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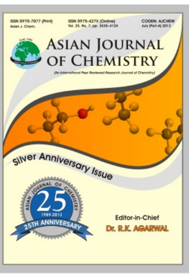

Emulsion Waterproof Agent and Its Effects on Intrinsic Properties of Gypsum

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A core-shell structural emulsion waterproof agent containing fluorine and silicone was prepared by gradual emulsion polymerization and its structure and properties were analyzed by fourier transform infrared spectrophotometer, integral-rotation contact angle measuring device and X-ray photoelectron spectrometer. Then the waterproof agent was added into gypsum slurry. Its modification effects on the 2 and 24 h water absorption and 24 h flexural, compressive softening coefficient of gypsum were studied and the action mechanisms were investigated. The research indicates that the fluorine and silicone monomers were effectively introduced into the molecular structure of the waterproof agent during the process of synthesis, which gave the latex film excellent hydrophobicity. When the dosage of waterproof agent reached to 9 %, the water-resistance of gypsum sample was improved significantly compared with the blank sample.

Key Words: Waterproof agent, Gypsum, Contact angle, Water-resistance.

INTRODUCTION

Gypsum is a non-hydraulic cementing material. As a green building material, gypsum products perform well in thermal insulation, sound absorption, fire resistance as well as pseudo "respiratory function" and have been widely used in architectural decoration field. However, gypsum has poor water-resistance. When the products are damp, their strength would be lost greatly and they will become easy to warp. Therefore, a scientific method to effectively improve the water-resistance of gypsum is an important research topic.

Research has shown that three main factors weigh heavily for the poor water-resistance of gypsum. The first factor is the fact that each liter of water can dissolve about 2.05 g of $CaSO_4$ at 20 ºC; therefore, this implies that the solubility of gypsum in water is relatively high. The second factor is that the internal surface of pores in hardened gypsum paste would cause strong adsorption of water. The third contributing factor is that there are large amounts of porosity in gypsum[1-3]. In this article, we tried to improve its water-resistance by both reducing the internal surface energy of pores and improving the density degree of gypsum-hardened. An emulsion waterproof agent containing fluorine and silicone was prepared and the effect on water-resistance of gypsum was observed and presented.

EXPERIMENTAL

Organic materials used to prepare the waterproof agent include monomers, initiator, emulsifier, solvent, *etc*. Butyl acrylate (BA) and methyl methacrylate (MMA) are soft monomer and hard monomer, respectively. Hexafluorobutyl methacrylate (HFMA), dodecafluoroheptyl methacrylate (DFHMA), acrylic acid (AA) and an acrylic monomer containing silicon are used as functional monomers. Ammonium persulfate (AP) is initiator. Nonylphenol polyoxyethylene ether (OP-10) and sodium dodecyl sulfate (SDS) are used as emulsifiers. Sodium bicarbonate and ammonia water are pH buffers. All of the substances above are analytical reagent and commercially available. Vinyl acetate ethylene (VAE) emulsion was used to contrast with the waterproof agent. Deionized water is industrial pure and used as solvent.

Gypsum: Flue gas desulfurization (FGD) gypsum whose chemical composition is shown in Table-1 is pale yellow powdery solid and it was obtained from Jinan Huangtai power plant in Shandong province, China. In the experiment, flue gas desulfurization gypsum, whose main component was $CaSO_4·2H_2O$, was calcined at temperature of 180 ºC for 2 h to transform to building gypsum ($CaSO_4·0.5H_2O$), then the calcined gypsum was aged for 7 days under natural conditions to prepare for subsequent use.

TABLE-1
CHEMICAL COMPOSITION OF DESULFURIZATION GYPSUM

SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	LOI	Crystal water
1.25	0.07	0.79	31.5	2.07	39.1	22.43	19.87

Synthesis and characterization of the waterproof agent

Synthesis: The waterproof agent was synthesized using a four-necked 250 mL flask fitted with a reflux condenser, a Teflon stirrer, a gas inlet and a peristaltic pump for the addition of starved-feed monomer. A typical polymerization procedure was as follows:

Firstly, the flask was fed with 50 % mixed emulsifier (OP-10: SDS = 2:1, w/w) and purged with nitrogen for *ca.* 15 min.

