

Hydrophobic Modification of Dickite and Salt Spray Test Study on LLDPE/Modified Dickite Composite

Bing Xue,¹ Yinshan Jiang,¹ Fangfei Li,¹ Maosheng Xia,¹ Mengmeng Sun,¹
Darui Liu,¹ Xuguang Zhang,¹ Lixin Yu²

¹Key Laboratory of Automobile Materials of Ministry of Education and Department of Materials Science and Engineering, Jilin University, Changchun 130025, China

²School of Materials Science and Engineering, Department of Inorganic Nonmetal Materials Science, Nanchang University, Nanchang, 330031, China

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ABSTRACT: Dickite particles were modified by silane coupling agent, hexadecyl phosphate, oleic acid, and stearic acid (SA), respectively. Modified dickite was composed with linear low-density polyethylene (LLDPE) to prepare a series of LLDPE/modified dickite composites. Hydrophilicity of modified dickite was characterized by dispersion experiments and contact angle tests. The results indicated that hydrophilicity of modified dickite decreases sharply, compared with nonmodified dickite. Among four modifying agents, SA had obvious effect on hydrophobic modification of dickite. Fourier-transform infrared spectra results suggested that chemical bonding between modify-

ing agent and dickite was beneficial to the hydrophobic modification. Results of salt spray tests illustrated that the introduction of modified dickite into LLDPE improved the anticorrosion properties of the polymer universally. The anticorrosion mechanism of LLDPE/modified dickite was analyzed by scanning electron microscope micrograph. The mechanical properties of the resultant composites displayed a fact of reinforcement of modified dickite. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 3480–3488, 2010

Key words: dickite; clay; fillers; modification; anticorrosion

INTRODUCTION

Corrosion is a natural process of a metal to return to its original state through an electrochemical process. Although corrosion is a natural process, certain atmospheric conditions to which the metal is exposed during its manufacture, processing, storage, or shipment can aggressively accelerate the degradation. Most notable of these factors are sulfur dioxide (typically associated with the burning of coal, oil, and gas), acids in packaging materials, and temperature and humidity fluctuations during transit. To combat the devastating effects of corrosion, several efficient methods have been developed, such as antirust oil seal,¹ vapor phase corrosion inhibitor,^{2,3} and dryness packaging. Vapor phase corrosion inhibitor technology has been widely used today, because it was first tested for the mothballing of boilers and similar structures on warships in the late 1940s.⁴ Although a

similar nitrite-based chemistry is still widely used today, there is an environmentally sound and safer alternative. Barrier composite film without harm to environment, which functions by altering an ever-changing environment surrounding the metal, will be another corrosion-inhibiting strategy.

Since Okada et al. synthesized nylon 6-clay hybrid by intercalating montmorillonite in 1987,⁵ which had greatly improved the barrier properties, many authors prepared various polymer/montmorillonite composites with better barrier properties.^{6–9} Now, the attention is being focused on the choice of fillers with barrier function. It is reported that kaolin,¹⁰ vermiculite,¹¹ and mica¹² have been the fillers used for the preparation barrier composite. Up to now, dickite has not attracted people's attention for its possible barrier function.

Dickite is a clay mineral of the kaolinite group with a 1 : 1 dioctahedral structure characterized by the common chemical formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$.¹³ Natural dickite is usually a white mineral with high purity and low water absorption. It may be used as excellent filler, especially barrier filler because of its layer structure. In recent years, main researches about dickite were paid to several aspects as followed: hydroxyl-stretching mode,^{14–17} thermal behavior,^{18–21} adsorption,^{22–25} and intercalation^{18,20,21,26} of organic molecule. In addition, the formation,^{27,28} distribution,^{29–31} and mineralogy

Correspondence to: Y. Jiang (yinshan_jiang@yahoo.com.cn).

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character³² of dickite were also studied. However, the reports on the utilization of dickite as filler for polymer, especially barrier filler, have not been seen yet. The study on the utilization of dickite as a barrier filler will be very significant for developing new barrier material.

In this article, surface modification^{33–39} is used to treat the dickite raw materials. Mechanochemical grinding, which could form new surfaces, create lattice defects, and increase the reactivity of the mineral, may play an important role on hydrophobic modification. The purpose of surface modification is to achieve the change of surface character of dickite, from hydrophilicity to hydrophobicity, improving the compatibility with the nonpolarity LLDPE resin. Dickite particles modified by several modifying agent were first used as barrier filler for LLDPE with the expectation of a certain anticorrosion function. Salt spray tests were used to evaluate the anticorrosion properties of LLDPE/modified dickite film.

