



Surface Modification of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ Crystals with Epoxy Resins at Normal Temperature Through a Mechanical Dry Method

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In order to solve problem of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals easy deliquescence at normal temperature, the surface modification of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals with epoxy resins by a mechanical dry encapsulation process taken diethylenetriamine as curing agent in ethanol was investigated through FTIR, TG/DTA, optical microscopy and moisture absorption performance test in atmosphere. The results showed that the curing time of the epoxy resin was shortened sharply with the increase of its concentration and the increase of the concentration of curing agent. The optimized formula for $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals coated is of epoxy resin, ethanol and diethylenetriamine at the mass ratio of 7:1:1.05. About 5-7 % weight of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals for formula coating materials has the best effects. It is suggested that the moisture absorption growth rate of these separate white granules increased slowly and effectively avoided $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals deliquescent at normal temperature. Furthermore, the thermal stability of the materials was enhanced dramatically.

Key Words: Surface coating, Calcium nitrate tetrahydrate, Epoxy resin, Curing agent, Deliquesce.

INTRODUCTION

As chemical industrial materials, calcium nitrate crystallizing in a white columnar crystal form of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in the range 0-40 °C has been widely used in many fields¹. With the development of advance technology, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ can often use as refrigerant and accelerant for cement², raw materials for hydroxyapatite synthesis³, surface phosphatizing fluid in the steelworks, as well as to manufacture fireworks and other nitrates. $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystal and its mixture with some other inorganic salts and organic compounds has high latent heat of fusion and low melting point. Moreover, the mixture has been considered to be the phase change materials (PCMs) for thermal energy storage⁴. For example, it can be combined with the traditional building materials to construct environmental-friendly phase change building materials (PCBM)⁵. However, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ has a low melting point (39.7 °C) and decomposes at ca. 40 °C. Especially, the critical suction humidity of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ is very low⁶ so that it would be extremely easy deliquescence into solution under normal temperature and dissolved in water and ethanol. Furthermore, the application of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals is inconvenient in some areas because of its physical and chemical properties sensitive to the environment. $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ is also available fertilizer for acidic soil and nutrient fluid components for plant soilless culture and can provide calcium ions for both cell structure

materials and as a second signal ion to participate in regulating different plant physiological process⁷. If free Ca^{2+} and NO_3^- ions were too high, the plant would happen to disease easily⁸, so the surface modification of the $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals is necessary for control-release fertilizer. According to the physical and chemical properties of the $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystal, the surface coating treatment technology to prevent the deliquescent loss and pertinently control-release would have important practical applications, whether the $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals are as a multifunctional phase change energy storage materials or control-release fertilizer⁹.

Recently, the technologies of surface treatment of inorganic crystalline materials have been developed. The common methods are using coupling agents, such as the silane coupling agent or the titanate coupling agent^{10,11} and surface encapsulation coating technology. However, the reaction temperature of the former is generally higher than 40 °C and usually use large amounts of water or alcohol as a solvent, as a result, it is unsuitable for handling the surface performance of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals, which has a low-melting temperature and easily soluble in water and ethanol. In contrast, the encapsulation coating methods are taken place by co-precipitation methods¹², microemulsion method¹³, *in situ* chemical modification grafted method¹⁴, spray pyrolysis process¹⁵, graft copolymerization¹⁶⁻¹⁸, suspension-like polymerization method¹⁹, *in situ* polymerization method²⁰ and electro-

less plating²¹. But the most reaction operating conditions were unsuitable for treating $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals because of the usage temperature and solvent nature. Therefore, for the special physical properties of this material, it is essential to seek a surface treatment methods-like mechanical dry coating encapsulation process for $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals under normal temperature.

For the surface properties' modification of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals, the coating to change the crystal surface performance is a effective method²². Epoxy resins can be used as the surface modification wall materials of the $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystal materials at normal temperature because of their superior mechanical properties, excellent chemical resistance, low shrinkage and good cohesiveness compared to many materials as coatings, adhesives, substrate materials²³, especially as surface coating materials can be rapidly cured at normal temperature. In this work, the optimum curing parameters of epoxy resin formation and the surface coating process of calcium nitrate tetrahydrate were investigated. Through the FTIR spectra, TG/DTA analysis, optical microscopy and moisture absorption performance test in atmosphere, the results is inferred that the mechanical dry coating technology is very effective for the surface modification of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals. Moreover, the thermal stability and deliquescence at normal temperature of the crystals are improved. Meanwhile, the surface mechanical dry coating processes of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals with epoxy resins at normal temperature has not been reported in related literature so far.

