Effect of polyurethane/nanosilica composite coating on water resistance of paper substrate

K. S. Ching¹, Y. C. Ching*¹, C. A. Ng², N. Ishenny³ and M. T. H. Beg⁴

The effect of nanosilica particles on the water resistance of a polyurethane/nanosilica composite coated paper substrate was investigated. The polyurethane/nanosilica composite coating was prepared by dispersing nanosilica powder into solvent-based polyurethane using high mechanical stirring force. Paper substrate was coated with polyurethane/nanosilica composite using a Rod Mayer technique. Various compositions of polyurethane/nanosilica composite coatings on paper substrate were prepared. The total thickness of the paper coated with polyurethane/nanosilica composite was 0.3 mm. The field emission scanning electron microscopy images indicated that the presence of nanosilica has improved the surface roughness and porosity of paper substrate. The addition of nanosilica in polyurethane coating had increased the water resistance ability of the coated paper. It was demonstrated that polyurethane/nanosilica-6% shows better water resistance and exhibits better thermal stability than the nanocomposites with lower nanosilica loading. Fourier transform infrared spectroscopy result shows that there was no chemical reaction between nanosilica and polyurethane.

Keywords: Polyurethane, Nanosilica, Coating, Paper, Water resistance

Introduction

Applying a coating material onto the paper substrate is widely practiced around the world.¹ According to European Standard EN 971-1 (1996), it is defined that the coating material which comprises paints and varnishes as a product in liquid, paste or powder form that, when applied to a substrate, forms a film possessing protective, decorative and/or other specific properties.¹–³ As stated above, the application of coating material is to provide the necessary protection to the paper substrate. The protection could be against water, thermal and also mechanical force. Polyurethane is proved as a high performance engineering materials that exhibit higher modulus, better adhesion, higher heat durability, better elasticity, abrasion resistance, hardness, flexibility, chemical and solvent resistance, gloss and low temperature film.⁴,⁵ However, it has low water resistance capability.⁶ Therefore, another method has been suggested that could improve the properties of the layer that is hybridised with other materials.⁶

Hybridising of nanoparticles, especially the inorganic ones, into the coating layer can help improve the properties of pristine coating. Among the improved properties via nanoparticle additions are high modulus, higher mechanical strength, increased tensile strength and heat resistance, the decreased elongation at break and gas permeability.⁴–⁷ The mechanical properties such as hardness and tensile strength are increased as the content of nanoparticle is increased.⁶ The improvement in the mechanical properties of polyurethane/silicate (PU/SiO₂) nanocomposites also suggested that there exists a strong interaction between the silicate surface and the surrounding polymer chains.⁸

Nanosilica will improve the water resistance of polyurethane.⁵ It is found that nanosilica formed after drying plays a remarkable role in improving water resistance, aging resistance and the finish of coating.⁴ This is mainly because of the maximised interfacial contact between the organic and inorganic phases within the nanostructured organic/inorganic composites.⁸–¹¹ Besides that the swelling percentages of films also reduced with an increase in nanoparticles such as clay and silica content.⁸ This shows that the inorganic materials such as nanoclay and nanosilica could improve the water resistance properties of the coating.⁸–¹² The water resistant layer is necessary in
impeding water from direct contact to the protected substrate.

Recently, many researches have been performed to improve the PU coating with the addition of nanosilica. However, there was still lack of studies on the performance of the PU/nanosilica composite coating on the paper substrates for numerous applications such as paper-making sector and food-packaging industry. Thus, this study focuses on the effect of different concentration of nanosilica contents on the water resistance and water-swelling properties of paper substrates. The development of nanosilica reinforced polyurethane composite coating was attempted using the blending method. In this study, a thin layer of PU/nanosilica composite coating with an uniform thickness of 4 μm was applied on the paper substrate using the Rod Mayer method. The water penetration test, water-swelling test, Fourier transform infrared (FTIR) and field emission scanning electron microscope (FESEM) analysis were conducted on the PU/SiO2 composite to determine the effect of the composite on paper substrate. The optimum PU/SiO2 composition for excellent water resistance and swelling properties of paper substrate was investigated in this study.