EXPERIMENT

Chemical

Silane coupling agent [3-aminopropyltriethoxysilane, $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$], hexadecyl phosphate [$\text{C}_{16}\text{H}_{33}\text{OPO}(\text{OH})_2$], oleic acid ($\text{C}_{17}\text{H}_{33}\text{COOH}$), stearic acid ($\text{C}_{17}\text{H}_{35}\text{COOH}$), and ethanol are analytical pure reagents and purchased from the Shanghai chemical reagents company. Kerosene (solvent oil, hexadecane, mixture of isomer) is obtained from Exxon Mobil. Linear low-density polyethylene (LLDPE) is provided from Jilin petrochemical. Compatilizer (maleic anhydride-grafted LLDPE) and antioxidant-LH (tetra-[methylene- β -(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionate]methane) are obtained from Nanjing Deba chemical. All chemicals are used as received without further purification. The dickite powder comes from Chang Bai (Baishan, Jilin province, China) with diameter in the range of 0.4–40 μm . This raw material is quite pure, and little impurity is detected by FTIR [Fig. 5(a)]. It is dried at 120°C for 4 h and kept in the desiccator.

TABLE I
Preparation Conditions of Modified Dickite
(Various Content of Modifying Agent)

Samples	Modifying agent	Content of modifying agent (wt %)	Grind time (min)
SCA-dickite	SCA	0.5, 1, 3, 5	30
HP-dickite	HP	0.5, 1, 3, 5	30
OA-dickite	OA	0.5, 1, 3, 5	30
SA-dickite	SA	0.5, 1, 3, 5	30

TABLE II
Preparation Conditions of Modified Dickite
(Various Grind Time)

Samples	Modifying agent	Content of modifying agent (wt %)	Grind time (min)
SCA-dickite	SCA	1	0, 15, 30, 45
HP-dickite	HP	1	0, 15, 30, 45
OA-dickite	OA	3	0, 15, 30, 45
SA-dickite	SA	3	0, 15, 30, 45

Surface modification of dickite

Modifying agent [silane coupling agent (SCA), hexadecyl phosphate (HP), oleic acid (OA), stearic acid (SA), 0.015 g (0.5 wt %)-0.15 g (5 wt %)] and ethanol (about 20 mL) were mixed with magnetically stirring, respectively, then 3 g dickite powder was added into them. The mixture was heated at 60°C for about 4 h to evaporate the ethanol. The dry mixture was ground in an agate mortar for a period of time (15–45 min), and then it was extracted with ethanol for three times to remove the remnants modifying agent. The solid powder was dried at 60°C. A white powder was obtained, which was the surface-modified dickite. By changing the content of modifying agent (Table I) to dickite particles and grinding time (Table II), a series of samples were prepared.

Preparation of LLDPE/modified dickite composite

LLDPE/SCA-dickite composite, LLDPE/HP-dickite composite, LLDPE/OA-dickite composite, and LLDPE/SA-dickite composite were prepared by internal mixer. Modified dickite (10 wt %), compatilizer (5 wt %), antioxidant-LH (1 wt %), and LLDPE (84 wt %) were mixed in a SLJ-40 internal mixer (Education apparatus, Changchun, China) at 170°C for 30 min at the speed of 50 rpm. The total quantity of modified dickite, LLDPE, compatilizer, and antioxidant-LH added into the internal mixer was 40 g.

Characterization

Dry dickite particles with modification at different condition were investigated by means of dispersion experiments. A total of 0.5 g solid sample (nonmodified dickite or modified dickite) and 5 mL solvent (water or kerosene) were introduced into a dried and clean test tube. The whole system was agitated for about 2 min. After agitating, the sedimentation of dickite particles was studied. When the volume of deposits reached half of the volume of solvent, the time it cost was defined as $T_{1/2}$ here. A big $T_{1/2}$ value will display a better dispersibility for dickite in solvent.

The contact angle was investigated using a contact angle meter GSA100 (KRÜSS) according to the sessile drop method. First, the sample particles were pressed into compacting piece with the diameter at 20 mm and thickness about 5 mm using preforming machine. Then, a droplet of distilled water (4 μ L) was dropped on the surface of the compacting piece. The contact angles were recorded immediately after the droplets touched the compacting piece.

FTIR of the samples was carried out on a Nexus 670 auto Fourier transform infrared spectrometer for which samples were palletized with KBr powder.

The particle-size distribution of dickite was determined by JL9200 laser particle size analyzer (Weina, Jinan, China). The samples were measured for at least 10 times, respectively. The average results were obtained.

Microscopic observations of the surface and the cross section of LLDPE/modified dickite composite film were performed in a Quanta200 environmental scanning electron microscope.

As this kind of composite may be used as an anti-corrosion packaging film for shipping, salt spray test, which can simulate ocean environment, was performed to evaluate the anticorrosion properties. The salt spray test was performed at a YW/R-150 salt mist corrosion testing box (Surui technology development, Tianjin, China) according to ASTM B-117 (natural salt spray test) with the following conditions: the NaCl concentration of the sprayed solution was 50 g/L (5% NaCl) with the pH between 6.5 and 7.2, the temperature remained at 35°C. Samples were prepared by the following process. First, as-prepared LLDPE/modified dickite composite was pressed into thin film with the thickness about 0.2 mm at a X-20 heat former machine (Education apparatus, Changchun, China). Second, the film was made into small bags with the size of 40 \times 40 mm². Then, round iron (Q195 steel) coupon, which had been washed by ethanol and dried, was sealed in the bags. These bags were hung inside the testing box using plastic strings in a free standing mode to ensure that both sides of the bags got sprayed uniformly. After 168 h test duration, the round iron coupon was taken out from the bags. The corrosion surface of the round iron coupon was analyzed to evaluate the corrosion level.

