

# Polymer Clay Self-Assembly Complexes on Paper

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**ABSTRACT:** Layer-by-layer (LBL) self-assembly was used to form polymer/clay complexes on paper to enhance its wet strength properties. Initially, alternating layers of poly(allylamine hydrochloride) (PAH) and Kaolin clay were sequentially deposited on quartz substrate and characterized by UV/Vis/NIR spectroscopy as a model system. The same procedure was then applied to a paper test sheet to form multilayered coatings, which were examined with scanning electron microscopy. The wettability of the LBL coated paper test sheet was shown to change

from hydrophilic to hydrophobic with increased number of multilayers and if the terminating layer was Kaolin clay. The wet strength of the coated test sheet was improved by more than 270% over the uncoated test sheet with 16 bilayers of PAH/kaolin complex on the surface. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1987–1992, 2007

**Key words:** layer-by-layer; self-assembly; polyelectrolytes; clay; paper

## INTRODUCTION

Recent advances in the science and engineering of nanotechnology are impacting a variety of industries including: aerospace, defense, automotive, textiles, and the paper-industry.<sup>1</sup> Innovative materials and systems have emerged from nanotechnology that can not be readily achieved when engineered on the micron or larger scale.<sup>2</sup> One of the areas that the paper industry can benefit from the nanotechnology breakthrough is the development of high value added coatings that are made of highly organized structure on a nanoscale.

Layer-by-layer (LBL) self-assembly from aqueous solution is a versatile and relatively straight forward strategy for the construction of an organized structure onto a solid substrate.<sup>3</sup> The driving force for multilayer synthesis is the electrostatic attraction between oppositely charged molecules. Multilayer structures of polyelectrolytes,<sup>4–9</sup> polyelectrolytes and nanoplatelets (clay<sup>10–12</sup> and graphite oxide<sup>13</sup>), polyelectrolytes and nanospheres,<sup>14–16</sup> polyelectrolytes and carbon nanotubes<sup>17</sup> have been reported. The advantages of the LBL technique include its environ-

mental friendliness, its ability to incorporate a host of different materials on the solid substrate and a relatively facile, direct methodology of modifying surface properties.

The LBL self-assembly technique has been used to increase dry paper strength by building multilayer polyelectrolytes on wood fibers. Wågberg<sup>18,19</sup> showed a steady build-up of multilayers on wood fibers from weak polyelectrolytes and the build-up of the multilayer could be made either linear or exponential by altering pH. Significant improvements in dry paper strength ranging from 60 to 200% were found depending on both pH during adsorption and the type of polyelectrolyte in the outer layer. Lvov<sup>20,21</sup> used LBL on lignocellulose fibers to produce negatively and positively charged fibers. The modified fibers were added to standard fibers at varying proportions and resulted in dry paper strength increase of 120%. Besides dry paper strength, wet paper strength is important in certain paper products such as hygiene and packaging products, which require strength when they are wet. Sheets prepared from the modified fibers exhibited 120% increase in the dry strength of the paper.<sup>20</sup> This study examines the use of LBL technique to build multilayers of polyelectrolyte/clay complexes on paper to modify its water repelling properties and to increase wet paper strength. As compared with the conventional single coating treatment, the LBL technique produces a coating whose thickness and terminating surface can be easily controlled by the number of self-assembly

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layers. The choice of clay as a major component in the coating is motivated by nature. Sea shells, for example, have an intricate organic/inorganic hybrid laminate structure that provides both strength and luster.<sup>22</sup> Clay materials are also inexpensive source of a polyanionic material.

In this article, the sequential development of multilayers was first demonstrated through multilayer formation on quartz. Then the morphological features of the modified paper test sheets are presented, followed by their surface properties and mechanical properties.

## EXPERIMENTAL

### Materials

Poly(allylamine hydrochloride) (PAH) was acquired from Aldrich with an average molecular weight of 70,000. The Kaolin clay, InFilm 939, was provided by Imerys and had a particle size information of 90% < 0.325 microns, 50% < 0.175 microns, and 30% < 0.141 microns. Quartz slides were acquired from SPI Supplies. An industrially produced elementally chlorine-free (ECF) softwood (SW) kraft pulp was used for making the test sheets of paper which had an initial Tappi brightness<sup>23</sup> of 84.3. Test sheets of paper were prepared according to Tappi standard T-205.<sup>24</sup> Water was purified by the Millipore system.

