INFLUENCE OF NANOPARTICLES COATING ON PAPER DURABILITY

NURUL H. FITHRIYAH¹*, ERDAWATI²

¹Department of Chemical Engineering, Universitas Muhammadiyah Jakarta
²Department of Chemistry, Universitas Negeri Jakarta, Indonesia

*Corresponding Author: nurul.fithriyah@gmail.com

Abstract

An environmentally friendly process were employed to prepare samples of recycled paper, as well as the coating solution of chitosan nanoparticles and dispersion of Ca(OH)₂ particles. The nanomaterial was tested for antibacterial and acidity neutralising functions to preserve the strength and colour of paper samples. The paper samples were then characterised for physical and morphological characteristics, as well as chemical and mechanical properties. At concentrations of 0.125 and 0.25 mg/L, the chitosan nanoparticles (23-62 nm) were observed to retard the propagation of E. Coli and S. Aureus bacteria up to 22 and 26 mm in diameter, respectively. This propagation was also hindered by an increase in acidity introduced by Ca(OH)₂ nanoparticles. The grammage, firmness, and colour of coated paper samples were not significantly influenced by nanoparticles concentration or coating thickness due to the low mass-to-area ratio of coating. Nevertheless, the tear strengths and cracking resistance of coated paper were improved. Chitosan nanoparticles in the coating potentially functioned as a sizing agent by diffusing into the pores of paper fibres and increasing the interfibrillar bonding, while the nanoparticles of Ca(OH)₂ apparently preserved the strength and colour of paper samples by neutralising the acidity and thus preventing microbiological attacks.

Keywords: Chitosan nanoparticles, Ca(OH)₂ dispersion, Coating, Properties, Paper.

1. Introduction

Paper durability depends on its physico-mechanical characteristics as well as other properties. These properties can be improved after an application of water-soluble polymeric materials, either synthetic or natural [1], as an additive or coating. Since paper consists of cellulosic fibres, these polymers are able to bond with the fibres by electrostatic or non-electrostatic interaction. Natural polysaccharides are promising
additives in papermaking processes, due to their biodegradability and thus environmentally friendly. They can also serve as moisture, grease, and oxygen barriers in many food-packaging applications. Biodegradable packaging can be developed by inclusion matrices of antimicrobial agents [2].

2. Literature Review

Chitosan is one of the most interesting and most studied polysaccharides available for paper coatings [3]. Its use as a paper making additive or paper surface treatment agent has been around for decades owing particularly to its good compatibility with cellulose-based substrates and high retention. This compatibility is attributed to its cellulose-like structure, allowing fast absorption onto cellulosic surfaces as supported by steric factors and chemical affinity. Chitosan has also been used as edible films or coating due to its film-forming and bioactive properties either in polymeric or oligomeric form [4]. The physico-mechanical properties of greaseproof paper’s wet end were improved when chitosan was applied [5-7]. Moreover, chitosan is biodegradable, non-toxic, antifungal, and antibacterial renewable material with excellent grease and oxygen barrier properties [8] because of it is high in crystallinity and forms hydrogen bonds between molecular chains [9].

Polymeric nanoparticles have attracted much application, particularly in pharmaceutical [10], biomedical [11], and food industries [12]. Nanoparticle chitosan was selected for paper coating because it is readily compatible with the cellulosic-fibres of paper, and is therefore a good comparison for the analysis of other biopolymer-paper system. Chitosan nanoparticles are usually prepared through an ionic gelation between positively-charged chitosan and negatively-charged sodium tripolyphosphate.

Dispersion of Ca(OH)₂ (calcium hydroxide) nanoparticles in non-aqueous solution like isopropanol is capable of absorbing CO₂ and forming CaCO₃. The calcium carbonate then acts as an acid neutraliser. Ca(OH)₂ and Mg(OH)₂ were used to maintain cellulosic fibre of church organ parts made of wood [13]. By coating the wood using Ca(OH)₂, emission of gasses from organic acid and other volatile organic substances were prevented.

3. Methods

3.1. Preparation of chitosan nanoparticles

Chitosan nanoparticles were prepared via ionic gelation of 0.2% (w/v) chitosan (BATAN) dissolved in 1% (v/v) acetic acid (Aldrich), with 1%
solution of tripolyphosphate (TPP) anions in water. Under magnetic stirring at room temperature, 1 mL of TPP solution was added dropwise to 25 mL of chitosan solution. The mixture was stirred for a further 20 minutes prior to sonication. The resulting suspension was subsequently centrifuged at 12,000 rpm for 10 minutes. The precipitate was suspended in water, centrifuged again, and then freeze-dried. The freeze-dried chitosan nanoparticles were then resuspended for coating purpose.