The mechanical properties of the composite were evaluated by the tensile test and steat test at room temperature. Samples were cut to dumbbell shape according to ISO/R 527-1966E. The thickness of each sample was measured at six different points with a micrometer, and the average was taken. Samples were then drawn with a universal testing machine (AG-IS, Shimadzu) at a stretching speed of 20 mm/min. The results presented were the mean values of six independent measurements.

RESULTS AND DISCUSSION

Particle dispersion experiments

Figure 1 indicates the dispersibility of dickite modified by several common modifying agents at different content. It can be seen that similar laws have appeared for all the modified dickite. With the increase of the content of modifying agent, $T_{1/2}$ values of all the modified dickite increase gradually and reach the maximum at a certain content. After the peak value, $T_{1/2}$ values begin to decrease. The maximal $T_{1/2}$ values of HP-dickite and SCA-dickite have appeared at the content of 1 wt %, whereas SA-dickite and OA-dickite at 3 wt %. For modification of dickite in this study, no matter what modifying agent is used and what interaction between modifying agents and dickite is occurred, the optimal content of modifying agent still appears. A lower content of modifying agent will not modify dickite effectively, whereas excessive modifying agent existed on the surface of dickite may intertwine with each other leading to flocculation process. It is determined that the optimal content of modifying agent is 1 wt % for HP-dickite and SCA-dickite, 3 wt % for SA-dickite and OA-dickite to make a better dispersibility in kerosene.

Figure 2 illustrates the results of the impact of grinding time on dispersibility of modified dickite. As shown in Figure 2, the dispersibility of four modified dickite increases gradually with the increasing of grinding time. The reason causing the enhancement of dispersibility of SA-dickite is that grinding has activated the crystal lattice of dickite and created some new active spots on the surface of dickite with the increase of grinding time.⁴⁰ More modifying agents existed at the active spots help to enhance the dispersibility of the modified dickite. It

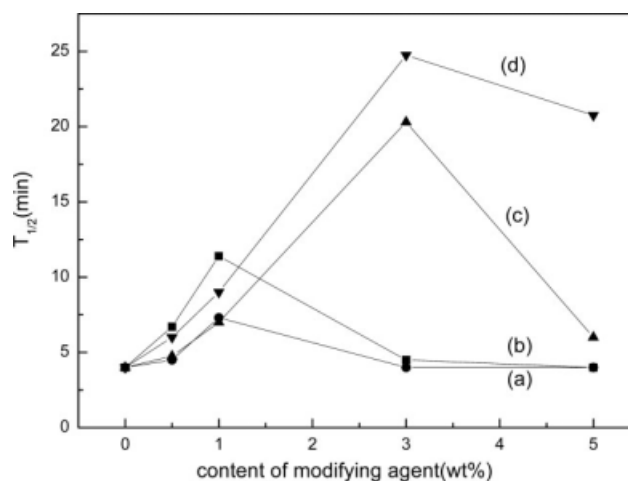


Figure 1 Dispersion experiments of dickite modified by several kinds of modifying agent. (a) SCA-dickite, (b) HP-dickite, (c) OA-dickite, and (d) SA-dickite.

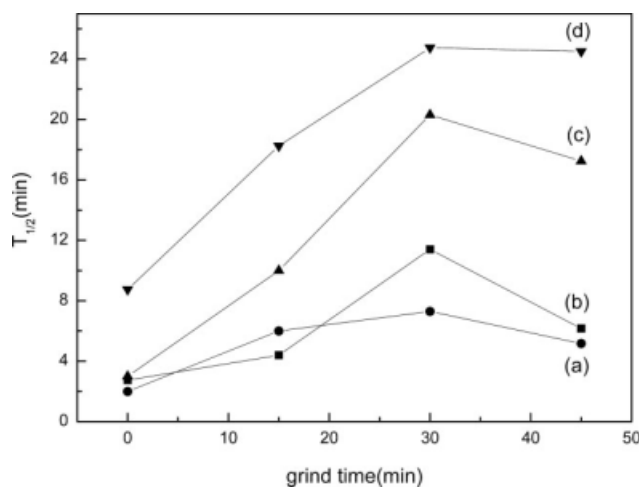


Figure 2 Effect of grinding time on dispersibility of modified dickite in kerosene. (a) SCA-dickite (at the content of 1 wt %), (b) HP-dickite (1 wt %), (c) OA-dickite (3 wt %), and (d) SA-dickite (3 wt %).

is interesting that the maximal $T_{1/2}$ values of four modified dickite (Fig. 2) appear concurrently when grind time reaches 30 min. The results show that the most active spots of dickite are produced when grinded for 30 min. The $T_{1/2}$ value of four modified dickite is no longer improved, when the grinding time overruns 30 min. It is possible that more new active spots created by grinding process may enhance the sorption between dickite particles and cause agglomeration, which weaken the interaction between modifying agents and dickite.

