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Effects of Montmorillonite Clay on Properties of Paper Coating Additives

Yoon Seok Seo† and Changwoon Nah

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ABSTRACT

A new composition of paper coating adhesives was prepared by using a nano-filler of an organically-modified montmorillonite (O-MMT). The new O-MMT coating adhesives were applied to the paper, and the properties of coated papers including surface morphology, optical and physical properties, and printing properties were investigated. The use of O-MMT improved the mechanical properties, such as folding endurance, tearing strength, and tensile strength, while the surface smoothness decreased. It decreased especially when the dosage was high enough, approximately above 6 parts. The printing properties such as wet- and dry-pick were enhanced with addition of O-MMT.

Keywords: clay, montmorillonite, paper coating adhesive, properties

1. Introduction

Montmorillonite(MMT) is a sort of layered-silicate with natural nanometer structure (1). The polymer/layered silicate nanocomposites have been widely studied by many research groups so far. It has been reported that the layered-silicates are mostly applied as structural materials based on various polymeric materials such as plastics, rubbers, and fibers, since they have many advantages including thermal resistance, mechanical property, gas barrier property, ease of manufacturing, conductivity, and optical property. However, not many attempts have been made on the application in the adhesive field, such as paper coating adhesives, although they can affect a lot of properties of coated-papers.

The structure of currently-available MMT is pyrophyllite, as proposed by Hoffmann et al (2). The lattice is distorted, and it consists of two fused-silica tetrahedral sheets sandwiching an edge-shared octahedral sheet of either aluminium or magnesium hydroxide. Isomorphous substitutions on Si^{4+} for Al^{3+} in the tetrahedral lattice and on Al^{3+} for Mg^{2+} in the octahedral sheet cause an excessive negative charges between the MMT layers. Water molecules are also present between the layers due to the hydrophilicity of the layered

• Department of Advanced Materials Engineering, Chonbuk National University, Jeonju 561-756, Korea
† Corresponding author: E-mail; sys@panasiakorea.com

silicates. Stacking of the layers lead to typical van Der Waals gaps called interlayers or galleries. The sum of the single layer thickness(9.6 Å) and the interlayer represents the repeating unit of the multiplayered material, so called d-spacing or basal spacing which can be determined from the X-ray diffraction patterns using the Bragg law. The reported d-spacing between silica-alumina-silica units for a sodium montmorillonite(Na-MMT) varies from 9.6 Å for the clay in the collapsed state to 20 Å when the clay is dispersed in water (3). The structure of layered silicate is shown in Fig.1.

Basically, the coating adhesive liquid is composed of pigment, water-soluble latex polymer as a binder, and various additives for enhancing the effectiveness of pulp fibers. The composition of pigments and binders in paper coating adhesives is numerous (4). Especially in color formulation, the role of pigments is very important because they greatly affect the important optical and printing properties of coated papers such as brightness, smoothness, and printability. Generally, the application of pigments leads to the improvement of printing properties, such as optical properties including paper surface smoothness, brightness, opacity, gloss, and ink absorption. Also, there is some disadvantage including loss of strength and dusting tendency, especially when the filler particles are not well bonded in the sheet (5).

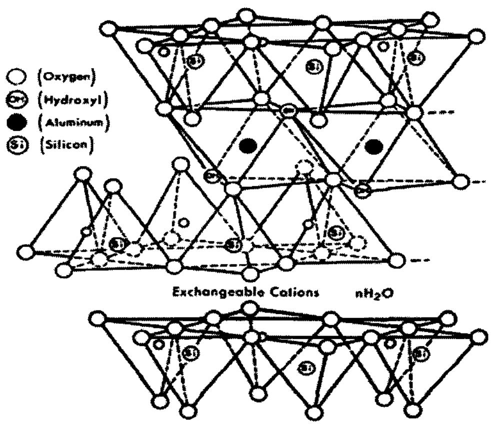


Fig. 1. Structure of layered silicates.

The objective of this study is to investigate the effects of organically-modified MMT (O-MMT) on the various properties of paper coating adhesives and the coated papers. All the properties were monitored as a function of the amount of O-MMT, which was varied up to 10 parts. The rheological property of coating adhesive liquid was also reported.

2. Materials and Methods

2.1 Materials and preparation of coating adhesives

An organically-modified montmorillonite (O-MMT) was supplied from Southern Clay, Inc. in the U.S.A. The grade was Cloisite® 15A, which was modified with a quaternary ammonium salt. The typical size of dry particles was ~13 microns, and the cation exchange capacity (CEC) was 125 mequiv/100 g of clay. The Cloisite® 15A has higher hydrophobicity than other Cloisites grades, and easily mixes with other polymers. The general clay and calcium carboxide for pigment composition was HG-90 #1 and SETA95 (Omya co., Switzerland). The latex used in this work was Styrene-Butadiene (SB) from Kumho Chemical Co., Ltd.