3.2. Preparation of Ca(OH)$_2$ nanodispersion

Solution of NaOH 0.2 M and CaCl$_2$ 0.1 M at 90 °C was mixed with solution of CaCl$_2$ in ethylene glycol at 150 °C and stirred at 5000 rpm. Reaction was constrained in an oxygen-free atmosphere by continuously flowing nitrogen to control the size of Ca(OH)$_2$ particles. Deposit of Ca(OH)$_2$ nanoparticles is purified by dissolution in NaCl and storage in dialysis bag for 72 hours. Water in the bag was replaced every 18 hours until the solution was free from chloride ions. The nanoparticles was then dispersed in isopropanol.

3.3. Paper materials and coating method

The nanoparticle solution was applied as a dip coating for standard paper grade of calendered kraft paper (Mondi, 100 g/m$^2$, thickness 125 µm), using a laboratory bar coater with bar speed of 6 mm/s and bar number 2 (type K303 Multi-coater from RP-Print Coat Instruments, Ltd). The samples were dried in a hot-air oven to remove the water solvent and further stabilised under room environment for at least one day. The dry coat weight equals 6 g/m$^2$ (determined by weighing). These samples were subject to mechanical tests.

As for colour change and morphology tests, recycled paper samples were used. Ethanol amine was added to control acidity during boiling of torn waste paper into pulp at 100 °C for 150 minutes. Solution of 5% polyvinyl pyrolidon (Povidon K30) was added to the pulp as a binding agent. The pulp was then subjected to screening process prior to drying. Steel plate was used to press the dried paper into an A4 size samples which were evenly flat and considerably thin. Particle dispersion was then sprayed onto both surfaces of samples, which were vertically clamped and air dried.

3.4. Characterisation of chitosan nanoparticle

3.4.1. X-Ray diffraction

The size of nanoparticles can be approached using the Bragg's law:

$$2d_{001}\sin\theta = nl$$

(1)

where $d_{001}$ is the nanoparticle size in nm and $\theta$ is the Bragg's angle of incident and reflected X-ray. For CuK$\alpha$ column and Ni filter used, $n$ and $l$ are the order and wavelength of X-ray, which are 1 nm and 0.1541 nm, respectively.
3.4.2. Antibacterial test
As much as 20 mL of sterilised Mueller-Hinton medium was left to firmly gelled in a petri dish. Onto the medium, 1 mL of bacterial suspension was applied evenly. The medium was put in a laminar air-flow for 10 minutes. Circular cuts of paper samples were placed in the dish and underwent incubation for 24 hours at 37 °C. Observations of translucent zones were conducted afterwards for triplicate samples.

3.5. Quality tests of nanoparticle-coated paper

3.5.1. Grammage test
Paper samples sized 200×250 mm were weighed and measured for their area. Grammage value is the mass for every m² area of paper.

3.5.2. Firmness test
Paper samples were formed into wavy surface and placed in an L & W crush tester vertically. The pressure needed to press the upper parts of samples was measured by the instrument, which showed the paper firmness against external pressure.

3.5.3. Crack resistance test
Paper samples were clamped in Mullen Bursting tester and pressed upward until they were torn. The measured pressure defined the crack resistance of paper.

3.5.4. Tear resistance test
Tear resistance is the maximum strength of paper prior to tearing or the required force to tear paper at standard condition. Tear index (gfmN) is calculated based on tear resistance compared to paper grammage.

3.6. Morphological analysis
Morphological analysis was conducted to understand the surface properties of the nanoparticle-coated paper samples using desktop SEM instrument (Phenom Pro-X, with charge-reduction sample holder for organic samples).

3.7. Colorimetry
Colorimetric measurements CIE L*a*b* using the colorimeter Data Colour International® in the D65/10 mode were performed with the aid of a Melinex mask in order to maintain the same examined areas. Samples were exposed to acetic acid, ammonia, or UV light for 7 consecutive days prior to measurement.

4. Results and Discussion
To ensure the validity and accuracy of the measurements, the results of coated paper samples were compared to those of uncoated ones and presented as averages of triplicate samples.
4.1. Characterisation of chitosan nanoparticle

4.1.1. X-Ray diffraction

Figure 1 shows X-ray diffraction pattern of chitosan nanoparticles at 20 - 80° (2θ). The peak of diffraction was observed at about 30° (2θ) which shows that the TPP (tripolyphosphate) intermolecular spacing is about 0.3 nm, based on equation (1). This result indicates that nano-sized particles of chitosan were formed. This short distance (about the three times of hydrogen size) will only possible in the presence of tight interaction like hydrogen-bonding among chitosan structures attached to the TPP molecules.

![Fig. 1. XRD pattern of chitosan nanoparticles.](image)

4.1.2. Antibacterial test

The results of chitosan nanoparticle test against the attack of Gram-positive *Escherichia coli* and *Staphylococcus aureus* bacteria (see Fig. 2 and Table 1) shows a reasonably low minimum inhibitory concentration (MIC), that is the lowest sample concentration to inhibit 90% of bacterial growth activity.