### Self-assembly procedures on quartz and paper

Quartz slides were cleaned by immersion in a 3% Alconox solution and ultrasonicated for 20 min. After being rinsed with purified water, the slides were ultrasonicated for an additional 20 min in purified water. They were then dried by a stream of hot air immediately before use for self-assembly. Test sheets of paper were directly used for self-assembly.

Kaolin slurries were prepared as fresh and treated dispersions. A fresh slurry was prepared by dispersing Kaolin (1.00 g) under stirring in 200.00 mL deionized water. To obtain a treated slurry, the fresh dispersion was centrifuged at 2800 rpm for 20 min and the large clay particles (>1  $\mu\text{m}$ ) were removed. The supernatant was ultrasonicated for 30 min and then kept for 24 h before use. The average size of the clay particles in the treated dispersion was 235.7 nm as measured by a Malvern 3000 Zetasizer and the  $\zeta$ -potential measured by the same instrument was -47.8 mV. The pH value of the Kaolin dispersions was 7.0. Except mentioned otherwise, the Kaolin dispersion in this paper refers to the treated dispersion. An aqueous PAH solution was prepared by dissolving 0.50 g of PAH in 100.00 g of purified water. The pH value of the PAH solution was 5.0.

The LBL self-assembly of polyelectrolyte-clay nanoplatelets onto substrates involves the following steps: (i) immersion of substrate (quartz slide or test sheet of paper) into an aqueous PAH solution (0.50%) for 5.0 min; (ii) rinsing in purified water and drying in oven at 105°C for 10.0 min; (iii) immersion into Kaolin dispersion mentioned above for 10.0 min; (iv) rinsing in purified water and drying in oven at 105°C for 10.0 min. Repeating steps (i)–(iv)  $n$  times produces an ultrathin film containing alternating  $n$  layers of PAH and  $n$  layers of Kaolin nanoplatelets.

### Methods

Absorbance spectra of PAH/Kaolin complex on a quartz slide was taken using a double-beam spectrophotometer (Lambda 900 UV/Vis/NIR Spectrometer, Perkin–Elmer). The background spectrum of quartz was subtracted from the measured spectra.

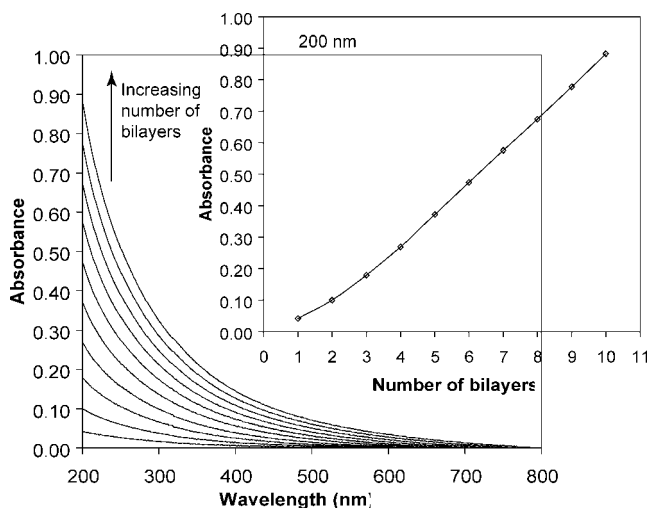
Scanning electron microscopy (SEM) was performed on a LEO 1530 thermally-assisted field emission (TFE) microscope at 10 kV. The coated quartz slide and the smooth side of the paper test sheets were gold coated before being examined.

Contact angle measurement was performed on a FTÅ200 Dynamic Contact Angle Analyzer. The test paper sheet (smooth surface facing up) was placed onto a platform underneath a syringe with a flat-tipped needle and in front of a camera. The syringe and camera were computer controlled. The syringe was programmed to deliver a drop of deionized water at 3.00  $\mu\text{L/s}$  onto the paper sample, and the camera captured an image every 0.033 s. Typically, after deposition of the water droplet on the surface, the droplet shape equilibrated within 6–8 picture frames. All the contact angles were analyzed based on images 0.2–0.3 s after water was in contact with test sheet surface. The mean value was calculated from at least 5 individual measurements with a standard deviation below 5°.