Then appropriate amount of deionized water was added. The mixture was stirred at 600 rpm for 0.5 h at the reaction temperature of 60 ºC to dissolve the mixed surfactant under a nitrogen atmosphere.

After that, mixed monomers of butyl acrylate, methyl methacrylate and acrylic acid were added. Then the mixture was stirred for a further 45 min to allow the monomers to emulsify.

Following this, the monomers of hexafluorobutyl methacrylate (HFMA), dodecafluoroheptyl methacrylate (DFHMA) and the acrylic monomer containing silicon were, respectively emulsified with totally one quarter mixed emulsifier.

After forming the pre-emulsions, they were divided into three parts. One part contained 2/5 of mixed monomers pre-emulsion and 3/10 dissolved radical initiator (typically 0.3 g of ammonium persulfate in 3 mL of deionized water). Another part contained 1/3 of hexafluorobutyl methacrylate pre-emulsion, 1/3 of dodecafluoroheptyl methacrylate pre-emulsion, the total pre-emulsion of the acrylic monomer containing silicon, 2/5 of mixed monomers pre-emulsion and 3/10 dissolved radical initiator. The third part contained the remaining pre-emulsions except the remaining mixed emulsifier and 3/10 dissolved radical initiator.

Then another identical flask was fed with right amount of sodium bicarbonate and the remaining mixed emulsifier and was degassed using a nitrogen purge.

After that, three parts of the pre-emulsions were added into the flask in order under starved-feed conditions at a rate of 1.2 mL/min with continuous stirring at 800 rpm. At the reaction temperature of 80 ºC, the reaction mixture was vigorously stirred under a nitrogen atmosphere.

After the addition of the third pre-emulsions was completed, the mixture was allowed to react for 2 h. Then the remaining 1/10 dissolved initiator was added.

At last, the mixture was allowed to react for another 2 h. When the prepared emulsion was cooled to room temperature and was filtered, ammonia water was used to regulate pH value to the range between 7 and 8. Finally, the waterproof agent, which was named safety first aid (SFA), was obtained.

Characterization: Fourier Transform Infrared (FTIR) spectrum. FTIR spectrum studies were carried out on samples dispersed in KBr disks using a Nicolet 380 IR spectrometer. Samples were prepared by drying right amount of the waterproof agent in a watch-glass. Deionized water was used to wipe off the mixed emulsifier by soaking the film for 12 h and acetone was used to wipe off the remaining monomers.

Contact angle (CA): Contact angle measurements were carried out using a JC2000D3X integral-rotation contact angle measuring device produced by the Shanghai Zhongchen digital technology equipment Co., Ltd. of China. Samples were prepared by drying right amount of the waterproof agent onto a glass slide.

X-Ray photoelectron spectrometer (XPS): XPS studies were carried out using a ESCALAB250 X-ray photoelectron spectrometer. Samples were made by drying a certain amount of the latex on the surface of the blank gypsum sample to form a piece of film (5 mm × 5 mm).

Gypsum samples shaping and testing: Six experiments from A0 to A5 were conducted (Table-2). First, gypsum power, SFA waterproof agent and water were, respectively weighed according to the table (in order to keep the water demand for normal consistency, the amounts of added water were decreased accordingly due to the solid content of the SFA waterproof agent is 50 %). Then they were added into a SJB-137 stirrer with water and stirred evenly. After stirred for 2 min, the plaster was poured into triplicate models to shape by vibration. Next, the gypsum samples were unmolded from the models after 1 h. When the samples were dried in oven, the effects of the waterproof agent on the 2 and 24 h water absorption and 24 h flexural, compressive softening coefficient of gypsum were investigated. QUANTA FEG 250 scanning electron microscope was used to observe the crystal shape appearance.