Compared with nonmodified dickite, the dispersibility of modified dickite in two typical solvents (polar water and nonpolar kerosene) is displayed in Figure 3. As shown in Figure 3, nonmodified dickite displays a better dispersibility in water than in kerosene because of hydrophilic hydroxyl groups ($-\text{OH}$) on the surface of dickite. Polar particles easily disperse in polar solvents, whereas it is difficult for them to disperse in nonpolar solvents. On the contrary, dickite particles modified by SA and OA are prone to disperse in kerosene, whereas they hardly disperse in water. The reason is as following, the hydroxyl groups ($-\text{OH}$) of dickite surface may interact with carboxyl groups ($-\text{COOH}$) of SA and OA. The other terminal of SA and OA, the long organic alkyl chain, which points to oil phase, ensures the lipophilicity of modified dickite particles. At the same time the alkyl chain fulfills steric hindrance between inorganic particles. All these factors improve the dispersibility of SA-dickite and OA-dickite in kerosene. In addition, HP and SCA modification also improve the dispersibility of dickite in kerosene and meanwhile decrease the dispersibility of dickite in water. It may be the result that HP and

SCA have not bonded on the surface of dickite or only a spot of modifying agents is absorbed on the surface of dickite. Therefore, the ability of interfering with the aggregation of dickite particles is weaker than that of SA and OA. Furthermore, because of the length of alkyl chain possessed by SCA is shorter than that of HP, the modification effect is worse than that of HP.

Wetting properties

Microphotographs taken immediately after dispensing the droplets on the surfaces of compacting piece are shown in Figure 4, presenting different wetting behaviors of distilled water and modified dickite. The distilled water permeates into nonmodified dickite immediately without leaving any residue, showing zero contact angle [Fig. 4(a)], suggesting the distilled water having the best wettability among all the studied dickite. In contrast, the distilled water forms clear droplets on the surface of the compacting piece with contact angles, 30.8° for SCA-dickite, 39.0° for HP-dickite, 83.1° for OA-dickite (wetting or hydrophilic, $0^\circ < \theta < 90^\circ$), and 147.3° for SA-dickite (nonwetting or hydrophobic, $90^\circ < \theta < 180^\circ$) [Fig. 4(b–e)]. These results clearly indicate that the wettability of dickite has been decreased due to surface modification. Among them, the surface of SA-dickite is changed obviously from hydrophilic to hydrophobic.

FTIR spectra of dickite

The surface groups of dickite particles before and after the modification are characterized by FTIR in Figure 5. In curve (a) the spectrum of nonmodified dickite exhibits the Si–O stretching bands at 1003,

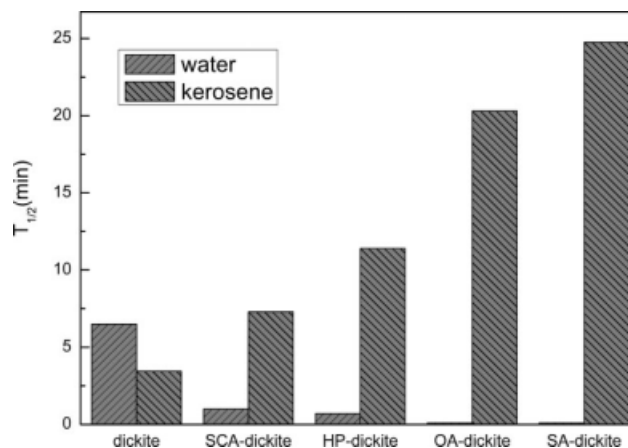


Figure 3 Dispersibility of nonmodified dickite and modified dickite prepared by four modifying agents at optimal condition (content of modifying agent and grind time) at two typical solvents.

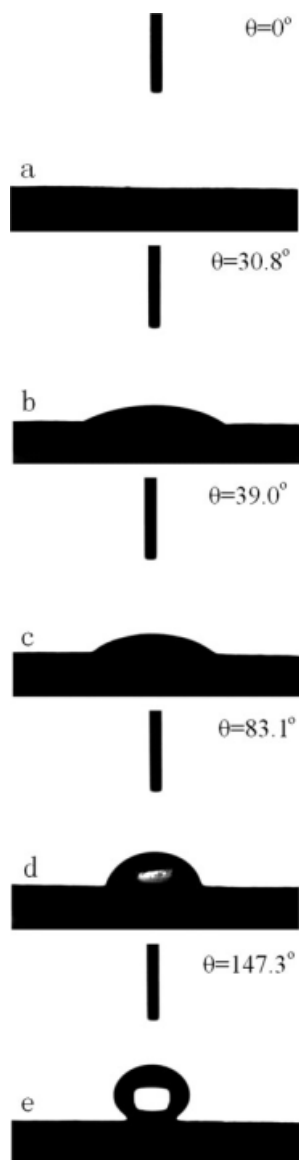


Figure 4 Contact angle of distilled water drops (4 μL) on the different compacting piece surface: (a) nonmodified dickite, (b) SCA-dickite, (c) HP-dickite, (d) OA-dickite, and (e) SA-dickite.