The preparation of the coating liquids was carried by the following procedure. 30 g of O-MMT were dissolved in 600 g water in a reaction vessel with stirring. A sodium silicate (Na_2SiO_2) was added into the O-MMT mixture to adjust the pH of 11~12. After stirring for 20 minutes, the prepared O-MMT solutions of 3,

Table 1. Composition of coating color adhesives with O-MMT Volume

Samples		Control	O-MMT-1	O-MMT-2	O-MMT-3
O-MMT (Units: Part)		-	3	7	10
Coating Color Ratio					
Pigment	Delaminate	40	40	40	40
	Amazon	20	20	20	20
	TiO_2	5	5	5	5
	$CaCO_3$	35	35	35	35
Binder	Latex	13	13	13	13
	Starch	3	3	3	3
Additives	Lubricant etc.	1	1	1	1

7, and 10 parts were mixed with a typical color pigment with fixed composition. The composition of the typical color pigment was 1,153.3 g of water, 40 g of 10% NaOH solution, 10 g of dispersant, 2,000 g of clay (delaminate and Amazon α-gloss), and 2,667 g of slurry $CaCO_3$. Then each ingredient was mixed step-by-step with a color dispersion mixer (PM-9030 CD with ~8,400 rpm) for 20 min. The total solid concentration (TSC) was 65wt%. The mixture of O-MMT solution and typical color pigment was then mixed with latex and water. The final TSC of the coating adhesives was around 61wt%. The composition investigated in this study is shown in Table 1.

2.2 Preparation of coated paper

The coating adhesives with various compositions were applied to a basic type of 63 gsm off-set paper (Hansol Paper Co., Korea) using a coating machine (CLC-6000TM, Simu Tech International Inc., USA) using a blade pond type. The coating condition is as follows; coating speed: 120 m/mim, drying condition: 150℃ /7 s, coating quantity: 11.7~11.8 g/㎡, pre-dry coating time: 20 s, power: 80%, post-dry coating time: 40 s, power: 100%, drying length: 3 m, and paper width: 950 mm. The coated paper was kept in a thermo-hygrostat room for 24 hrs and was calendared with a super calendar machine (SMT, Japan) under the calendaring force of 8.3 kN, temperature of 40℃, and speed of 10.4 m/min with two passes.

2.3 Measurements of properties

High viscosity: Tests were carried out by Hercules Hi shear viscometer (Hercules, Inc. U.S.A.). Low viscosity: Tests were carried out by Brookfield programmable digital viscometer DV-Ⅱ+Viscometer (Brookfield Engineering Laboratory, Inc. Switzerland) and test conditions were spindle #4, 60 rpm, 1 minute. Water retention: Tests were carried out by AA-GWR, U.S.A. Print-through test: Tests were carried out by applying ink to the ink unit followed by testing with IGT AIC2-5 and measuring ink density on the reverse side of the printed paper sample. Printing test: (Especially with O-MMT-2) Tests were carried out by Prufbau tester, SMT-PM902PT, (Kumagai Riki Koygo, Japan). Pick test: Tests were carried out by RI tester (Kumagai Riki Koygo, Japan). Wet receptivity and Set-off test: Tests were carried out by RI Tester RI-1 (Kumagai Riki Koygo, Japan).

3. Results and Discussion

3.1 Properties of color coating adhesives

Fig.2 shows the effects of O-MMT on the several properties of color coating adhesives. The viscosity, maximum torque (T-max), and thixotropy increased, while the water retention decreased with increasing O-MMT levels. The increase in viscosity, simply defined as the internal resistance to flow (6), can be explained by the nature of the O-MMT. The O-MMT in the coating adhesives will form highly exfoliated separated nano-sized platelets with an extremely high aspect ratio (~2,000). Thus, each platelet can resist the flow of coating liquids. Likewise, the maximum torque might be increased. The increase in thixotropy, defined as the dependence of viscosity on the speed of deformation, is also attributed to the plate structure of O-MMT. For instance, when the liquids with various thin plates are subjected to a deformation to flow, it is more difficult to deform the fluids because every plate can effectively act as a resisting obstacle against flow at increased speeds of deformation. However, the water retention decreased with increased O-MMT content.

