Preparation and Characterization of Muscovite Mica/UV Coating Materials for Steel

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This paper describes the exfoliation and surface modification of muscovite mica for UV coating formulation. For the exfoliation of the mica, hydrothermal process was used in the presence of lithium nitrate ($LiNO_3$). After the cation exchange with Li^+ ions, the surface of the mica was modified with several amphiphilic substances to increase compatibility and storage stability in UV coating formulation. Such a hydrophobic surface modification affected colloidal stability as well as dispersibility of the exfoliated mica in UV coating solution. Anticorrosive property of mica/UV coated steel plates was tested by salt spray test (SST) and compared with sodium montmorillonite (Na^+-MMT)/UV coated steel plates.

1. Introduction

Lamella-type inorganic fillers have been used for the enhancement of barrier properties in the steel coating formulations. Lamella- or sheet-type of inorganic fillers exhibit superior barrier properties as compared with other fillers of particle or spherical morphologies, since such fillers guarantee longer diffusion pathways under the same condition. Until now, various kinds of inorganic fillers have been studied in polymer/inorganic composite materials. Most extensively studied one can be montmorillonite (MMT) family. MMT is a soft phyllosilicate group of clays whose structure is a kind of smectite. MMT is usually composed of 2 tetrahedral sheets sandwiching a central octahedral sheet with having hydrate cations. MMT shows a high cation exchange capacity (CEC) and can absorb water to be exfoliated under mild conditions. For this reason, MMT has been widely investigated in the composites of various vinyl, acryl, and condensation polymers.[1)-5)]

On the other hand, micas are a different sort of minerals which have been studied as reinforcing fillers. Mica has longer sheet lengths more than 1 μm, which is usually bigger than the typical dimensions of MMT. In addition, mica shows better smoothness and hardness, lower heat expansion coefficients ($\sim 3\times10^{-5}$ ℃$^{-1}$), superior elastic modulus ($\sim$ 3 GPa) as compared with MMT.[6)] The structural formula of natural or muscovite mica is $K_2Al_4(Si_6Al_2)$ $O_{20}(OH)_4$ in which aluminum ions coordinated octahedrally by oxygen and hydroxyl ions sandwiched between $(Si, Al)O_4$ tetrahedral. In mica, the interlayer cations are potassium ions, and which are not hydrated; therefore, the micas do not swell in water under mild conditions.[7)-9)] Most of synthetic micas also have the highest layer charge density among the clays; however, natural mica is non-swelling. Therefore, swellable synthetic micas, which can be prepared by hydrothermal, solid state, and topotactic exchange methods, have been studied so far.[10)] In the case of synthetic mica, fluorinated or organically-modified mica nanocomposite systems are widely studied by many research groups.[11)-13)]

In this work, we used natural muscovite mica as inorganic filler in UV coating formulation for steel plate. Exfoliation of the mica was performed by using hydrothermal process in the presence of lithium nitrate and surface modification with several cationic surfactants and water-soluble polymers. Exfoliation degree, morphology, and dispersion stability of the mica as well as the barrier property of the exfoliated mica/UV coating films will be discussed in this paper.

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2. Experimental

2.1 Materials

Muscovite mica (300 mesh, white color, CEC = 1~5 meq/100 g) was purchased from Prakash Mica Exports in India. Urethane-acrylate UV coating solution, photo-initiator (Darocure 1173, Ciba Chemical), and GI steel plates (150 mm × 75 mm) were given by POSCO. Lithium nitrate ($LiNO_3$), cetyl trimethylammonium bromide (CTAB), dodecyl trimethylammonium bromide (DTAB), polyethyleneimine (PEI, Mn = 60,000 g/mol), and polyoxyethylene (PEO, Mn = 3,350 g/mol) were purchased from Aldrich and used without further purification. Ultra-pure water (resistivity > 18.2 MW·cm, Millipore Co.) was used all through the experiments.