Wet tensile strength was measured using the Lorentzen and Wettre Tensile Tester according to Tappi standard T494.<sup>25</sup> The treated sheets were soaked in deionized water for 15 s and excess water was removed with blotting paper, then the test sheets were immediately transferred to the tensile tester. Error was less than  $\pm 10\%$ .

## RESULTS AND DISCUSSION

Initially, a smooth and transparent quartz slide was used as a model paper test sheet substrate for LBL self-assembly, in part, because both surfaces are negatively charged and both possess hydroxyl groups. Self-assembly of the successive PAH/Kaolin layers onto a quartz slide was monitored by the UV/Vis/



**Figure 1** UV/Vis/NIR absorbance spectra of PAH/Kaolin multilayers on glass substrate. Inset shows absorbance at 200 nm against number of bilayers.

NIR absorption spectra (Fig. 1), which shows sequential increase of absorbance with the number of bilayers. Absorbance was measured in terms of bilayers instead of individual layers since PAH has no absorbance peak in the region of interest. The inset of Figure 1 presents the absorbance at 200 nm against the number of bilayers. A linear growth of absorbance with the number of bilayers is observed after the third bilayer. This indicates regularity of the polymer/clay multilayer formation.<sup>26</sup> An SEM photograph of 10 double layers of PAH/Kaolin on quartz is presented in Figure 2. The self assembled clay platelets uniformly populate the quartz surface. However, empty spaces can be found among the clay platelets and stacking of clay platelets can also be seen, showing that the clay/polymer multilayer structure is far from being ideal. Contact angle measurement reveals a change in the surface hydrophilicity with the polymer/clay complex formation. The surface of quartz coated with 8 double layers of PAH/Kaolin exhibits a contact angle of 80° while the untreated quartz has a contact angle of 16°. This effect will be discussed in more detail later.

Figure 3 shows the surface morphology of a paper sheet and a treated sheet on which PAH/Kaolin complexes (18 double layers) were self-assembled. On a pure paper sheet [Fig. 3(a)], the fibers could be clearly seen. Higher magnification of a fiber [Fig. 3(b)] reveals a relatively smooth surface. On coated test sheet [Fig. 3(c)], the individual fibers are still clearly seen, but their surfaces are covered by "frost-like" materials. Higher magnification [Fig. 3(d)] shows that the fiber surface is covered with clay platelets which are bound to the fiber surface tightly, much like fish scales. This self-assembly coating is different from the one-step coating used in industry

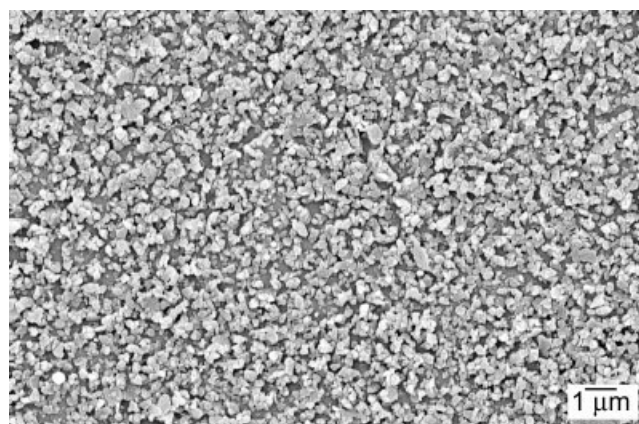
where the clay particles fill the spaces between fibers.

The surface properties of paper test sheet are significantly modified after it was coated with PAH/Kaolin complex. Figure 4 shows the measured contact angle on test sheet with the number of self-assembled layers. A general increase of contact angle with the number of layers is observed. After the 12th layer, the contact angle is stabilized.