**Experimental**

2 K polyurethane (SM 510n/60LG, 60% solid content) was purchased from Cytec. Hydrophobic fumed silica with a specific surface area of 130 m² g⁻¹ and the mean particle size of 16 nm (Aerosil R972) from Degussa Chemicals was used for the preparation of nanocomposites. The reagent grade solvents such as toluene, isopropanol and ethyl acetate were purchased from Eastern Printing Ink Co. Sdn. Bhd. All the raw materials were used as received. The PU solution was diluted using a mixture of solvent, namely, toluene, isopropanol and ethyl acetate in the ratio of 6:3:1. Nano silica was purchased from Cytec. Hydrophobic fumed silica with a specific surface area of 130 m² g⁻¹ and the mean particle size of 16 nm (Aerosil R972) from Degussa Chemicals was used for the preparation of nanocomposites. The reagent grade solvents such as toluene, isopropanol and ethyl acetate were used as received. The PU solution was diluted using a mixture of solvent, namely, toluene, isopropanol and ethyl acetate in the ratio of 6:3:1.2-6 Nano silica was dispersed in the polyurethane solution using a Cowles mechanical stirrer Dispermix DL-B (Olivery Battle S.A., Spain). All nanosilica was added into PU solution at a stirring speed of 2000 rev min⁻¹ for 30 minutes.2,3,5 The nanocomposite material was then deposited onto the paper substrate (60 g m⁻²) using the Rod Mayer technique.2-6 The coating would pass through the grooves between the wires of Rod Mayer and then levels off a uniform thickness of thin film on the surface of paper substrate.12-16 The coated paper was then left to cure under the standard room temperature. An uncoated paper substrate was prepared under the same condition and used as a blank.

The ability of polyurethane and PU/SiO2 nanocomposite coating in resisting water penetration was tested by applying a drop of water (0-05 mL) onto the samples. The time taken for water to penetrate through the coating material was recorded. The recorded time will show the water resistance ability of paper substrate coated with neat PU and PU/SiO2 nanocomposite coating. Fourier transform infrared spectra were performed using a FTIR Perkin-Elmer Spectrum 400 in the range of 4000–400 cm⁻¹ to study the chemical composition of the composite and to ascertain the interfacial interaction between the nanosilica particles and polyurethane. Field emission scanning electron microscope (JEOL JSM-7600F) was used to analyse the surface morphologies of paper coated with a nanocomposite coating containing various percentages of nanosilica. The adhesion as well as the thickness of the PU/SiO2 composite-coating layer on paper was observed through cross-sectional images from FESEM. Water swell, i.e. the degree of water absorption, was measured by preserving a film in water at room temperature for over 7 days. The water swell (%) was calculated by the following equation:

\[
\text{% swell} = \frac{W - W_0}{W_0} \times 100
\]

where \(W_0\) is the weight of dried film and \(W\) is the weight after water absorption.

**Results and discussion**

As observed in Fig. 1a, clear strands of fibres were seen for uncoated paper substrate. The morphology is true as the production of paper requires pressing of wood fibres together to form paper sheets.4 Figure 1b illustrates the morphology of paper substrate after coated with a neat polyurethane layer. The coat of PU layer appears tough to spread evenly on the paper surface. The paper surface was less covered and revealed the texture of the paper fibres.14 However, the PU coating was spread more smoothly on the surface of paper substrate with the introduction of nanosilica (Fig. 1c). This was due to the reduction viscosity of polyurethane binder after blended with small amount of nanosilica. Figure 1d illustrates that the surface texture of paper substrate became less visible with the increasing of the nanosilica content in PU/SiO2 composite coating from 4 to 6 wt-%. The morphology of paper coated with PU/SiO2-6% coating shows a rough surface because of the presence of high amount of nanosilica particles.14,15

The first penetration test was performed by leaving a drop of liquid comprising water and water-based ink on the top of the sample and left overnight. The time taken for water to pass through the blank paper, paper coated with a polyurethane coating and paper coated with PU/SiO2 composite coating were tabulated in Table 1. It was found that the water takes the least time to go through the blank paper, followed by paper coated with a polyurethane coating and a PU/SiO2 composite coating. The water penetrated through the uncoated paper substrate and left behind the water stain at the back of uncoated paper after 0-05 hour. This is because polar molecules such as water are more attracted to form polar–polar interaction with other polar groups. Hence water molecules are easier to go through the blank paper because they contain polar groups.16,19

For paper substrate coated with polyurethane coating, the water stain was observed on the back of the paper after 3 hours. This is probably because of application of the PU-coating materials onto the surface of the paper provides a barrier and reduces the porosity between the wood fibres.12,14 This effect increases the water resistance ability of the paper. With the addition of nanosilica particles in the polyurethane coating, the water barrier rate was further increased with the increasing of nanosilica content. This indicates that the addition of nanosilica particles to polyurethane composite coating had further reduced the polarity of paper, and lowered its tendency...
to interact with water molecules.\textsuperscript{18,19} Thus, the water molecules are unable to pass through the porosity. This explains why the small water stains only found at the back of the paper coated with PU/SiO\textsubscript{2}-6\% composite coating after 10 hours of the water penetration test.

Table 2 shows the result of the water-swelling test on PU/SiO\textsubscript{2} composites with varying nanosilica contents. From the result, it was found that the addition of nanosilica increases the water resistance of the PU/SiO\textsubscript{2} composite coating. This was proved when the paper coated with a neat polyurethane coating experiences the largest of water swelling.\textsuperscript{14,18,19} 30.8\% of the swelling for paper coated with polyurethane after a period of 7 days was observed. For the same period of time, 17.3, 9.8 and 3.5\% of swelling were observed for PU/SiO\textsubscript{2}-2\% composite, PU/SiO\textsubscript{2}-4\% composite and PU/SiO\textsubscript{2}-6\% composite, respectively.