3.2 Structural properties of coated paper

Structural characteristics describe how the components are arranged in a sheet of paper (7). The structure and surface of the paper sheet play a fundamental role in the interaction between the paper and the ink during and to some extent after the printing process. Fig. 3 shows scanning electron microscopy (SEM)

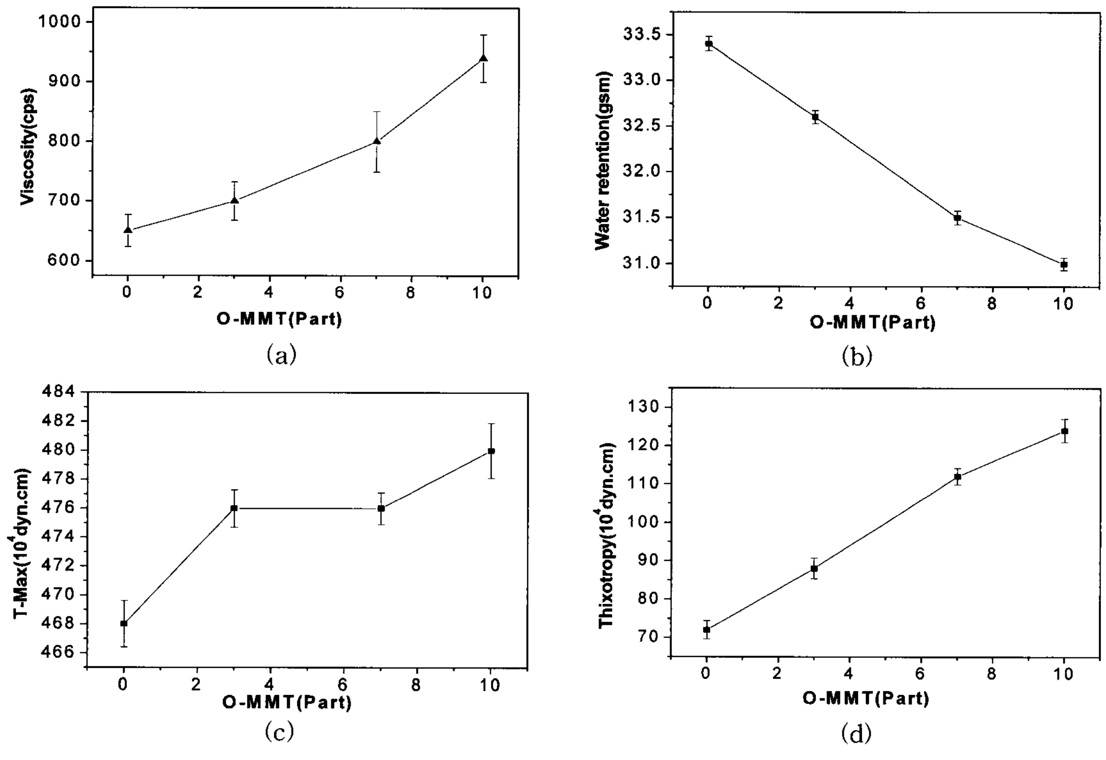
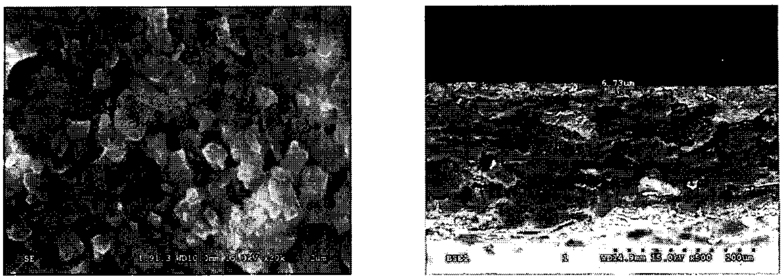
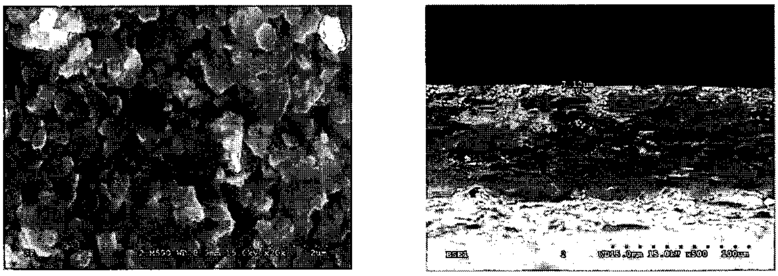


Fig. 2. Properties of color coating adhesives as a function of O-MMT contents:
(a)Viscosity, (b) Water retention, (c) T-max, and (d) Thixotropy.