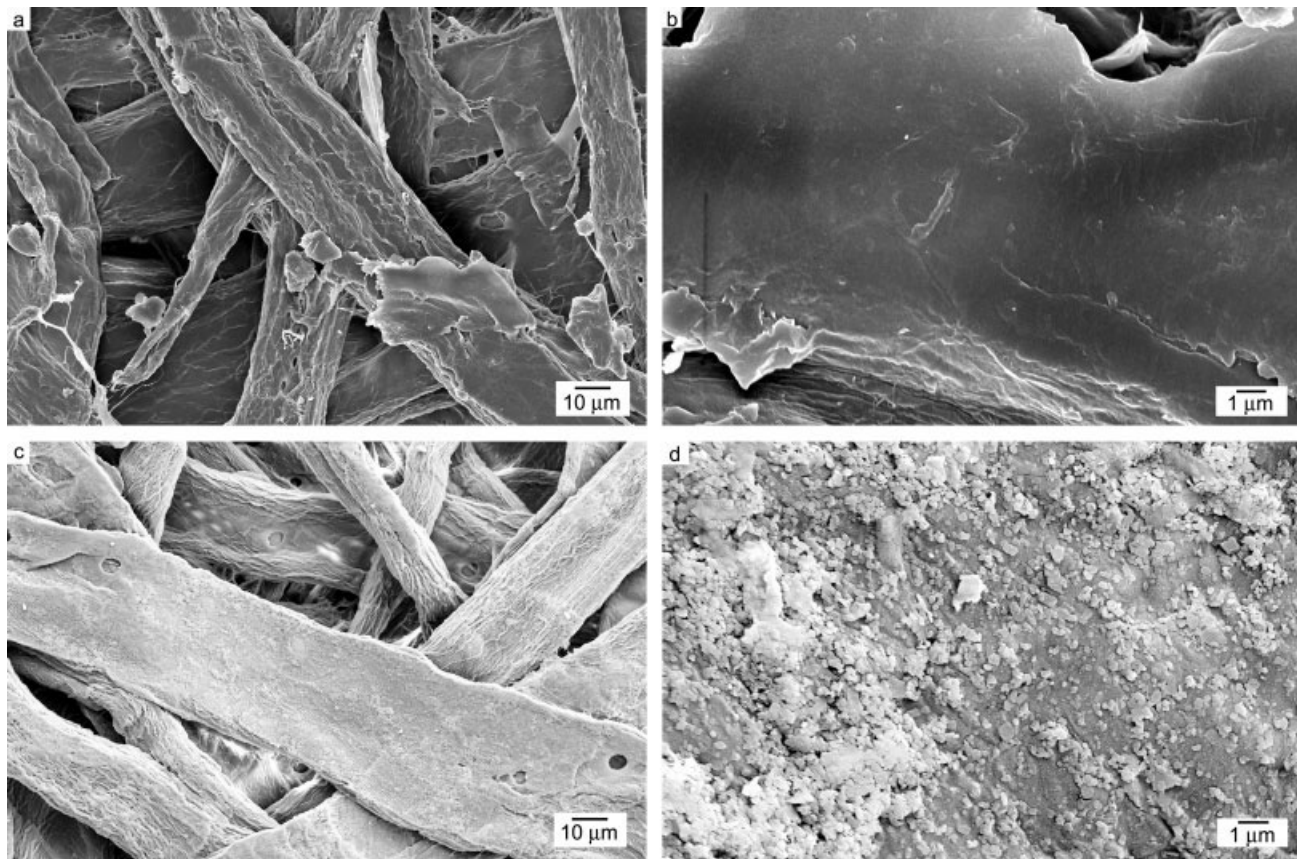
A close look at Figure 4 reveals that the curve follows a zigzag pattern. This is more clear after the 10th cycle. It should be mentioned that odd number layer is a PAH terminated surface and an even number layer is a Kaolin terminated surface. Thus it seems that the Kaolin terminated surface is more hydrophobic than the PAH terminated surface.

To evaluate the stability of the water droplet on a LBL coated paper sheet the contact angle measurement was performed as a function of time for a test sheet coated with 18 double layers of PAH/Kaolin (see Fig. 5). There is only a small decrease of contact angle for the first 20 min after which the contact angle drops more rapidly as water gets absorbed into the test sheet. This is a great improvement over uncoated sheet where water is absorbed very fast and the contact angle reaches zero in less than 1 s. The inset of Figure 5 shows the shape a water droplet on the test sheet coated with 18 double layers of PAH/Kaolin taken immediately after the water droplet is deposited on the LBL coated sheet.