The PU/SiO\textsubscript{2}-6\% composite exhibited the greatest water resistance ability. As seen from Table 2, PU/SiO\textsubscript{2}-6\% composite was impermeable to water swelling during the first 5 days of the test. This result is similar to the previous water-swelling test conducted on polyurethane/organoclay composites.\textsuperscript{19} According to Chen et al.,\textsuperscript{19} the mean free path of water molecules to pass through the composite of polyurethane/organoclay would increase when the organoclay layers are dispersed in nanometre scale in the polyurethane matrix.

Figure 2 illustrates that Fourier transform infrared (FTIR) spectra of uncoated paper yields peak at 1640 cm\textsuperscript{-1}, NH (amines) stretching at 3300 cm\textsuperscript{-1} and CH (alkanes) stretching at 2900 cm\textsuperscript{-1}.\textsuperscript{20} With the introduction of PU coating on paper substrate, peak at 1730 cm\textsuperscript{-1} emerged. Paper coated with PU/SiO\textsubscript{2} nanocomposite containing 2 wt-% of nanosilica displayed new peak at around 1060, 960 and 810 cm\textsuperscript{-1}, indicating the absorption of Si–O. For paper coated with PU/SiO\textsubscript{2}-4\% and PU/SiO\textsubscript{2}-6\% nanocomposite, the FTIR spectra show the existence of the same peaks as PU/SiO\textsubscript{2}-2\% nanocomposite-coated paper.

Besides, the region at 1060–1160 cm\textsuperscript{-1} becomes broader with the increasing of the nanosilica content. This can be associated with overlapping of bands from

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time taken (hour)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank paper</td>
<td>0.05</td>
</tr>
<tr>
<td>Paper with polyurethane coating</td>
<td>3</td>
</tr>
<tr>
<td>Paper with PU/SiO\textsubscript{2}-4% composite coating</td>
<td>6</td>
</tr>
<tr>
<td>Paper with PU/SiO\textsubscript{2}-6% composite coating</td>
<td>10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water swell (%) after 1 day</th>
<th>2 days</th>
<th>3 days</th>
<th>4 days</th>
<th>5 days</th>
<th>6 days</th>
<th>7 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PU</td>
<td>10.2</td>
<td>11.3</td>
<td>13.5</td>
<td>16.9</td>
<td>20.4</td>
<td>25.6</td>
<td>30.8</td>
</tr>
<tr>
<td>PU/SiO\textsubscript{2}-2%</td>
<td>5.6</td>
<td>6.8</td>
<td>8.0</td>
<td>10.7</td>
<td>12.8</td>
<td>14.1</td>
<td>17.3</td>
</tr>
<tr>
<td>PU/SiO\textsubscript{2}-4%</td>
<td>2.0</td>
<td>2.6</td>
<td>3.3</td>
<td>4.5</td>
<td>5.8</td>
<td>6.5</td>
<td>9.8</td>
</tr>
<tr>
<td>PU/SiO\textsubscript{2}-6%</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>2.2</td>
<td>3.5</td>
</tr>
</tbody>
</table>
thus, contributes to the water resistance capability of the polyurethane has created a barrier for water movement, the addition of nanosilica particles into polyurethane has, successfully, covered the porosity of the paper composites with lower nanosilica loading. The site layer shows better water resistance than that of nanosilica. The introduction of the polyurethane coating for water resistance of the paper substrate. The effect of nanosilica-filled acrylic-based polyurethane coating successfully onto the paper substrate by the Rod Mayer technique. The nanocomposite. Hence, the incorporation of nanosilica did not alter the chemical structure of polyurethane.

Conclusion

The polyurethane/nanosilica composites were coated successfully onto the paper substrate by the Rod Mayer technique. The effect of nanosilica-filled acrylic-based polyurethane coating for water resistance of the paper substrate was investigated. Both the water penetration test and the swelling test methods were carried out to determine the ability of the polyurethane/nanosilica coatings in resisting water permeability of the paper substrate. Introduction of the polyurethane/nanosilica-6% composite layer shows better water resistance than that of nanocomposites with lower nanosilica loading. Nanocomposite coating with 6 wt-% of nanosilica contents has, successfully, covered the porosity of the paper and has increased the resistance of the paper to water penetration. The addition of nanosilica particles into polyurethane has created a barrier for water movement, thus, contributes to the water resistance capability of the composite layer to the paper substrate.

Acknowledgements

The authors acknowledge financial support from research grants: CG013-2013, RP024C-13AET, RU022A-2014, FP030-2013A and ER014-2012A.

References