1034, 1107, and 1117 cm^{-1} , which together with OH stretching vibration at 3622, 3651, and 3701 cm^{-1} , are characteristic for dickite mineral. Little impurity is detected by FTIR. In Figure 5(g–i), two sharp bands at 2921 and 2852 cm^{-1} are attributed to the asymmetric and symmetric CH_2 stretch, respectively. The O–H in-plane band appears at 1469 cm^{-1} . In curve (c–e), the obvious two sharp bands and the O–H in-plane band appear in the same position. As the modified dickite particles are thoroughly washed with ethanol, no free modifying agents are believed to exist in the sample. Therefore, the obvious adsorption bands at 1469, 2921, and 2852 cm^{-1} that appear in the sample spectra confirm the existence of the modifying agent molecules HP, OA, SA in

the dickite particles. In Figure 5(i), a band near 1700 cm^{-1} attributes to the stretching vibration band of C=O in SA, whereas in Figure 5(e) this band disappears. At the same time a new peak at 1560 cm^{-1} corresponding to $-\text{COO}^-$ appears. Thus, it can be concluded that the $-\text{COOH}$ in SA has reacted with the $-\text{OH}$ of dickite and the product is carboxylate.⁴¹ The same situation happens at OA-dickite, but a bit different. The characteristic peak of carboxylate appearing in the spectra of OA-dickite is a little fuzzy, indicating a weak bonding reactivity. The observation suggests that the reactivity activity of OA is weaker than that of SA for chemical bonding dickite. As shown in Figure 5(c), no new peak is observed by IR, leading to the conclusion that HP is physically adsorbed on the surface of dickite particles. In Figure 5(b), little difference between nonmodified dickite and SCA-dickite indicates that the interaction between SCA molecules and dickite particles may be very weak.

In Figure 5(a), dickite has three absorption bands in the OH stretching region. Inner hydroxyl groups, lying between the tetrahedral and the octahedral sheets, give the absorption near 3622 cm^{-1} . The other two OH groups reside at the octahedral surface of the silicate layers and form weak hydrogen bonds with the oxygens of the Si–O–Si bonds on the lower surface of the next layer.⁴² Compared with nonmodified dickite, the position and the intensity of the three OH stretching bands in Figure 5(c–e) have no change, indicating that the modified dickite still keeps the layer stacking arrangement, thus leading to the conclusion that modified dickite has not been intercalated. Therefore, it can be concluded that inner hydroxyl groups and hydroxyl between the silicate layers have not reacted with the carboxyl of OA and SA. For OA-dickite and SA-dickite, only some hydroxyl groups on the surface of dickite react with the carboxyl of OA and SA. The spectrum of dickite shows two bands at 1635 and 3442 cm^{-1} owing to OH stretching vibrations of H_2O adsorbed on the surface of dickite particles [Fig. 5(a)]. As can be seen from Figure 5(e), SA surface modification causes the reduction of the intensity of H_2O bands, suggesting a formation of hydrophobic surface of SA-dickite. This result is in accordance with the contact angle test. There are at least two reasons why SA-dickite contains less water than nonmodified dickite—the larger size organic carboxylic acid molecule physically takes up room that water would occupy in an inorganic system, and has much lower hydration energies.⁴² As a result, the amount of water in SA-dickite is considerably reduced. An important consequence of surface modification is that the dickite surface takes on hydrophobic character, which will greatly enhance the compatibility with nonpolar polymer.