These results suggest that the LBL coating of Kaolin clay on the paper surface changes the surface from hydrophilic to hydrophobic, however, further analysis suggests that this effect is not that simple. As a control, a test sheet with Kaolin clay coated on the surface (coating layer composed of 90% of Kaolin bound with 10% PAH) was prepared. This coated paper exhibits a very hydrophilic surface with a contact angle around 10°. Also, when a fresh Kaolin



**Figure 2** SEM photograph of 10 bilayers of PAH/Kaolin on quartz.

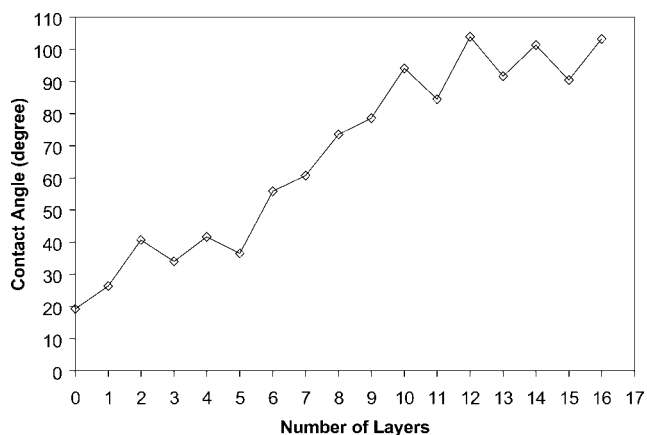


**Figure 3** SEM photographs of pure test sheet ((a) and (b)) and 18 bilayers of PAH/Kaolin on ECF SW Kraft test sheet ((c) and (d)).

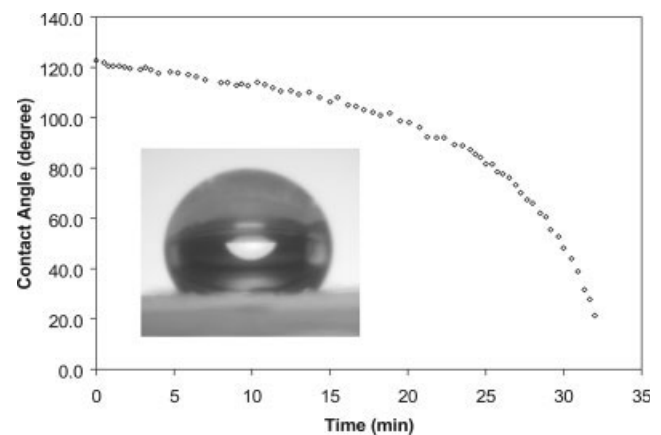
clay dispersion is used in the LBL self-assembly the resulting test paper sheet surface is hydrophilic.

To understand this behavior, it is necessary to examine the Kaolin structure (see Fig. 6).<sup>27</sup> The ideal structural formula of kaolinite crystal is  $[\text{Al}_4\text{Si}_4\text{O}_{10}](\text{OH})_8$ . A kaolinite crystal is composed of two types of sheets, namely the tetrahedral (designated T) and the octahedral (designated O), stacked

one above the other. The tetrahedral sheet is a planar network of continuous linkage of  $\text{SiO}_4$  tetrahedra formed by sharing three of the O atoms with adjacent tetrahedra. An octahedral sheet is obtained through condensation of  $\text{Al}(\text{OH})_6^{3-}$  octahedra. The mineral layer of Kaolin is composed of a single tetrahedral sheet condensed with a single octahedral



**Figure 4** Contact angle of PAH/Kaolin self-assembled multilayers on ECF SW Kraft test sheet.

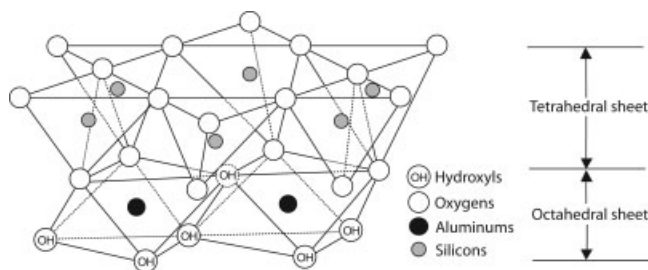


**Figure 5** Contact angle versus time for test sheet of paper coated with 18 double layers of PAH/Kaolin. Inset is the shape of a water droplet on the test sheet at 0 min.