![Fig. 2. Gram-positive *E. coli* in medium without (a) and with (c) chitosan nanoparticles; and *S. aureus* in medium without (b) and with (d) chitosan nanoparticles.](image)

<table>
<thead>
<tr>
<th>Table 1. MIC of chitosan nanoparticle (mg/L).</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bacteria</strong></td>
</tr>
<tr>
<td><em>E. coli</em> (K 88)</td>
</tr>
<tr>
<td><em>S. aureus</em> (ATCC 25923)</td>
</tr>
</tbody>
</table>

Moreover, the antibacterial property of chitosan nanoparticle was also tested by measuring the diameter of inhibition zone, that is the distance from the centre to the edge of chitosan nanoparticle medium area not attacked by bacteria. As shown in Table 2 and Fig. 3, the increase in nanoparticle concentration extended the diameter of...
inhibition zone. A maximum diameter of inhibition zone was obtained at 4% concentration of chitosan nanoparticle.

<table>
<thead>
<tr>
<th>Chitosan Nanoparticle concentration (%)</th>
<th>E. coli medium</th>
<th>S. aureus medium</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>12</td>
</tr>
<tr>
<td>4</td>
<td>22</td>
<td>26</td>
</tr>
<tr>
<td>6</td>
<td>22</td>
<td>25</td>
</tr>
</tbody>
</table>

Fig. 3. Inhibition zone of bacterial growth on chitosan nanoparticle medium (translucent circle) at: (a) 4%; (b) 2%; (c) 6%; (d) 0% concentration.

4.2. Paper quality tests

4.2.1. Grammage measurement

Grammage in g/m² is a known paper property expressing the weight of paper per unit area. The result of paper sheet grammage test is shown in Fig. 4. It can be observed that the coating reduced the paper's grammage. This grammage complies with Indonesian National Standard (SNI 14-0094-1987) around 125-140 g/cm².

Fig. 4. Paper grammage vs. chitosan nanoparticle concentration (%).

There was no considerable difference, however, in the paper grammage of varied chitosan nanoparticle concentration. There was uneven grammage across the sample due to uneven expulsion of suspension water during the pressing of paper pulp. Besides, the low mass-to-area ratio of the nanoparticle coating layer also contributes to this result.
4.2.2. Firmness test

Paper firmness is measured based on the bending moment in gram-force per centimetre (g/cm) required to bend the sample paper at 15° bending angle and standard condition. Firmness is one of paper quality measure that is very important for cardboard paper. It is expected that cardboards can bear loads without much bending. Paper firmness is positively correlated with paper grammage and thickness. The higher the grammage and thickness are, the higher the firmness and thickness of papers will be.

The influence of chitosan nanoparticle concentration on the paper firmness is shown in Fig. 5. It was observed that the higher the concentration of chitosan nanoparticle, the higher the firmness of paper would be. This firmness was, however, still lower than that of uncoated paper.

![Figure 5: Paper firmness vs. chitosan nanoparticle concentration (%).](image)

The chitosan nanoparticles may have increased or strengthened interfibrillar bonds by forming a film-thin layer on the fibres surface to prevent stress concentration or build-up, so that any external pressure will be distributed throughout the surface evenly. Besides, firmness may also increase because the flexible structure of chitosan nanoparticle facilitated its diffusion through the pores of fibres so that the nanoparticle can freely bind and adhere the fibres together, that is acting as a 'sizing agent' to the cellulose, which will in turn strengthen the overall structure and contribute to bear the load of fibres crosslinking.

4.2.3. Crack resistance test

Crack resistance is the required force to crack a piece of paper as measured in kg/cm or kPa at standard condition. The measure of paper quality prior to a crack is called crack index. Crack index is calculated based on the crack resistance value compared to its grammage. This crack index value is particularly important for wrapping paper or paper bag.

Fibres length and interfibrillar bonds are the factors affecting crack strength, and the interfibrillar bonds is the most influential in increasing crack resistance. The longer the milling process is, the lower the crack resistance will be. The crack resistance is also affected by the fibre dimension especially the wall thickness and
diameter. Thin and wide fibres will easily be cracked and milled into flat paper with high crack resistance.

Although crack index value is excluded from the SNI, the Ministry of Industry regulated that this index is one of paper quality parameter, which value ranges from 2.55-2.43. This research proved that the crack index of coated papers was higher than that of uncoated papers, as seen in Fig. 6, and also complied with the regulation.

Crack resistance is related to 'sizing' into paper. Sizing is the addition of certain chemicals into paper to attain desired properties. It is inferred that chitosan has sizing property since it can bind and adhere the interfibrillar bonds via the fibres outer layer. Apart from that, chitosan may also form protective coating on the paper surface to enhance the paper resistance against external factors, such as pressure and water penetration.