2.2 Preparation of exfoliated Mica/UV coating solution

Pristine mica was rinsed with acetone and water, and followed by heating in an IR furnace for 1 hr at 800 ℃ under Ar atmosphere. After the heat treatment, the mica powder was added into an autoclave reactor (< 5 bar) with 100 mL pure water and 170 g $LiNO_3$. The concentrations of mica were 0.5, 1.0, and 3.0 wt.% based on total weight. The reaction mixture was then vigorously stirred at 170 ℃ and the reaction time was varied from 48 to 96 hr. After the hydrothermal treatment, the product was washed with excess amount of pure water in the filtration unit equipped with an aspirator. Then the mica was dried in a vacuum oven. Surface modification of the mica was performed with DTAB, CTAB or PEI/PEO (1:1 w/w) mixture. First, 0.1 g the mica was dispersed in 10 mL pure water with varying concentration of DTAB from 16.7 to 133.3 wt.% based on the mica solid. Second, ultrasonic energy was applied to the dispersion by using a probe-type ultrasonic processor (Vibracell 750VCX, 750W) for 30 min (1 sec on/ 1 sec off cycle) at 70% load. Then the mica dispersion was washed again and dried with the same method aforementioned. Mica/UV coating solution was prepared by ultrasonication. The concentrations of the mica were 0, 1.0, and 3.0 wt.%, respectively. The method was the same as above.

2.3 Characterizations

Concentration of the cations (Li^+ or K^+) in mica was analyzed by using an atomic absorption spectrometer (AAnalyst 700, Perkin Elmer). X-ray diffraction (XRD) patterns of micas before and after the treatments were obtained by using a Rigaku D/MAX 2500 X-ray diffractometer with Cu Kα radiation source (λ = 0.154 nm), operated at 40 kV and 20 mA. Morphology and size of mica were studied by using SEM/EDX (S-570, Hitachi

Co.) and TEM (H-7600, Hitachi Co.). TEM micrographs of mica/UV coating layer were observed after the ultra-microtoming with 60 nm sample thickness. Dispersion stability of mica in UV coating solution was measured by using an on-line turbidity meter (Turbiscan Lab, Formulaction Co.) for 24 hr. Barrier property of mica/UV coating films was tested according to salt spray test (SST, 10 wt.% NaCl aq. solution). After the coating (UV mercury lamp, 400 W for 30 sec) of mica/UV coating solution onto GI steel plate, the test samples were kept in an incubator for 72 hr. The average thickness of the coating layer was 5 ± 0.5 mm.

3. Results and discussion

3.1 Exfoliation of pristine mica

Fig. 1 shows the basal spacing of mica powders before and after the hydrothermal treatment. The XRD patterns of pristine and heat treated micas are almost identical, in which a typical basal sheet distance of 9.98 Å can be observed. After the hydrothermal process, the basal spacing increases and this can be proved by the peaks at ca. 4° and 8° angles, and which correspond to 22.07 Å and 11.04 Å, respectively. This value seems remarkable as compared with previous reports.[14],[15] During the hydrothermal process, K^+ ions can be replaced by small Li^+ ions, and they can be hydrated. The radius of Li^+ ions is 0.068 nm, which is a half of K^+ ions (0.133 nm); however, the hydration number of Li^+ ions is 5-6, and which is bigger than that (3-4) of K^+ ions. Due to the hydration, mica sheets are swollen and they can be delaminated. In Table 1, the effect of hydrothermal process time on the
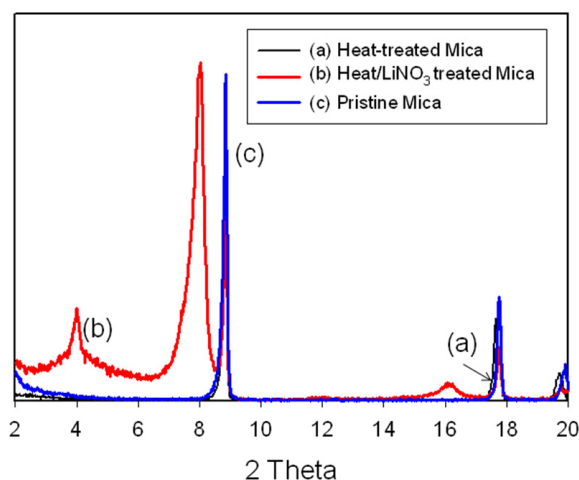

Fig. 1. XRD patterns of (a) heat treated mica at 700 ℃ for 1 hr, (b) heat and $LiNO_3$ (hydrothermal) treated mica, and (c) pristine mica samples.