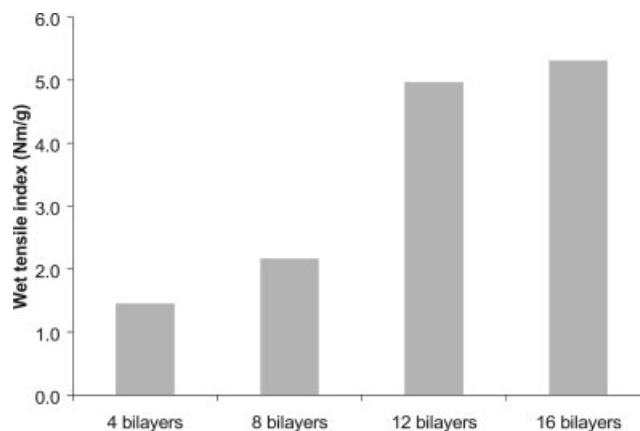
sheet into one unit layer, designated TO. Although only one TO layer is shown in Figure 6 for simplicity, the actual clay platelets consist of many TO layers. The external surface of Kaolin clay platelet always consists of a hydroxyl plane on one side and an oxygen plane on the other side. In addition to the uppermost and lowest faces, the external surface of a clay crystal also consists of the edges of all the layers and these are called the "broken bonds surfaces." The edges of kaolinite constitute up to about 20% of its total area, whereas the two faces each make up about 40% of the external surface.<sup>27</sup>

Although there is no general agreement on the wettability of the different clay surfaces, it is known that the edge surface, or the broken bond surface, has exposed functional groups that are very active and may react as electron pair donors or acceptors.<sup>27</sup> Tunega et al.<sup>28</sup> analyzed kaolinite surfaces using *ab initio* molecular dynamics and concluded that the octahedral surface (hydroxyl plane) and tetrahedral surface (oxygen plane) of the kaolinite layer are of different chemical nature and can be considered as hydrophilic and hydrophobic, respectively.

Given these findings, it is reasonable to suggest that during the LBL self-assembly, the ultrasonicated Kaolin clay platelets are assembled onto the paper surface in such a way that the hydrophobic surfaces are predominantly exposed to the external surface. Such an arrangement would increase the hydrophobicity of the paper surface, which would require that the Kaolin clay platelets are on average faced down to the substrate so that the edges are not exposed to the outside surface as is suggested by the SEM graph [see Fig. 3(d)]. This preferred orientation of clay platelet is only possible with the self-assembly process. On a surface randomly coated by Kaolin clay, the platelet surfaces, hydrophobic (oxygen plane) or hydrophilic (hydroxyl plane), are indiscriminately exposed to the outside together with some hydrophilic edges so that a relatively hydrophilic surface will be created. A fresh Kaolin dispersion, without ultrasonic agitation, consists of Kaolin aggregates<sup>28,29,30</sup> and the aggregates behave in a similar way to the randomly coated clay platelets and thus a hydrophilic surface is generally obtained.



**Figure 6** Schematic diagram of the structure of kaolinite.



**Figure 7** Wet tensile index of ECF SW Kraft testsheet modified by PAH/Kaolin multilayers.

The wet tensile index of the paper sheet coated by the multilayered PAH/Kaolin complex is shown in Figure 7. It can be seen that the wet tensile index increased with the number of bilayers. Espy has highlighted two mechanisms that contribute to improve wet strength, (1) a protective mechanism by which water is prevented from interrupting hydrogen bonding and (2) a covalent crosslinking mechanism.<sup>31</sup> The increase in wet-strength reported in this study is due partly to improved hydrophobicity of the test sheet surface, which slows down the attack of water. Another strength enhancing factor comes from PAH, which had been documented as a strength enhancing additive.<sup>32</sup>

## CONCLUSIONS

This study has shown that LBL self-assembly can be directly applied to a paper test sheet and results in significant modification of its surface properties. Alternating layers of PAH and Kaolin clay were sequentially deposited on paper test sheet. The LBL self-assembly technique has the obvious advantage of precisely controlling the amount of materials coated on paper. In addition, the obtained dense layer of nanoparticles by means of LBL self-assembly produce a hydrophobic surface that cannot be attained from simple coating with Kaolin clay platelets. The enhanced hydrophobicity gives rise to improved wet strength of the modified test sheet.

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