4.2.4. Tear resistance test

It was observed that the tear index of coated paper is higher than uncoated paper and generally the increase in chitosan concentration will increase the tear index (Fig. 7). There is no SNI value for tear index despite its common use as a quality parameter in paper industry.
4.3. Morphological analysis

Morphological properties of paper were analysed using SEM. In Fig. 8, SEM image shows the distribution of calcium particles around the cellulosic fibres of recycled paper sample. The dispersion of Ca(OH)$_2$ coating sprayed onto the surface of recycled paper sample was represented by an object labelled as spot 1. The EDS elemental analysis results confirming the presence of Ca(OH)$_2$ particles appearing as long slim block with neat edges. The element sulphur might had come from printing ink on the waste paper. The widely distributed spherical white lumps, as represented by an object labelled as spot 2, were attributed to Ca(OH)$_2$ added during the original paper processing and contributed to the bright white colour of paper. This finding was supported by EDS elemental analysis result (level of confidence 100% and maximum error 1.8%).

<table>
<thead>
<tr>
<th>Element Name</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphur</td>
<td>16.6</td>
</tr>
<tr>
<td>Calcium</td>
<td>20.7</td>
</tr>
<tr>
<td>Oxygen</td>
<td>62.7</td>
</tr>
<tr>
<td>Spot 1</td>
<td>0.0</td>
</tr>
<tr>
<td>Spot 2</td>
<td>22.3</td>
</tr>
<tr>
<td>Spot 2</td>
<td>77.7</td>
</tr>
</tbody>
</table>

Fig. 8. SEM image and its corresponding EDS elemental analysis of nanoparticles-coated recycled paper surface.

4.4. Colour changes

Molecular modifications in the cellulose polymer caused by degradation reactions can outcome in chromatic changes. The chromatic coordinates were measured by the CIE L*a*b* system - the standard colour model established by the Commission Internationale d’Eclairage. The three parameters (L*, a* and b*) in the model represent the brightness (L*) of the colour (the smallest value indicating black), a* for its position between red and green (the smallest value corresponds to green), and b* for its position between yellow and blue (the smallest b corresponds to blue).

The colour of recycled paper is composed of significantly higher yellow with slightly lower red and lower brightness compared to fresh paper. The high yellow component is probably due to the paper oxidation level during period of use of waste paper, since the carbonyl groups formed in the cellulose oxidation reactions are chromophores, that cause changes in the polymer colour from nearly colourless to yellow and even brown when they present as a part of a conjugated system [14]. This yellowish colour of paper is recommended for printing or writing, since less contrast against the ink colour can provide higher comfort of reading and reduce eye fatigue.
Before coating, the recycled paper samples showed a high brightness while its red and yellow values are close to zero, meaning that the colour of these samples is visibly white (Table 3). After coating, the paper brightness slightly increased, as also the green and blue value. The variation was insignificant, indicating the transparency of nanoparticle coating. Various exposures of coated paper to acid, base, and UV light showed no significant change of colour. This result suggests an effective protection of nanoparticles coating towards the exposures. It appears that the nanoparticles coating were able to maintain the bright white colour of recycled paper samples by providing barrier against penetration of acid and base or UV light into the cellulosic fibres underneath.

Table 3. Colorimetric coordinates before and after coating treatment tests.

<table>
<thead>
<tr>
<th>No</th>
<th>Remark</th>
<th>Colour Coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>L*</td>
</tr>
<tr>
<td>1</td>
<td>Kraft Paper</td>
<td>92.01</td>
</tr>
<tr>
<td>2</td>
<td>Recycled Paper</td>
<td>87.89</td>
</tr>
<tr>
<td>3</td>
<td>Coated Paper</td>
<td>90.61</td>
</tr>
<tr>
<td>4</td>
<td>Acetic Acid Exposure</td>
<td>91.22</td>
</tr>
<tr>
<td>5</td>
<td>Ammonia Exposure</td>
<td>90.87</td>
</tr>
<tr>
<td>6</td>
<td>UV Exposure</td>
<td>90.66</td>
</tr>
</tbody>
</table>

5. Conclusions

An investigation has been made of the effects of nanoparticles coating on the durability of coated paper samples in terms of strength and colour. This study clearly demonstrated that chitosan nanoparticles coating increased interfibrillar bonding and prevented microbiological attacks, while nanoparticles of Ca(OH)$_2$ neutralised the acidity of paper and protected it against base and UV radiation.

As the tear strengths and cracking resistance of coated paper were improved, it is recommended for lightweight packaging. Relatively more yellowish colour of recycled paper suggests a suitability of use for notebook and printing.

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References