TABLE-2
USE LEVELS (BY MASS) OF SFA WATERPROOF AGENT IN GYPSUM SAMPLE

Experiment code	Gypsum	SFA waterproof agent	Water
A0	100	0	100
A1	100	3	98.5
A2	100	6	97.0
A3	100	9	95.5
A4	100	12	94.0
A5	100	15	92.5

RESULTS AND DISCUSSION

Characterization of the SFA waterproof agent

Structure: Fig. 1 shows the FTIR spectra obtained for SFA waterproof agent sample, which characterizes some typical bands. The appearance of bands at 1065 and 1141 cm^{-1} can be due to the characteristic absorption of Si-O, while the Si-CH$_3$ flexural vibration occurs at 748 and 802 cm^{-1}. In addition, the band observed at 689 cm^{-1} is associated with stretching vibration of C-F and the other one contributes to a broadening band in the 1265-1141 cm^{-1} region under the influence of ester groups. The complete reaction of added monomers is obvious and indicated by the disappearance of the C=C stretching vibration at 1645 cm^{-1} and the band found at 1720 cm^{-1} is characteristic absorption peak of -COOH. The results confirm that hexafluorobutyl methacrylate (HFMA), dodecafluoro heptyl methacrylate (DFHMA), acrylic acid (AA) and an acrylic monomer containing silicon have been indeed introduced into the molecular structure of the SFA waterproof agent.

Hydrophobic property: The angle θ showed in Fig. 2 is the contact angle on solid-liquid interface and when the liquid is water, it is called water contact angle. Water contact angle can characterize the hydrophobicity of the solid surface directly and effectively. The smaller the contact angle is, the easier the droplet soak into the solid material, which means that the solid

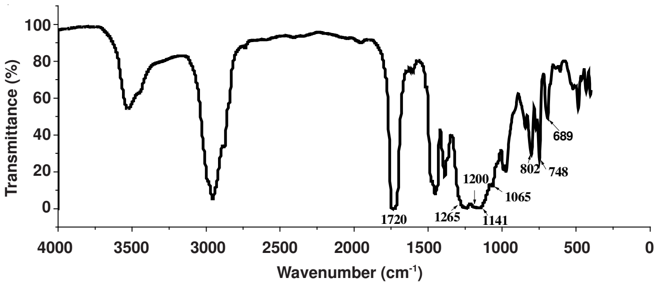


Fig. 1. FTIR spectra of SFA waterproof agent

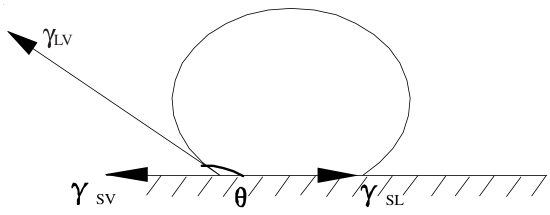
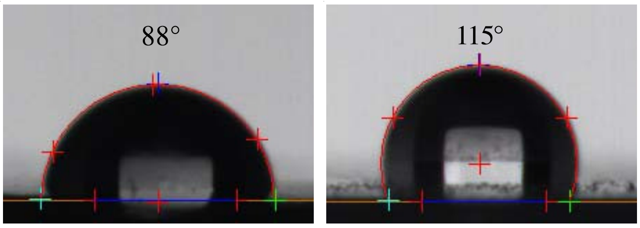


Fig. 2. Scheme for contact angle

becomes more absorbent. The higher the contact angle is, the more likely the droplet shrunk to a removable ball on the solid surface, which impedes access to the capillary porosity of the solid and which means it has good hydrophobicity[4].