(a)



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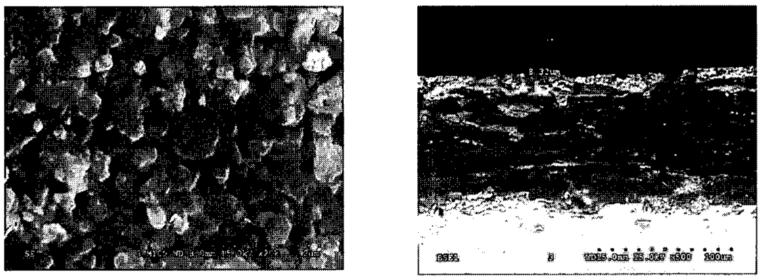

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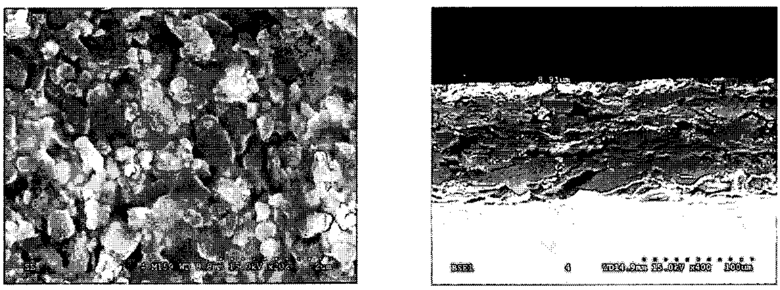

(d)

Fig. 3. SEM micrographs of paper surface(x10,000) and cross-sectional view(x500): (a) Control, (b) O-MMT-1, (c) O-MMT-2, and (d) O-MMT-3.

images of surfaces and their cross-sections for different specimens. No significant difference in the over-view surfaces were detected in the SEM photos. But, in the case of cross-sectional views, the degree of packing of coating layers improved with addition of O-MMT. For in-

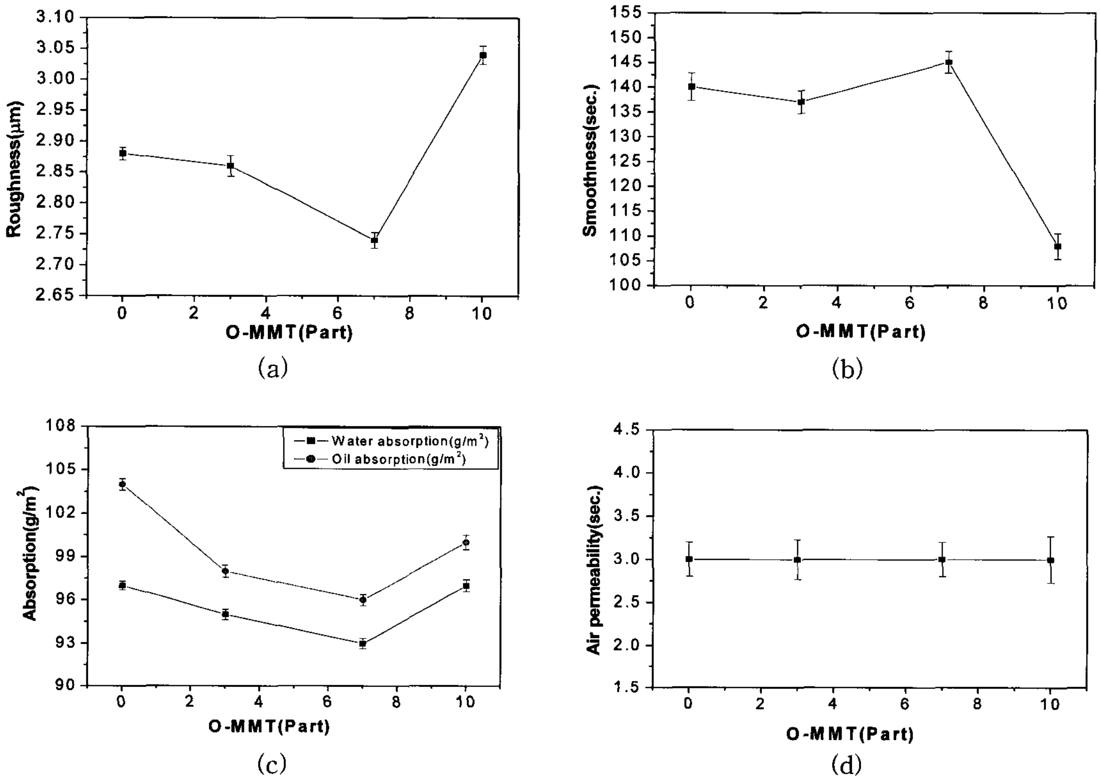

Fig. 4. Several structural properties of coated paper with O-MMT:
(a) roughness, (b) smoothness, (c) water & oil absorption, and (d) air permeability.

stance, the cavity of the coating layer became small. This can greatly affect the various structural properties of coated papers, as shown in Fig. 4.