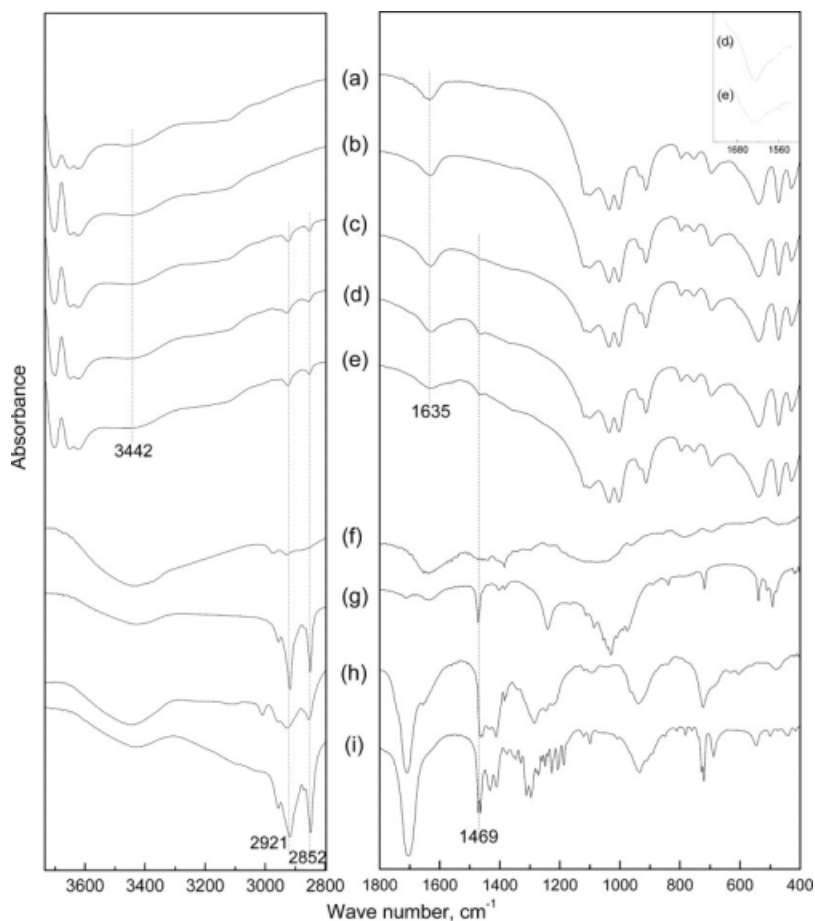


Figure 5 FTIR spectra of (a) nonmodified dickite, (b) SCA-dickite, (c) HP-dickite, (d) OA-dickite, (e) SA-dickite, (f) SCA, (g) HP, (h) OA, and (i) SA.

Size analysis of dickite

Figure 6 shows the particle-size distribution in terms of percentage of total particle volume versus particle diameter of dickite particles with and without modification. The particle-size distribution of nontreated dickite [Fig. 6(a)] shows the presence of a population of particles, which is formed by particles of 0.4–40 μm , with a modal size of 10.5 μm . The distribution curves of modified dickite [Fig. 6(b–e)] indicate that the surface modification treatment causes the reduction of the modal size of the dickite particles. Compared with nontreated dickite, grinding has decreased the particle size of dickite, activated the crystal lattice of dickite, and created some new active spots on the surface of dickite.⁴⁰ These active spots are likely to reunite with each other and cause aggregation. The introduction of modifying agents can interfere with the aggregation of dickite particles by reacting with the active spots and coating the particles. Meanwhile, different modifying agents could affect the size of modified dickite. For SA-dickite, strong interaction has happened between SA and dickite, and dickite particles have been fully coated by SA, so a smaller modal size of SA-dickite

is formed, whereas other modified dickite cannot show a smaller modal size because of weak interaction between modifying agents and dickite.

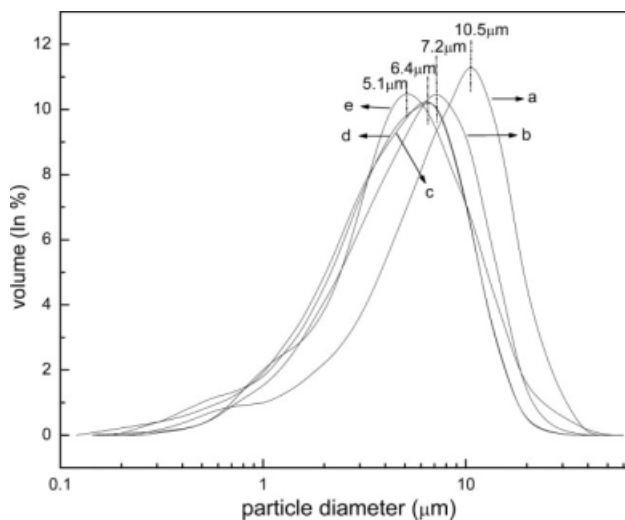


Figure 6 Particle-size distribution versus percentage of particle volume for (a) nontreated dickite, (b) SCA-dickite, (c) HP-dickite, (d) OA-dickite, and (e) SA-dickite.

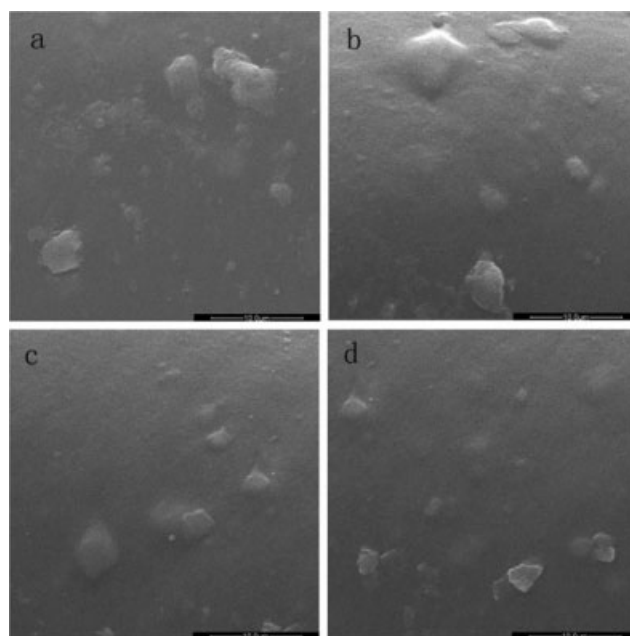


Figure 7 SEM micrograph of the surface of the composites film, (a) LLDPE/SCA-dickite composite, (b) LLDPE/HP-dickite composite, (c) LLDPE/OA-dickite composite, and (d) LLDPE/SA-dickite composite.