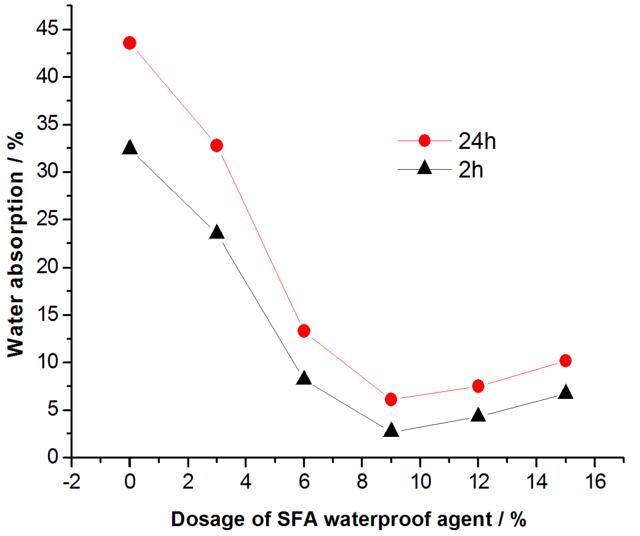
Fig. 3 shows the water contact angle images obtained on the latex surfaces of VAE and SFA waterproof agent, respectively. The angle on VAE latex surface is only 88°, whereas, it can reach to 115° for the SFA waterproof agent. This proves the latex film of SFA waterproof agent to be more excellent with hydrophobicity and low in surface energy than that of VAE latex.



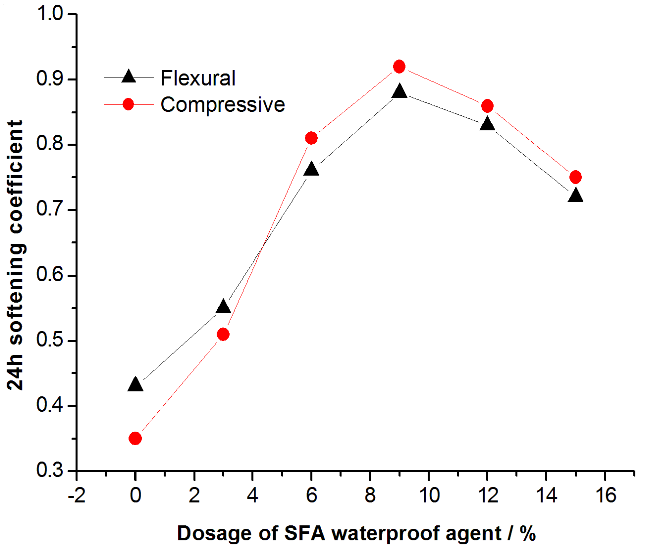
(a) VAE (b) SFA

Fig. 3. Contact angle of water on latex film surface

Influence of SFA waterproof agent on gypsum water-resistance and its action mechanism: The effects of SFA waterproof agent on gypsum water-resistance (such as 2 h water absorption, 24 h water absorption, 24 h flexural softening coefficient, 24 h compressive softening coefficient) are shown in Fig. 4. As shown in the figure, the water absorption declined gradually with the increase of the dosage of SFA waterproof agent, while the softening coefficient went up. This clearly indicated that SFA waterproof agent could improve gypsum water-resistance significantly. It went for a maximum effect at the point of 9 % where 2 and 24 h water absorption of gypsum sample reduced by 91.7 and 86 %, respectively and its 24 h flexural, compressive softening coefficient were increased by 104.7 and 162.9 %, respectively. The water resistance of the gypsum sample showed a downward trend when exceeding 9 % amount, which was due to the strong air-entraining effect caused by adding large amount of SFA waterproof agent.