The roughness (or smoothness) slightly improved until 7 parts of O-MMT were added, but further increase of O-MMT caused a severe increase in roughness. The water and oil absorbance showed a similar trend with that of roughness. The abrupt change in properties at 10 parts might be due to the re-aggregation of O-MMT platelets after drying. It has been known that the optimum concentration of O-MMT is only around ~3 wt% for the best performance in mechanical properties of polymer/clay composites, if the clay platelets are well dispersed in the polymer matrix (8). Further addition of O-MMT can cause a clustering of O-MMT platelets, resulting in a weak point in the matrix. Therefore, the amount of O-MMT in the coating adhesives should be maintained below 7 parts to maximize the effect of O-MMT in view of surface roughness and resistance to water and oil. Another point to be mentioned here is that the air permeability of the coated papers remained stable throughout the experiment, although it was expected to be improved somewhat. This was described in other literature concerning previous experiments. This seems to be due to the extremely high composition of inorganic pigments including O-MMT compared with polymer component such as SB latex and starch. The main composition was inorganic particles.

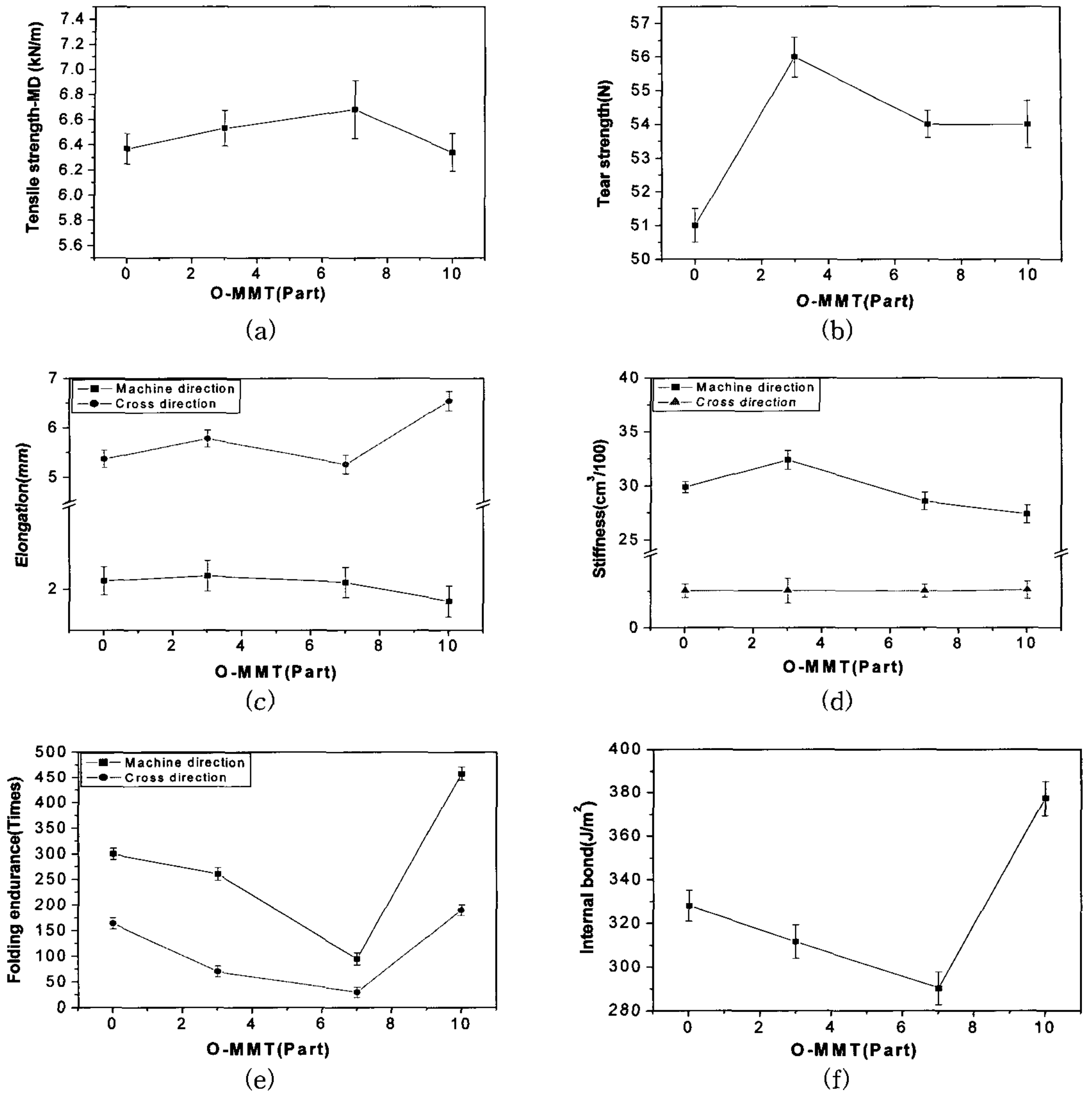

Fig. 5. Mechanical properties of coated paper with O-MMT:
(a) tensile strength, (b) tear strength, (c) elongation at break, (d) stiffness, (e) folding endurance, and (f) internal bond.