Morphology of modified dickite in LLDPE matrix

Figure 7 presents the morphology of modified dickite particles in LLDPE matrix. Lamellar particles were observed in all samples. This situation may be due to the fact that hot pressing film formation has induced layered structure of dickite to parallel to the composite film surface. We can clearly see this distribution from the SEM micrograph of cross section of LLDPE/SA-dickite composite film in Figure 8. However, different modified dickite displays different distribution in LLDPE matrix. As can be seen from Figure 7(a,b), SCA-dickite and HP-dickite are not uniformly distributed throughout the LLDPE

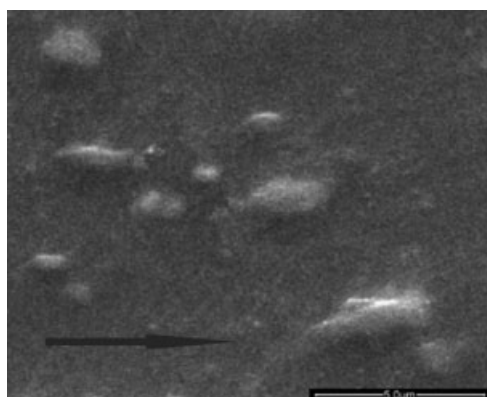


Figure 8 SEM micrograph of the cross section of the LLDPE/SA-dickite composite film (the arrow is oriented parallel to the film surface).

matrix, and aggregations of dickite particles have appeared. By contrast, OA-dickite and SA-dickite are more uniformly distributed in the LLDPE matrix [Fig. 7(c,d)]. Among four kinds of modified dickite, SA-dickite shows a smaller size distribution, and the results are consistent with particle size analysis, indicating that different modifying agents have an obvious impact on the dispersion of dickite particles into LLDPE matrix.

Performance in salt spray test

Figure 9 shows the photographs of iron coupon without and with a certain treatment. As iron cannot withstand the aggressive Cl^- and H_2O corrosion medium for 168 h, the bare iron coupon in testing box is badly corroded as shown in Figure 9(a). The massive corrosion products are accumulated on the corrosion surface. Corrosion degree has decreased after iron coupon is packed with LLDPE bag. However, massive rust still appears on the surface of iron

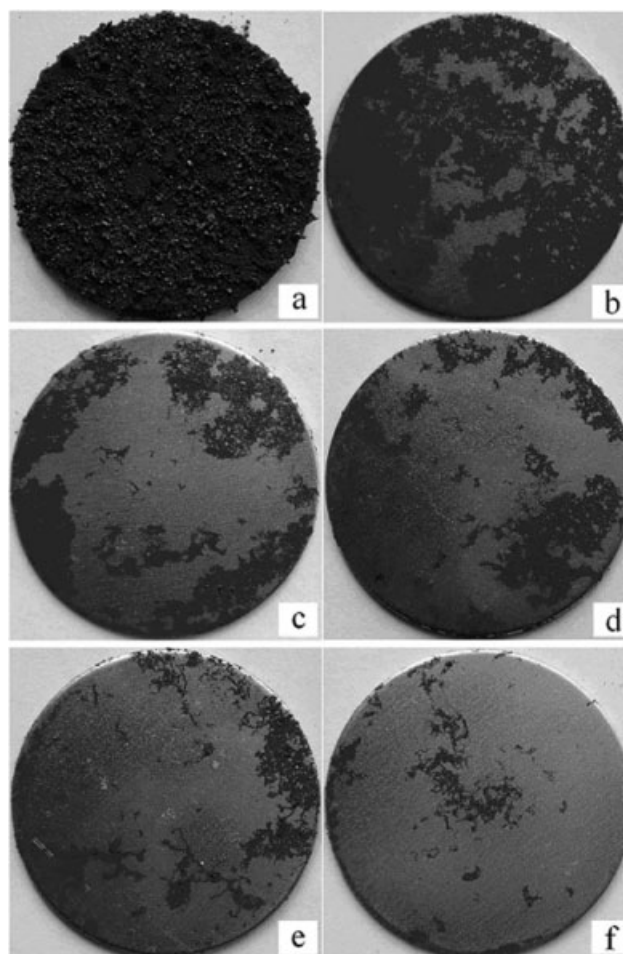


Figure 9 Photographs of iron coupon, (a) naked, packed with (b) LLDPE, (c) LLDPE/SCA-dickite composite, (d) LLDPE/HP-dickite composite, (e) LLDPE/OA-dickite composite, and (f) LLDPE/SA-dickite composite.