EXPERIMENTAL

Industrial grade of Epoxy resin E-44 was purchased from Wuxi resin processing plant, China. Absolute ethyl alcohol (AR graded) was received from Chengdu union chemical industry reagent research institute, China. Diethylenetriamine and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ reagents (AR graded) were obtained from Chengdu Kelong chemical reagent factory, China and were used without further purification.

Curing parameters of the epoxy resins: The curing agent of diethylenetriamine (15 wt % of epoxy resins) was added in portions to a series of experiments and for a variety of concentrations in absolute ethanol (epoxy resin:ethanol = 9:1-1:9) at normal temperature and allowed to stir for 3 min. Then, the resulting solution was placed into vacuum drying chamber to be solidified. During a period of time, the curing time was confirmed with a knife to pick silk until without drawing out and the trait of cured epoxy resins was recorded; the best-quality ratios of ethanol and epoxy was obtained. Based on this proportion, the optimal diethylenetriamine content was ascertained with different mass proportion of epoxy resin by using the same process above. Finally, the optimum solidification formula to coat the surface of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals was determined.

Surface coating of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals: About 1-11 wt % of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals for coating formula materials gained above were added to a continuous reground $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ powder crystals (10 g) until consolidation. After vacuum desiccated, all the treated different specimens (each of 3 g) were precisely test moisture absorption rates at

15 min intervals for 4 h. Considering the experimental phenomena, moisture absorption data, FTIR spectroscopy and optical microscopy analysis, a surface coating optimization process for industrial application of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals could be obtained.

Characterizations: After all samples under vacuum dried at normal temperature, FTIR spectra was performed on an America Nicolet 5700 spectrometer in the range from 4000-500 cm^{-1} , KBr tableting, between sample and KBr at a mass ratio of 1:100. TG/DTA analysis was recorded on a Germany Netzsch STA-449-C at the heating rate of 10 $^{\circ}\text{C}/\text{min}$ in nitrogen atmosphere. The morphology of the granules was observed by using Japan Olympus Co. BX51-P multifunction optical microscopic examination. The moisture absorption growth rates of the granules were measured by America Ohaus corp. Pine Brook Co. AR1140 electronic analytical balance ranges from 0.0001-110 g.

RESULTS AND DISCUSSION

Curing parameters of epoxy resin formation analysis under normal temperature: Fig. 1 shows the variation of curing time with epoxy resin concentration. Transparent massive materials are produced with all proportional epoxy resin concentration in experimental process. As shown in Fig. 1, the concentration of the epoxy resins is higher, the curing time is shorter. Moreover, the curing time is rapidly delayed and the surface hardness of the resulting cured substances is also decreased obviously when its concentration is reduced. Because the curing time for low concentration of epoxy resins is too long and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals are easily soluble in ethanol, its low concentration prevents $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals from being coated. When the mass ratio of epoxy resin with ethanol is over 9:1, there are more cracks emerging on the surface of curing body. Calcium nitrate coated specimens are easily recrystallize on the coating surface because of this reason, so higher than this concentration of coating parameters cannot be adopted in this experiment. Taking into account all the factors above mentioned, the final selected parameters with epoxy resin and ethanol have a mass ratio of 7:1 in present work.