Therefore, the O-MMT in the polymer component might not influence the air permeability of coating adhesives.

3.3 Mechanical properties of coated paper

The mechanical properties of papers describe the ability of the paper web to sustain an applied load without suffering damage by fracture. In spite of their importance, the relationship between the mechanical properties and the performance of the papers in the press has not yet been fully clarified. Fig. 5 shows a series of mechanical properties of coated papers. The tensile strength improved slightly until 7

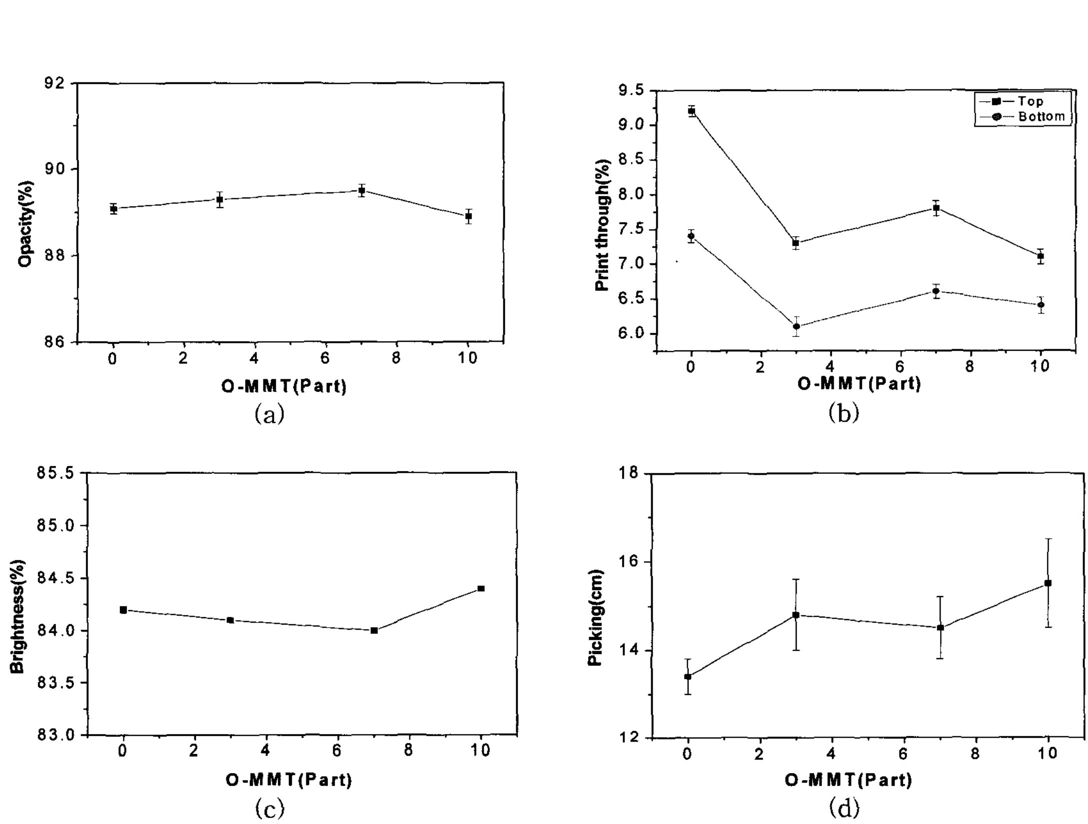

Fig. 6. Optical properties of coated paper with O-MMT:
(a) opacity, (b) print-through, (c) brightness, and (d) picking.

parts, then decreased with further increase of O-MMT. Even higher improvement was observed in tear strength regardless of O-MMT level. Elongation at break point in both machine direction (MD) and cross direction (CD) maintained until 7 parts of O-MMT, and a slight increase was observed for CD case. Stiffness in CD and MD were not considerably affected by the addition of O-MMT. The observed results strongly indicate an advantage to the addition of O-MMT in terms of mechanical strength of paper, unless the dosage of O-MMT exceeds critical levels, approximately 7 parts in our system. The folding endurance and internal bond showed a abrupt change at the similar critical concentration of O-MMT dosage. A further study is needed for finding an accurate critical concentration.