Table 1. Concentrations of Li$^+$ and K$^+$ ions analyzed by using AAS with varying the hydrothermal process time and the concentration of mica

Process time [hr]	Temperature [℃]	LiNO$_3$/H$_2$O [-]	Conc. of Mica [%]	Li$^+$ [%]	K$^+$ [%]
0	-	-	-	0.02	7.61
48	170	1.7	1.0	0.67	4.75
72	170	1.7	1.0	0.66	4.70
96	170	1.7	1.0	0.67	4.78
72	170	1.7	0.5	0.94	3.78
72	170	1.7	3.0	0.38	6.60

concentration of Li$^+$ ions in the mica was summarized. As a result, it was found that the process time of 48 hr was enough to exchange K$^+$ ions, in the case of 1.0% mica concentration. When the process time was 72 hr, a full delamination of mica was observed by analyzing XRD patterns; however, more than 72 hr was not required. The effect of mica concentration on the degree of cation exchange was also investigated and summarized in Table 1. As one can see, the cation exchange was significantly affected by the initial charge of mica. In the case of 0.5 wt.% mica concentration, Li$^+$ concentration was 0.94%. However, the mica concentration and the process time should be optimized in terms of process cost and the final properties of mica/UV coating layer.

Fig. 2 shows the effect of mica concentrations on the basal spacing changes during the hydrothermal process. As the mica concentration decreases, the intensity of initial typical basal spacing (002) decreases and the newly appeared peak around 8° angle becomes apparent and the angle value decreases. The *d*-spacing increases from 10.8 nm to 11.2 nm. The other peak around 4° angle (*d*-spacing, 21~22 nm) also becomes clear. These results prove that

the delamination or exfoliation of mica is significantly affected by the relative concentration between Li$^+$ and mica.

3.2 Surface modification of mica and dispersion stability

In this work, DTAB, CTAB, and PEI/PEO were used to modify the surface of mica after the hydrothermal treatment. We didn't present the XRD patterns of micas after the surface modification; however, DTAB exhibited the best result in terms of delamination and dispersion stability. Among the surface modifiers used in this work, DTAB has the smallest carbon number (C$_{12}$) as compared with those of other surface modifiers. Due to the limited molecular size, CTAB and PEI/PEO cannot be inserted in between the platelets of mica. When more than 33.3% DTAB (based on the mica solid) was used, new XRD peak was observed around 2.3°. Moreover, the intensity of peak around 8° decreased and shifted to 7°, and which implied the further exfoliation of mica proceeded due to the insertion of DTAB.

Fig. 3 shows the dispersion stability of mica/UV coating solution with varying the concentration of DTAB. The mica powder was re-dispersed in the UV coating solution
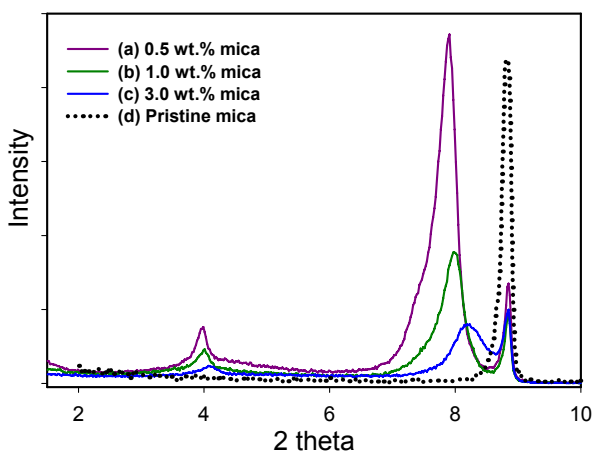

Fig. 2. XRD patterns of the hydrothermally treated mica with various concentrations.
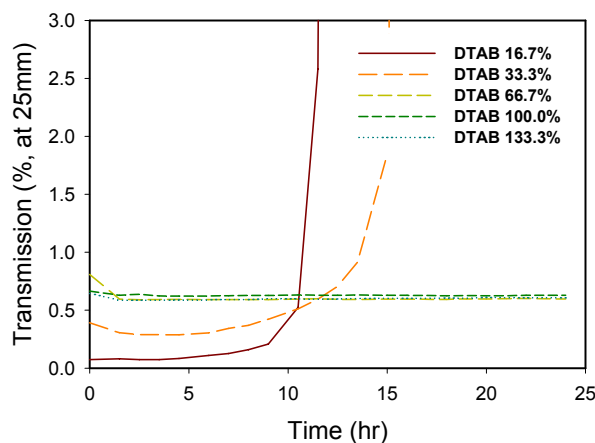