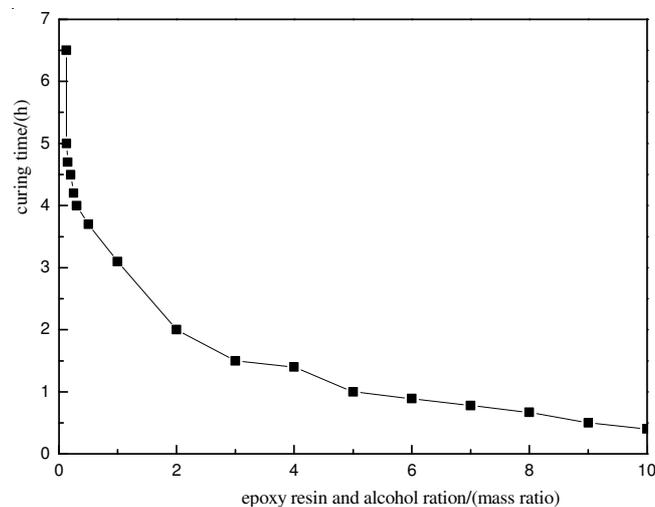


Fig. 1. Epoxy resin concentration *versus* the curing time

During the epoxy resin curing at normal temperature, the curing agent exerts very important influence on the properties of cured materials. As depicted in Fig. 2, we investigate the variant of curing time with diethylenetriamine concentration based on fixed epoxy and ethanol mass ratio of 7:1. Though the curing agent of diethylenetriamine has some toxicity, the epoxy resin cured products have good toughness and excellent adhesion under normal temperature²⁴. In addition, it is also beneficial to help $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals coated. Hence, the choice of diethylenetriamine as curing agent for epoxy resin coated is appropriate. In Fig. 2, the curing time decreases rapidly when the curing agent concentration is gradually increasing. While the curing agent concentration is higher than 12 wt %, it remains approximately constant. Upon addition with 15 wt % curing agent, the curing time is less than 0.5 h. Since the contents of curing agent is played an important role in the needed curing chemical reaction time, there has some unreacted epoxy groups in reaction solution in low concentration of curing agent. With this reason, the final selection of the optimum coated formation of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals treated is for epoxy resin, ethanol and diethylenetriamine at ratio of 7:1:1.05 and the formula of epoxy resin can be cured within 0.5 h.

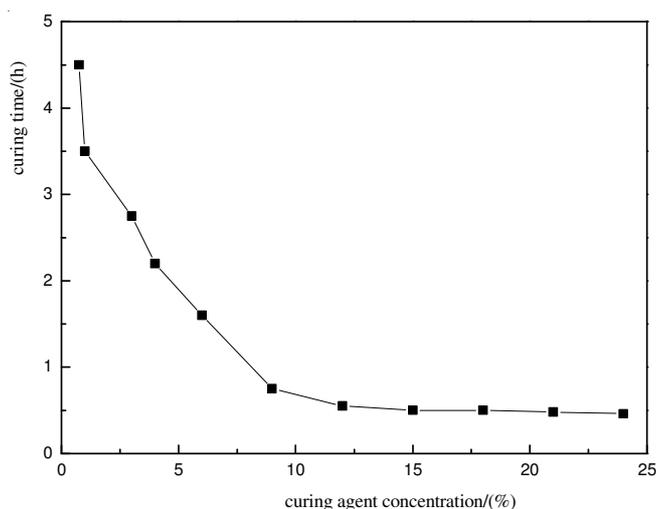


Fig. 2. Curing agent concentration versus the curing time

Results of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals coated: Optical microscopic images of coated and uncoated $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals are displayed in Fig. 3. Images indicated that most of the coated $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals are cladding with epoxy resins, but the degree of coated and surface smoothness of the samples are different due to the varied contents of epoxy resins. In contrast with Fig. 3(A), the covered layers are observed when there are *ca.* 3 wt % epoxy resins coatings in the treated specimens. However, there is a coated insufficiency in the surface as shown in Fig. 3(B) indicated by arrow. The surface coated degree of samples covers completely and high, when the coatings contents are more than 5 wt %. Furthermore, we found that $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals appeared in the surface of the samples with 9 wt % epoxy resins after the same tested time [the arrow location in Fig. 3(E)]. It is assumed that $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals generate in the coating surface because of the supersaturation concentration of calcium nitrate

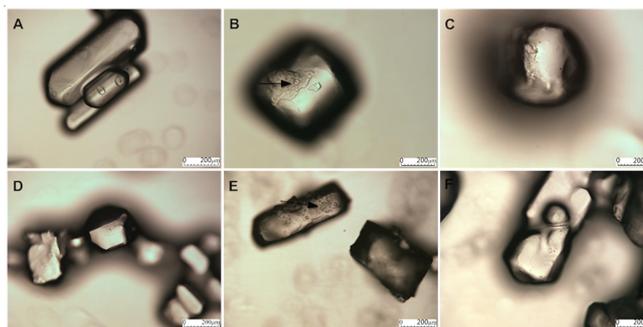


Fig. 3. Optical microscopy images of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals-coated with varies epoxy resin contents of (A) 0 %, (B) 3 %, (C) 5 %, (D) 7 %, (E) 9 %, (F) 11 %, hereinafter the same

which can be formed with ethanol solvent evaporation after the specimens coated over a period of time. Although the surface of samples Fig. 3(F) are coated completely, the particles agglomerated sharply and this is not an experiment required. Consequently, to obtain a dispersion coated entirely particles of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals, the incorporation amount of the coating materials would be a certain appropriate ratio. The results suggested that suitable coating material amounts (5-7 wt %) after vacuum drying could be stably existed in a fairly long period of time and the optimum coated samples have been gained with white dispersion and no recrystallization on the surface of particles.

In order to characterize the coated effects of all samples, it is an especially important step to check the moisture-absorption growth-rate of all specimens. The experimental test data are displayed in Fig. 4.