3.4 Optical and printing properties of coated paper

The optical properties of paper are of great importance to publishers because of their influence on both readers and advertisers, either directly by their perceptual impact or indirectly by their strong influence on the mechanical quality of the final printed products (9). The opacity increased until 7 parts, and decreased at 10 parts of O-MMT. The print-through considerably improved with increased O-MMT dosage. The brightness decreased until 7 parts, and then increased with higher dosage of O-MMT(10 parts), although the amount of change was negligible in view of industrial applications. The picking property was improved with addition of O-MMT. Generally the

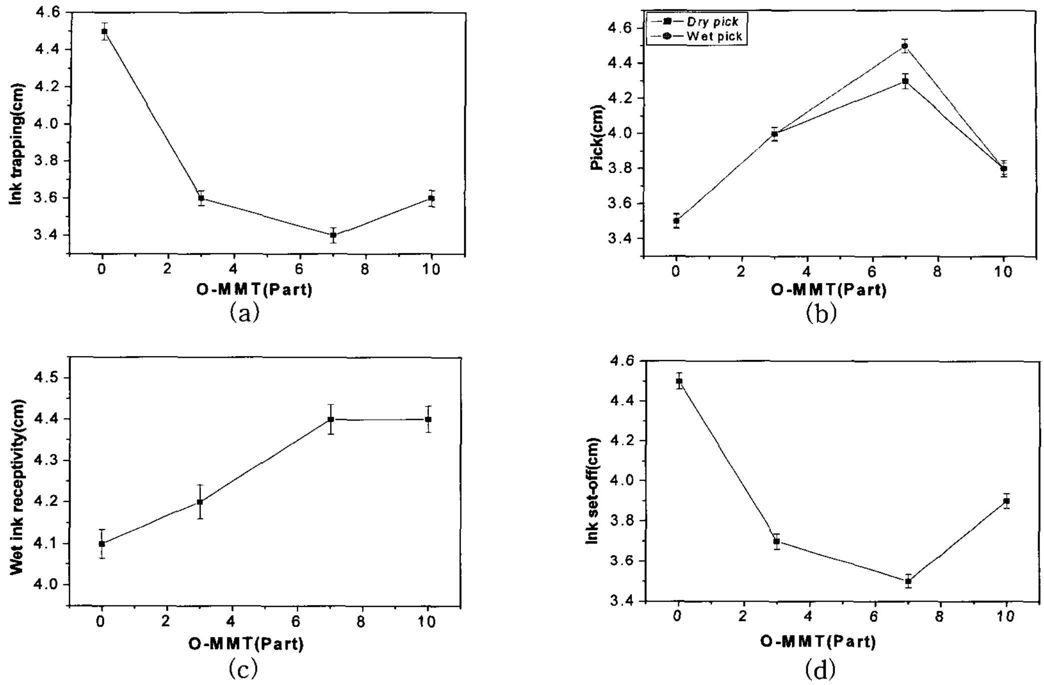

Fig. 7. Printing properties of coated paper with O-MMT:
(a) ink trapping, (b) pick, (c) wet ink receptivity, and (d) ink set-off.

picking appears when particles of paper are pulled apart as the web leaves the printing nip, because of either high ink tack or low surface strength of the paper. Thus, the improvement in picking seems to be due to enhancement of internal bond strength by O-MMT reinforcement.

Another important property required in the paper market for higher print quality is printing properties (10). The printing properties are shown in Fig. 7 and 8. The ink trap, amount of ink transferred from the printing plate to the paper as a result of a printing impression, was decreased with increasing O-MMT. Wet or dry pick are picking results with and without water, respectively, occurring in the printing process (11), where the picking results from a loss of surface strength due to dampening the sheet surface prior to the moment of impression. They improved remarkably with increasing O-MMT dosages until 7 parts, then decreased with further increase of O-MMT. The wet ink receptivity, ability of a paper surface to uniformly and adequately transfer ink from the printing plate or blanket, was improved with the addition of O-MMT. Thus, the O-MMT based coating adhesives can provide uniform ink coverage over a wide range of film thickness due to improved ink receptivity. The set-off, a measure of the tendency of a freshly-printed ink layer to be partly transferred to a substrate coming into frictionless contact with the print, also improved with the increased O-MMT.