(a) Water absorption



(b) 24 h softening coefficient

Fig. 4. Effects of SFA waterproof agent on gypsum sample water-resistance

When SFA waterproof agent was added into gypsum slurry, the latex particles were dispersed uniformly with vigorous stirring. Along with the hydration and evaporation, the adjacent latex particles were packed together and the protective layer on the particles surface was damaged. Following this, the gaps between the latex particles got smaller and smaller. Consequently, the particles deformed continuously until the interface between particles disappeared. Afterwards, one ends of the macromolecular chains in polymer, which contained the groups of -COOH originated from acrylic acid that would be combined with Ca^{2+} in gypsum through forming chemical bonds, were adsorbed to the surface of the gypsum crystal and the other ends contain a large number of C-F bonds originated in hexafluorobutyl methacrylate, dodecafluoroheptyl methacrylate. Fluorine atom is highly electronegative and its covalent radius is small. So the nucleus can strongly constrain the surrounding electron clouds formed *via* bonding and then result in the C-F bond with low polarizability. This led to weak interactions between the ends containing C-F bonds, which made it easy for the ends to migrate to the surface of the latex film in drying film-forming process. Then fluorine elements would gather on the surface and that gave it low surface energy. At the same time, the Si-O bond with high energy and flexibility could also migrate to the surface easily to further improve the hydrophobic property of the latex film. As a result, a layer of compact latex film was formed in the gypsum-hardened with the ends intertwined with each other, which improved the density degree of gypsum-hardened to a certain extent. In addition, a hydrophobic surface containing rich fluorine and silicon was formed by migration. As shown in Fig. 5, the formed latex film plugged up microscopic pore or changed the inner surface energy of macropores, which converted it from hydrophilic to hydrophobic. Thus, the water contact angle of the inner surface got larger. Consequently, when the gypsum samples contacts with water, the water in the macropores will not infiltrate to form the drops of water, so as to achieve water-resistance by holding up access of further penetration5-8.

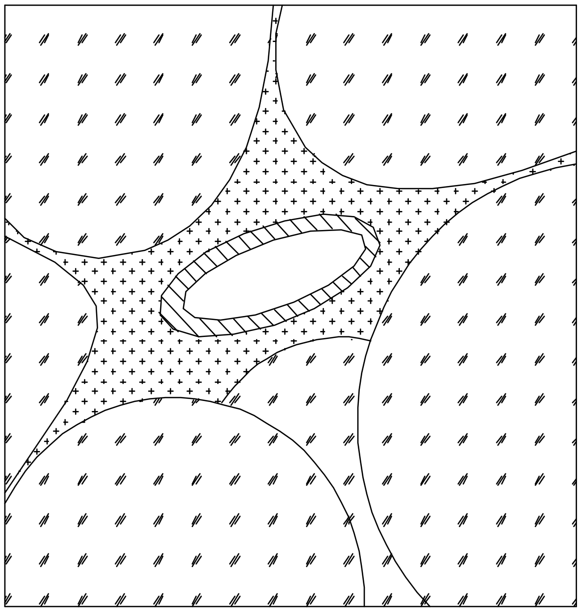
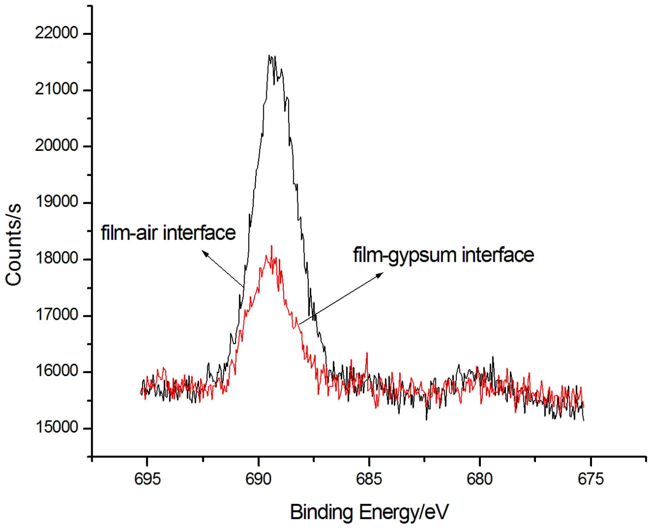


