. In the present article we study the possible use of chitosan coating on bricks as hydrophobic barrier and water repellent coating. The chitosan coatings were applied on small bricks from chitosan solution containing 1% or 2.5% of chitosan in acetic acid. The hydrophobic properties of the modified bricks were evaluated monitoring the time taken for a droplet to penetrate in the brick through the polymeric coating. The topography of the brick surface modified by the chitosan coating was also evaluated by scanning electron microscopy. The proposed coating could be used in application where some water resistant properties are needed, for example in bricks to be used in roofing or in bricks exposed to freeze/thaw cycles.

Experimental Method

Chemicals

Chitosan with a degree of deacetylation of 84%, sodium citrate, sodium sulfate and sodium tri-polyphosphate were all purchased from Aldrich, Thailand. Diluted solutions of acetic acid prepared from dilution of glacial acetic acid, from Carlo Erba Thailand, were used to adjust the pH of all solution to a value of 4. In all experiments double distilled water was used.

Brick Coating

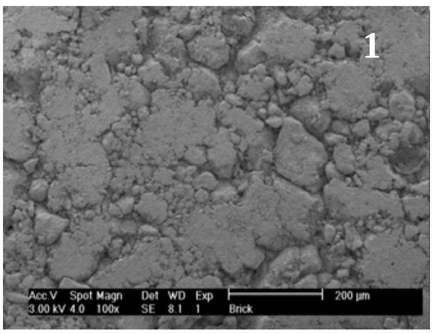
The bricks were purchased from a local store and had a dimension of 5x5x0.5 cm. The chitosan solutions used for coating the bricks were prepared as follow. Chitosan flakes with a degree of deacetillation of 84% were dissolved in 1% acetic acid overnight. The chitosan concentration was either 1% or 2.5 weight %. The next day, the chitosan solutions were filtered to remove undissolved chitosan solids and stored in a bottle prior to use. The bricks were coated with 1ml of the chitosan solution spread evenly and allowed to dry. The bricks were then dipped in a 1M NaOH solution, dried and then dipped for 1 min in a cross-linking 1% solution of either: sodium citrate, sodium sulfate or sodium tri-polyphosphate. A last drying step at room temperature was used prior to testing.

Characterization

The surface morphology of the coated bricks was obtained by a scanning electron microscope (model Phillips 1000s). For water permeability test, a drop of water (100μL) dispensed by a micropipette was deposited at the surface of the sample. The time for the droplets to completely permeate in the film was measured for each coating condition.

Results and Discussion

In Figure 1. SEM images of the bricks' surface after coating with various chitosan solutions are presented. The changes in porosity of the bricks' surface can be observed by the decrease in apparent roughness. The surface of the original uncoated brick (Figure 1 picture 1) shows extensive roughness which is typical in ceramic surfaces after sintering of the clay at high temperature. It is the brick's porosity which is the cause of its high water adsorption leading to potential cracking and failure after repetitive freeze/thaw cycles. The coating effect of the treatment proposed in this work on the surface roughness and porosity can be seen in Figure 1 pictures 2, 3, 4, 5. The efficiency of chitosan with the concentrations 1% (pictures 2, 3) and 2.5% (pictures 4, 5) to cover the pores can be seen with a decrease of the brick surface features. While the 1% solution provides some coverage of the pores, the 2.5% solution leads to the formation of a uniform coating which completely covers the bricks' surface. Although the chitosan coatings were cross-linked with sodium citrate, sodium sulfate or sodium tri–polyphosphate, only the SEM images of the citrate cross-linked bricks are shown since the other coatings displayed very similar features. It is interesting to note that the cross-linking of the chitosan film with the 1% sodium citrate solution does not induce any change in film morphology. This can be observed when comparing the 1% chitosan coating on picture 2 (uncross-linked) and picture 3 (1% citrate cross-linked) and the 2.5% chitosan coating picture 4 (uncross-linked) and picture 5 (1% citrate cross-linked). Since the 2.5% chitosan coating provided a more uniform and more complete coating of the brick's surface, we chose to use the 2.5% chitosan coating throughout the remainder of this research.



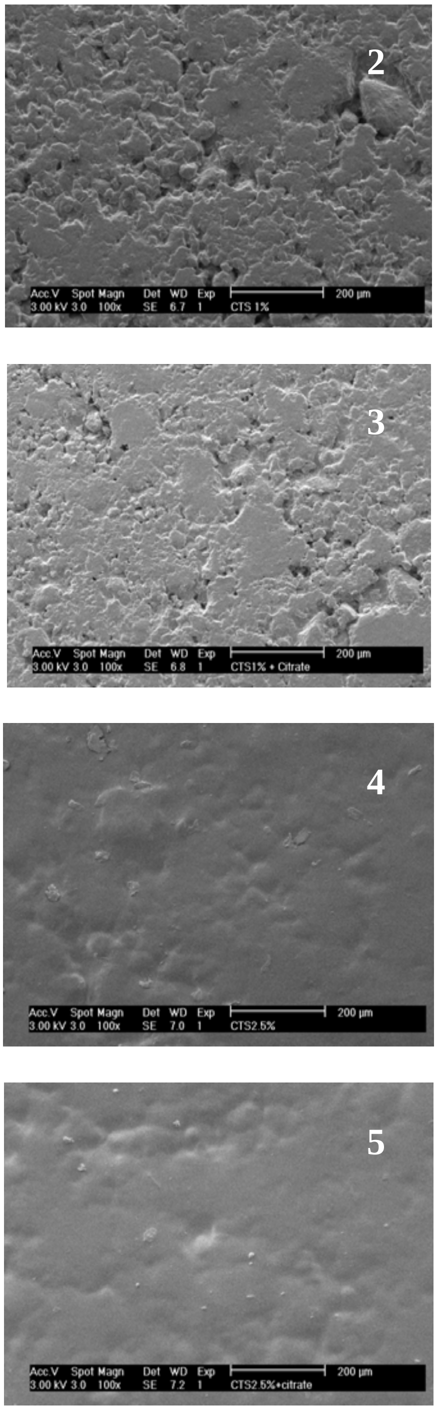


Figure 1. SEM of the bare brick surface (picture 1), brick surface modified with 1% (picture 2) and 2.5% (picture 4) solution of uncross-linked chitosan and the brick surface modified with 1% (picture 3) and 2.5% (picture 5) solution of chitosan cross-linked with 1% sodium citrate solutions.