Based on the results in this study, it can be concluded that the addition of a small amount (less than 7 parts) of O-MMT can generally improve the mechanical and printing properties

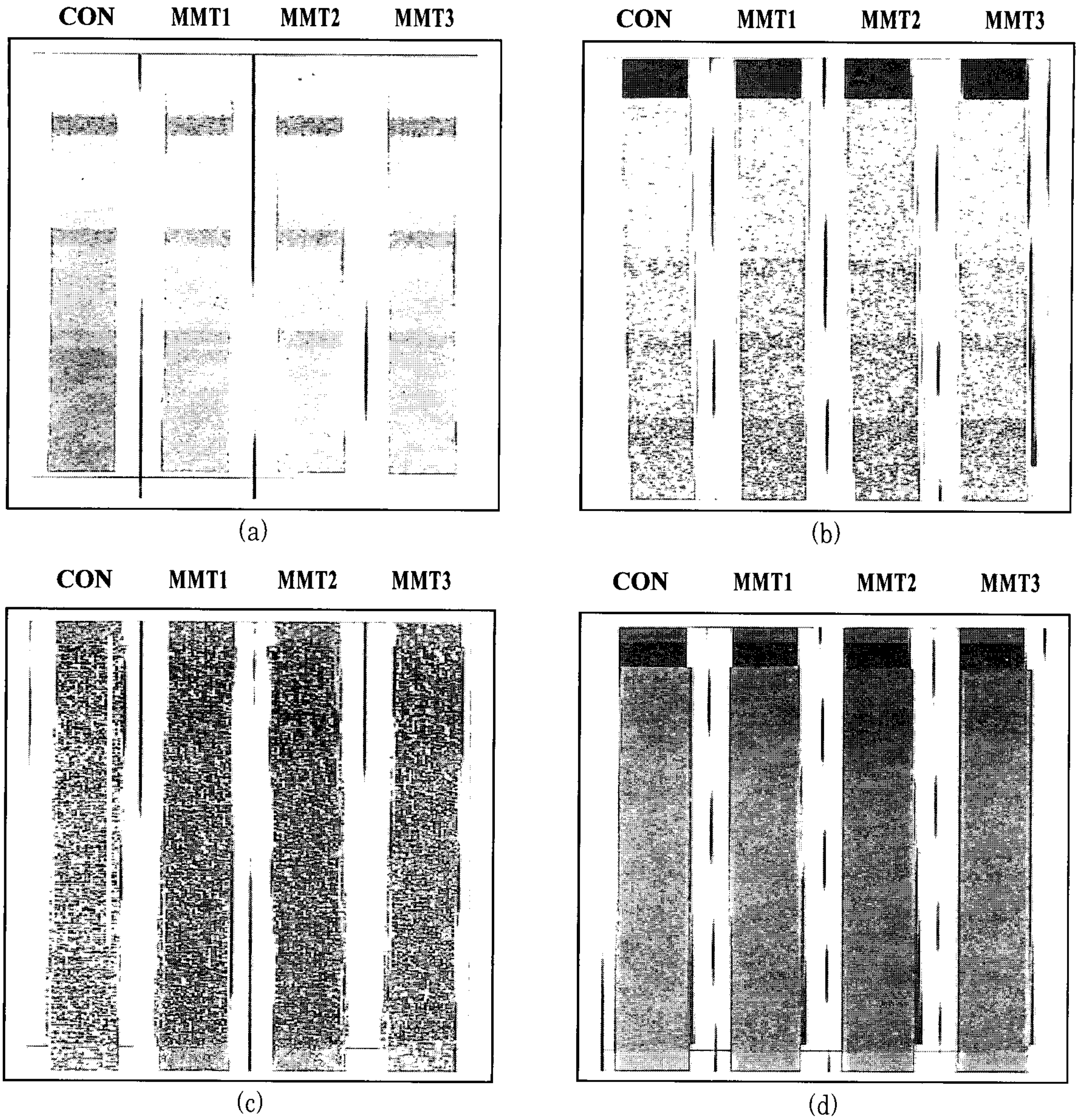

Fig. 8. Visual representation of printing properties:
(a) ink trap test, (b) set-off, (c) wet pick, and (d) dry pick.

of the coated paper. And the technique is a promising method to enhance the paper quality, if there is a compromising study between the performance and cost of O-MMT in terms of the O-MMT concentration.

4. Conclusions

This paper describes the results of a new paper coating adhesive based on an organically-modified montmorillonite (O-MMT).

The amount of O-MMT was varied by 0, 3, 7, and 10 parts, while all the other color coating formulations were fixed. The flow resistance such as viscosity, maximum torque, and thixotropy increased with increased amounts of O-MMT. In mechanical properties, tensile strength and tear strength, internal bond and folding endurance were improved remarkably with increasing levels of O-MMT. In printing properties the picking and print-through properties, some of the most important qualities in the paper market, were improved, while the opacity and brightness showed little improvement with the addition of O-MMT. Thus, the technique in this study can be a promising method to enhance the paper quality. But a more precise comparson of the composition of paper coating adhesives between the performance and cost of O-MMT in terms of the O-MMT concentration is needed.

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