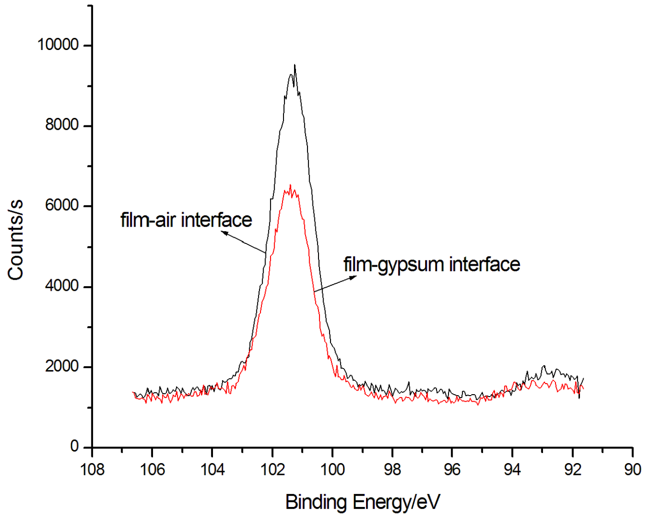
Fig. 5. Model for waterproof mechanism of SFA waterproof agent. ◌: Gypsum-hardened body, ◍: SFA latex film, ▨: Hydrophobic surface, ○:Pore

In order to prove the existence of hydrophobic surface containing rich fluorine and silicon, the specimen of SFA waterproof agent latex film coated on the surface of A_0 sample was analyzed by X-ray photoelectron spectroscopy. From Fig. 6(a), one can see that fluorine signal in the latex film-air interface was significantly stronger than that in the latex film-gypsum interface. In Fig. 6(b), the same thing applied for silicon signal. This was another demonstration of that fluorine and silicon with low surface energy gave priority to migrate to the latex film-air interface in the film-forming process and then resulted in a hydrophobic surface formed on the surface by the way of enrichment.

To further study the impact of SFA waterproof agent on water resistance, the fractures of A0, A3 sample eroded in water for 24 h were analyzed by SEM and EDS and the results were shown in Fig. 7. From Fig. 7(a) we can see obviously that the gypsum crystals were fractured and its length shortened, which