Fig. 3. Transmittance changes of mica/UV coating solution with varying the concentration of DTAB for 24 hr.

by using a ultrasonication for 10 min at 40% load of 750 W and its concentration was 1% based on the total weight. The dispersion stability was investigated by using an on-line turbidity meter in terms of the change in transmittance (%) at the certain height of sample vial for 24 hr. As shown in Fig. 3, the transmittance significantly changes when the concentrations of DTAB are 16.7 and 33.3%. However, no changes in the transmittance are observed when the concentration of DTAB is higher than 66.7%, and which indicates neither creaming nor precipitation occurs within measuring time.

3.3 Characterization of Mica/UV coating layer

SST was performed with a series of GI steel plates coated with 1.0 and 3.0% mica/UV coating solutions, respectively. For comparison, the same test was performed with the GI steel plates coated with the same concentrations of Na$^+$-MMT/UV coating solutions and these results were summarized in Table 2. As listed in Table 2, the average coating thickness was 5 ± 0.5 mm. The photographic im-

ages of coated steel plates are shown in Fig. 4. In all samples, white rust resulted from the oxidation of zinc were observed. Mica/UV coating solutions exhibited better results as compared with Na$^+$-MMT/UV or UV coating solution without filler. We didn't show the TEM micrographs of mica/UV or Na$^+$-MMT/UV coating layers; however, it was found that the size is platelet of mica was much bigger than that of Na$^+$-MMT. In both cases of mica and Na$^+$-MMT, several layers of sheets were observed in the TEM analysis. We believe that optimal coating condition is required to enhance the barrier properties in mica/UV coating formation, like mica concentration or coating thickness.

4. Summary

We demonstrated the synthesis and characteristics of delaminated muscovite mica/UV coating solutions for anti-corrosive steel coating applications. Hydrothermally treated mica showed better anticorrosive properties than Na$^+$-MMT as inorganic fillers. The hydrothermal process and surface modification with DTAB exhibited good dispersion stability of the mica in UV coating solution. The mica/UV coating system guarantees the high degree of exfoliation of mica as compared with mica/polymer composite system. Further optimizations in the surface modification of mica or coating formation are on-going in our group, and which will give us advanced barrier properties.

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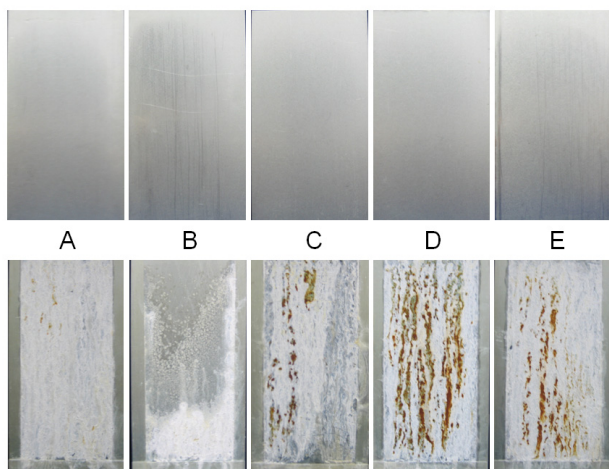2. H. Z. Friedlander and C. R. Frink, *J. Polym. Sci. B.*, **2**, 475 (1964).

Fig. 4. Photographic images of the GI steel plates coated with various UV coating solutions. The upper and lower images are before and after SST, respectively. The sample ID is listed in Table 2.

Table 2. UV coating conditions and SST results for mica/UV and Na$^+$-MMT/UV coated GI steel plates

Sample ID	UV coating conditions		Appearance after 72 hr SST / Area of red rust in steel plate [%]
	Coating thickness [μm]	Type / concentration of filler [wt.%]	
A	5±0.5	Mica / 1.0	Good (white rust) / < 1
B	5±0.5	Mica / 3.0	Good (partial white rust) / 0
C	5±0.5	Na$^+$ MMT / 1.0	Bad (white rust)/ ~8
D	5±0.5	Na$^+$ MMT / 3.0	Bad(white rust) / ~37
E	5±0.5	No filler	Bad (white rust)/ ~28

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