Although no morphology changes of the chitosan coating could be observed by SEM between uncross-linked and cross-linked, water permeability was greatly modified. Figure 2 shows the permeation times of a 100 µL water droplet through the 2.5% chitosan film after various treatments. The water droplet took only 30 min to penetrate the uncross-linked chitosan but 40, 50 and 53 min for the 1% tri-polyphosphate, sodium sulfate and sodium citrate cross-linked coatings. The superior efficiency of chitosan film cross-linking by citrate and sulfate over TPP has already been reported by Shu in chitosan beads used for targeted drug delivery systems.[10] The citrate which is composed of three carboxylic groups (COOH) has a strong affinity with the protonated amino groups ($NH3^+$) of the chitosan leading to a better cross-linking effect than other compounds used.

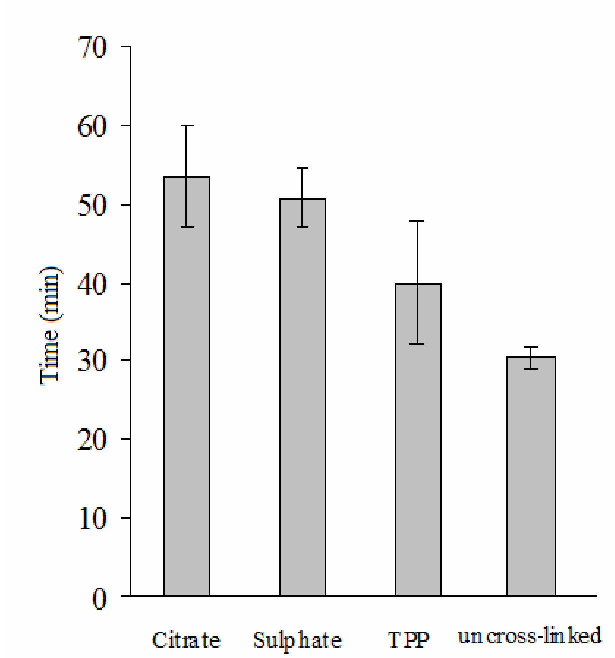


Figure 2. Time needed for a drop to penetrate the brick through the 2.5% w/w chitosan coating as a function of the cross-linking conditions used.

In Figure 3, the water repellent properties of the unmodified brick (picture A) and 2.5% chitosan coating cross-linked with a 1% solution of citrate (picture B) are compared. The superior water resistance of the cross-linked film can be seen as the water droplet remains intact while the unmodified brick allows water to permeate through the surface instantaneously. The water resistance is clearly provided by the film formed at the surface of the brick and closes the porosity, thus reducing water permeability. The cross-linked film shows superior hydrophobicity due to the complexation of the carboxylic groups and the amino groups from the citrate and chitosan, respectively. Although no covalent bonding occurs in the complexation process, the ionic association between carboxylic and amino groups is strong and results in a more hydrophobic character. The coated bricks display high hydrophobicity which could, reduce water absorption in outdoor usage. Further work is being pursued to investigate the long term stability of such coatings.

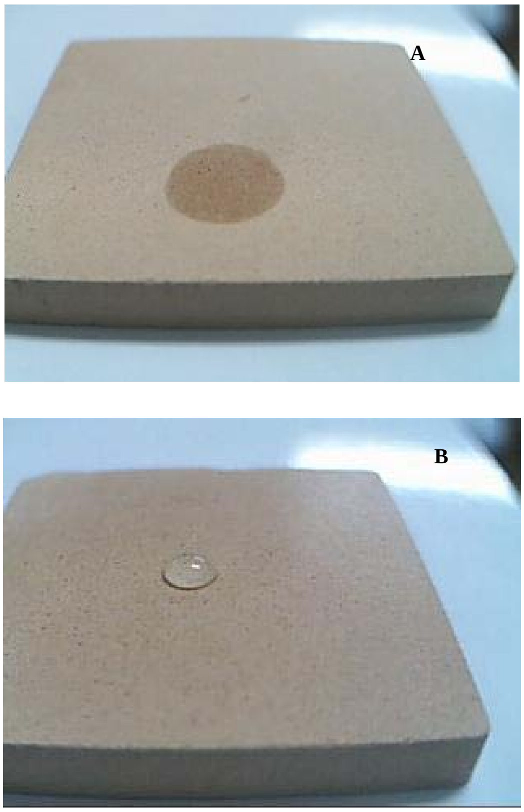


Figure 3. Contact angle pictures of the bare brick (picture A) and modified bricks with a 2.5% Chitosan coating cross-linked with 1% citrate (B).

Conclusion and Further Work

In conclusion we have demonstrated that chitosan can be used as a coating to reduce the porosity of bricks and provide hydrophobic character of usually very hydrophilic brick surface. The 2.5% chitosan solution provides the best coating and the 1% citrate solution gives the best cross-linking efficiency. The bricks' surface can be modified by simple dipping or spraying of chitosan solution which would render them useful in application where moist resistant bricks are needed.

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