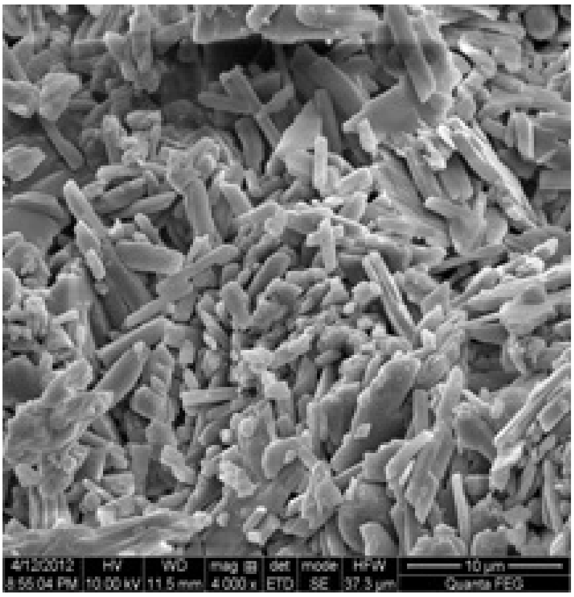


(a) F signal

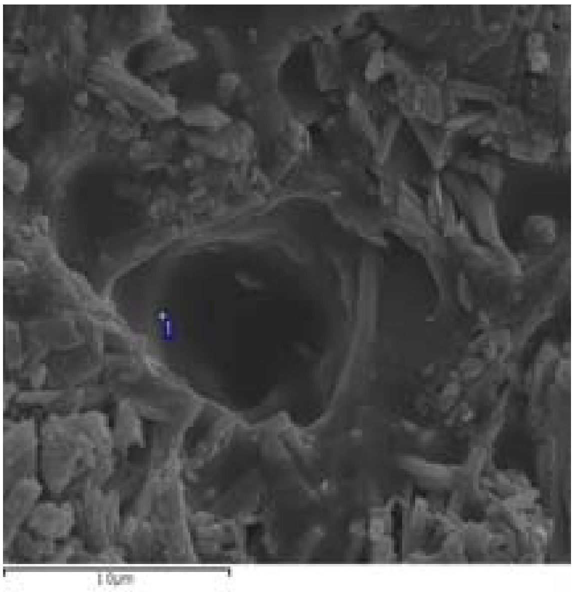


(b) Si signal

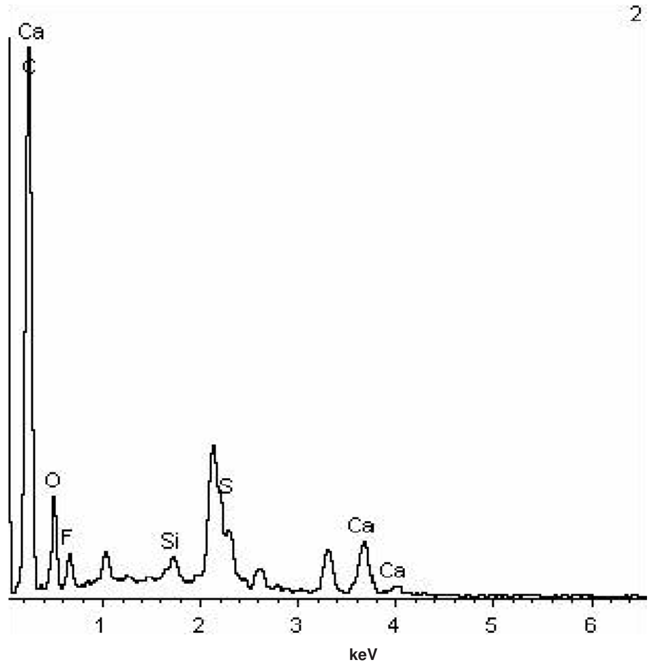
Fig. 6. XPS spectra for latex film of SFA waterproof agent



(a) A0 SEM



(b) A3 SEM



(c) A3 EDS

Fig. 7. SEM, EDS image of fracture in gypsum sample eroded in water

accounted for the serious dissolution of dehydrate gypsum crystal. In Fig. 7(b) and (c), the gypsum crystals of samples with the SFA waterproof agent were intact by the protection of the layer of compact latex film with a hydrophobic surface containing rich fluorine and silicon. This also showed that the latex film could block water invasion and improved the water resistance of gypsum effectively.

Conclusion

From above research experiments and analytical studies of results obtained, it is concluded the following empirical findings: A core-shell structural emulsion waterproof agent containing fluorine and silicone was prepared by gradual emulsion polymerization. FTIR analysis confirms that hexafluorobutyl methacrylate (HFMA), dodecafluoroheptyl methacrylate (DFHMA), acrylic acid (AA) and an acrylic monomer containing silicon have been indeed introduced into the molecular structure of the SFA waterproof agent. The latex film of SFA waterproof agent is more excellent with hydrophobicity and low surface energy, which can be observed by contact angle. When SFA waterproof agent was 9 %, we obtained a maximum effect as shown by the 2 and 24 h water absorption of gypsum samples which reduced by 91.7 and 86 %, respectively. At the same time, its flexural, compressive softening coefficient was increased by 104.7 and 162.9 %, respectively. The latex film formed by SFA waterproof agent plugged up microscopic pore or changed the inner surface energy of macropores, which converted it from hydrophilic to hydrophobic. Thus, the water contact angle of the inner surface got larger and the density degree of gypsum-hardened improved. Consequently, when the gypsum samples contacts with water, the water in the macropores will not infiltrate to form the drops of water, so as to achieve water-resistance by holding up access of further penetration.

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