University of Technology, Sydney

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INVESTIGATION INTO CLAY-BASED CONSOLIDANTS FOR CONSERVATION OF "YELLOW BLOCK SANDSTONES" IN SYDNEY'S HERITAGE BUILDINGS

PhD Thesis

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PhD THESIS

A thesis submitted in partial fulfilment of the requirement for the award of a PhD degree

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I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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AFM:	Atomic Force Microscopy
CRT:	Cathode Ray Tube
DRIFT:	Diffuse Reflectance Infrared Fourier Transform
DSC:	Differential Scanning Calorimetry
DTG:	Derivative Thermogravimetry
DTGS:	Deuterated Triglycine Sulfate
EDS:	Energy Dispersive Spectroscopy
ESCA:	Electron Spectroscopy for Chemical Analysis
ESEM:	Environmental Scanning Electron Microscopy
FTIR:	Fourier Transform Infrared
IR:	Infrared
NMR:	Nuclear Magnetic Resonance
PAA:	Poly acrylic acid
PAAMMT:	poly acrylic acid – montmorillonite
PEO:	Poly ethylene oxide
PEOBEN:	poly ethylene oxide - Bentone
PEOTIX:	poly ethylene oxide - Tixogel
PVAl:	Poly vinyl alcohol
PVAlMMTu:	Poly vinyl alcohol – montmorillonite from Unimin
PVAlMMTa:	Poly vinyl alcohol. – montmorillonite from Arumpo
SEM:	Scanning Electron Microscopy
TG:	Thermogravimetry
XPS:	X-ray Photoelectron Spectroscopy
XRD:	X-ray Diffraction

Abstract

Many of the 19th century heritage buildings, located in Sydney, were built from locally quarried sandstone. After more than a century of natural weathering, a number of the sandstone buildings are showing signs of deterioration. In order to ascertain the appropriate preservation techniques of such buildings, an understanding of the mechanisms of degradation of these buildings stones must first be sought before consolidation treatment is carried out. The objectives of the thesis are to first characterise the degradation processes of selected heritage yellow block sandstone, followed by the synthesis and characterisation of potential polymer-clay nanocomposites as stone consolidating systems. In order to target particular degradation problems in heritage sandstones, a thorough understanding of the degradation mechanisms of the sandstone is essential before suitable materials are synthesised to prevent or slow down further damages to the stones. The novel approach of this thesis is to use a large range of analytical techniques for the characterisation of degraded yellow block sandstone samples. The methods of preparation of a series of novel polymer-clay nanocomposite consolidating systems can then be optimised according to the characteristics of each stone, and potential consolidant systems can be identified. Although various materials have been employed as stone consolidants in the past, the proposed use of polymer-clay nanocomposites as potential stone consolidants is a novel approach.

A number of analytical methods including FTIR, NMR, XPS, XRD, SEM and thermal analysis were used to characterise the sandstone and to determine the degradation mechanisms of the sandstones in Sydney's heritage buildings. The yellow block sandstones were found to be composed of sand grains (60 – 68%) bound together by a kaolin-based cementing material (16 – 25%). As the silica sand is essentially

inert, the study focused on the clay component of the stone. An increase in iron concentration on the stone surface contributed to the discolouration of the stone and provided a source of Fe^{3+} for the isomorphous substitution of Al^{3+} in the octahedral sites and possible Si^{4+} in the tetrahedral sites of the aluminosilicate layers in the cementing clay. The substitution resulted in the brittleness of the stone, but preserved the layered structure of the clay binder and retained the overall integrity of the sandstone. A change in pore size distribution was observed on weathering of the sandstone, with an increase in population of large pores providing greater access to atmospheric pollutants, soluble salts and rainwater to the sandstone core, making the already weathered stones more vulnerable to further degradation.

Based on the model of degradation, the physical properties of Sydney sandstones and the aim to produce consolidants for easy application, hydrophilic polymer-clay nanocomposite systems were prepared. Montmorillonite was used as the clay component for its similar layer structure as the kaolinite presented in the cementing materials in the yellow block sandstone samples, while poly(vinyl alcohol), poly(acrylic acid) and poly(ethylene oxide) were used as the polymer component for their hydrophilic nature. AFM and XRD analysis were used to investigate the polymer-clay interactions in these composites. While the AFM analysis reveals the topography of the synthesised polymer-clay film without melting the samples, XRD analysis indicates the degree of separation of the montmorillonite clay platelets by the polymer chains through the detection of the shift of the XRD peaks. The intercalation and partial exfoliation of montmorillonite platelets in different hydrophilic polymer matrices was observed in both the solution and melt intercalation methods. PAAMMTa samples were found to be the best intercalated/exfoliated nanocomposites in the solution intercalation method. Although better separation of clay platelets was demonstrated in the XRD results using the melt intercalation method, it would not be considered a preferred method at present time due to the impractical nature of using solid products as stone consolidants. However, further research may provide solution for the dissolution of such materials in suitable solvents without affecting its consolidating ability. The hydrophilic nanocomposite materials investigated in this project show great potential as a new class of sandstone consolidants for the binding of porous weathered sandstones in Sydney's heritage buildings.