TABLE III
Corrosion Rate of Iron Coupon

Packed material	None	LLDPE	LLDPE/ SCA-dickite	LLDPE/ HP-dickite	LLDPE/ OA-dickite	LLDPE/ SA-dickite
Corrosion rate (%)	100	65	33	32	19	11

coupon, because aggressive salt spray can permeate through LLDPE matrix and corrode iron coupon. To quantify the corrosion degree, the corrosion rate of iron coupon was obtained by calculating the pixel proportion of pitting occupied in iron coupon from each photograph using Photoshop software. The corrosion rate of iron coupon has been evaluated and expressed as a percentage of corroded surfaces. In Table III, the corrosion rate of iron coupon packed with LLDPE bag has reached 65%. The introduction of the modified dickite into LLDPE has improved the anticorrosion properties of this polymer. The corrosion rate of iron coupon packed with these composite has significantly declined. In general, there are two reasons causing the enhancement of anticorrosion properties for LLDPE/modified dickite composite. First, it can be seen from Figures 7 and 8 that platelet structure, which consists of silicate layers with a certain thickness, has formed at the process of preparing LLDPE/modified dickite composite film. This kind of platelet structure nearly parallels to the composite film surface and is impermeable for gas and water. Therefore, a tortuous pathway, which retards the progress of salt spray through the composites film, is formed. Second, clay layer bundles strongly restrict the motion of polymer chains, probably reducing the coefficient of diffusion of the gas and water molecules.⁴³ Therefore, compared with pure LLDPE, the introduction of modified dickite into LLDPE matrix has improved the anticorrosion properties of the polymer by impeding the penetration of aggressive salt spray through composites film. However, anticorrosion properties vary with different modified dickite in these composites. The anticorrosion properties of LLDPE/SA-dickite composites and LLDPE/OA-dickite composites are better than that of LLDPE/SCA-dickite composites and LLDPE/HP-dickite composites. The minimum corrosion rate (11%) appears when iron coupon packed with LLDPE/SA-dickite composite bag. The reason may attribute to different dispersion situation of

modified dickite in LLDPE matrix. As shown in Figure 7, different modified dickite displays different distribution in LLDPE matrix. As the four LLDPE/modified dickite composites are prepared by keeping the same content of filler, big particles formed by aggregation of dickite are likely to decrease the amount of formed platelet structure and shorten the tortuous pathway, leading to reduced anticorrosion properties of LLDPE/modified dickite composite (Fig. 10). SA-dickite shows a smaller particle size and a uniform distribution in the LLDPE matrix, so a better anticorrosion properties of LLDPE/SA-dickite are obtained.

Mechanical properties

The results of the mechanical properties for the investigated LLDPE/modified dickite composite samples are listed in Table IV. Compared with LLDPE, the introduction of modified dickite into LLDPE resin has improved the tensile strength and tear strength of the polymer generally. Particularly, the reinforcement of SA-dickite for LLDPE is relatively remarkable. The reinforcement of SA-dickite is caused by the good dispersion in LLDPE as proved by SEM. The improved mechanical properties after the addition of SA-dickite could be mainly contributed to interactions between SA-dickite clay and LLDPE chains associated with larger contact surface. The SA-dickite layers interact with LLDPE chains to form a network in which SA-dickite acts as a physical crosslinking junctions.⁴⁴ For other modified dickite, the worse dispersion is in LLDPE, the smaller contact surface is obtained, and the interaction between modified dickite and LLDPE is weaker. Therefore, the effect of reinforcement for LLDPE is not as good as SA-dickite.

CONCLUSIONS

Four common modifying agents were used to modify dickite. The effect of hydrophobicity modification

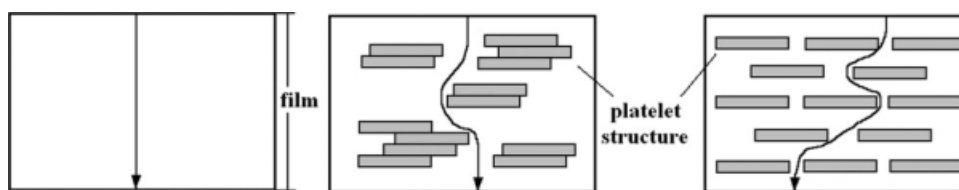


Figure 10 Sketch of barrier mechanism of LLDPE/modified dickite composite.

TABLE IV
Mechanical Properties of LLDPE/Modified
Dickite Composite

Modified dickite/LLDPE (filler content: 5 wt %)	Tensile strength (MPa)	Tear strength (KN/m)	Elongation at break (%)
LLDPE	19.79	129.29	292
LLDPE/SCA-dickite	20.49	129.67	305
LLDPE/HP-dickite	19.92	131.43	246
LLDPE/OA-dickite	21.43	130.21	287
LLDPE/SA-dickite	24.12	134.04	275

of dickite was analyzed and compared according to dispersion experiments and contact angle tests. The results show that the order of effective hydrophobicity modification of dickite for modifying agents is SA > OA > HP > SCA. Among them, SA modification achieves the change of the surface properties of dickite from hydrophilicity to hydrophobicity, and the contact angle of SA-dickite reaches 147.3°. The mechanism of interaction between modifying agents and dickite was discussed by FTIR. It is indicated that SA is chemically bonded on the surface of dickite, whereas HP, a modifying agent with poor modification effect, is physically absorbed on the surface of dickite. The results suggest that the chemical bonding between modifying agents and dickite is more beneficial than physical adsorption for the hydrophobic modification of dickite. SEM micrographs of the LLDPE/modified dickite show that modified dickite with hydrophobic surface could uniformly distribute in the LLDPE, where more platelet structure parallel to the composite film surface is formed, and the anticorrosion properties of composite are greatly improved.

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