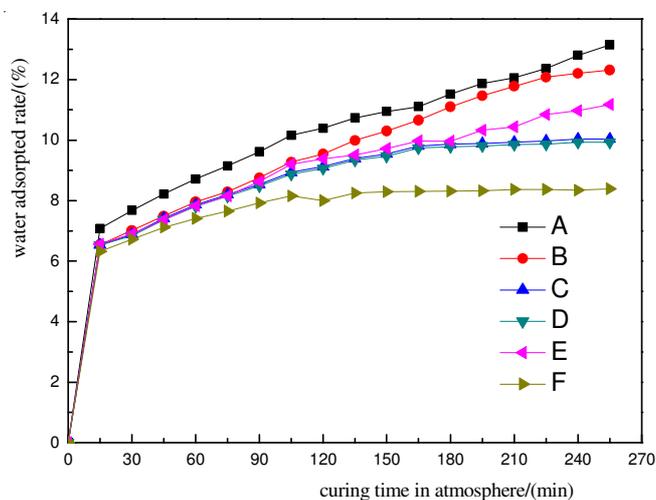


Fig. 4. Natural water absorption rate of growth versus time of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals-coated with different contents of epoxy resin samples

Fig. 4 showed that the moisture-absorption growth-rate of uncoated $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals has maximum change values with the extension of storage time. When the crystals are put at 25-35 °C in the air for more than one day, they all are deliquescent changed into the liquids. In spite of the moisture-absorption growth-rate of all the coated specimens increasing slightly, they remain approximately constant with time delayed after 15 min. Especially, they won't deliquescent into liquids in the air at normal temperature. The results indicate that the

surface coated of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals with epoxy resins has been very effective to resist moisture absorption deliquescence. The moisture absorption growth-rate of the 9 wt % coated sample is merely lower than uncoated specimen, but higher than other coated specimens. This is properly because of the recrystallization of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ with the ethanol solvent evaporation and the appearance of agglomerates. Although the moisture-absorption growth-rate of the 11 wt % coated sample is minimum, the crystals cannot be dispersed. Therefore, they are not required for us. The moisture-absorption growth-rates of the coating amount in 5-7 wt % of specimens have a smaller growth, which is in good agreement with the results from the optical microscopy analysis. As a result, these coating proportions are needed.

FT-IR spectra: Fig. 5 shows the FTIR spectra of the coated specimens, where A1 is the curing epoxy resins; samples of A, B, C, D, E and F are the same as above. In the spectra of epoxy resin (A1), a characteristic absorption band at 898 cm^{-1} belongs to epoxy group and the -OH appears at 3401 cm^{-1} . The alkyl C-H stretching region in epoxy resin is found around 2961 and 2873 cm^{-1} , respectively. The C-H antisymmetric stretching vibration in the methylene group is seen at 2929 cm^{-1} due to methylene bridges. At 1735 cm^{-1} are found -C=O stretching vibration peak. The C-O-C antisymmetric and symmetric stretching vibration of ether bond in the epoxy resin can be observed at 1103 and 1080 cm^{-1} , respectively. In contrast to the spectra of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals (A), the characteristic absorption band around 850 cm^{-1} is ascribed to the stretching vibration of C-N bond and at 600 cm^{-1} broad peak can be assigned to C-Br stretching vibration of KBr tablet. As exhibited in the FTIR spectra of these coated granules (B, C, D, E, F), not only the all characteristic absorption peaks of epoxy resin can be observed, but also at 1735 cm^{-1} of -C=O stretching vibration is strengthened. The results confirmed $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals have been successfully coated by epoxy resins and were in consistent with the results from the above experiments.

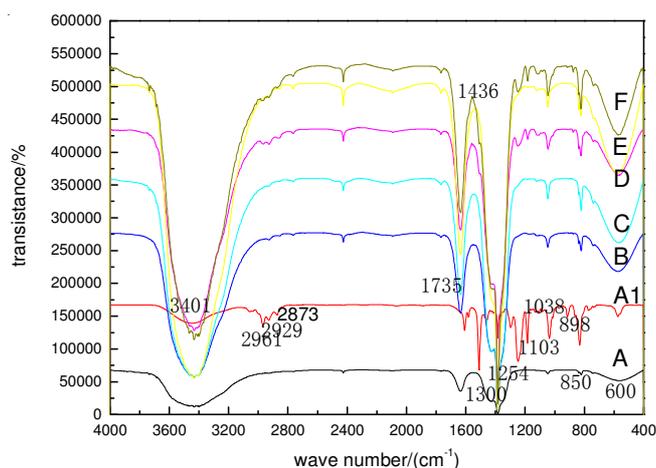


Fig. 5. FTIR spectra of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals-coated with different contents of epoxy resin samples

TG/DTA thermal stability of the optimum coated particles: TG/DTA thermographs of untreated and the best treated $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystal granules are displayed in Fig. 6. The weight loss of Fig. 6(A) happens in four endothermic stages,

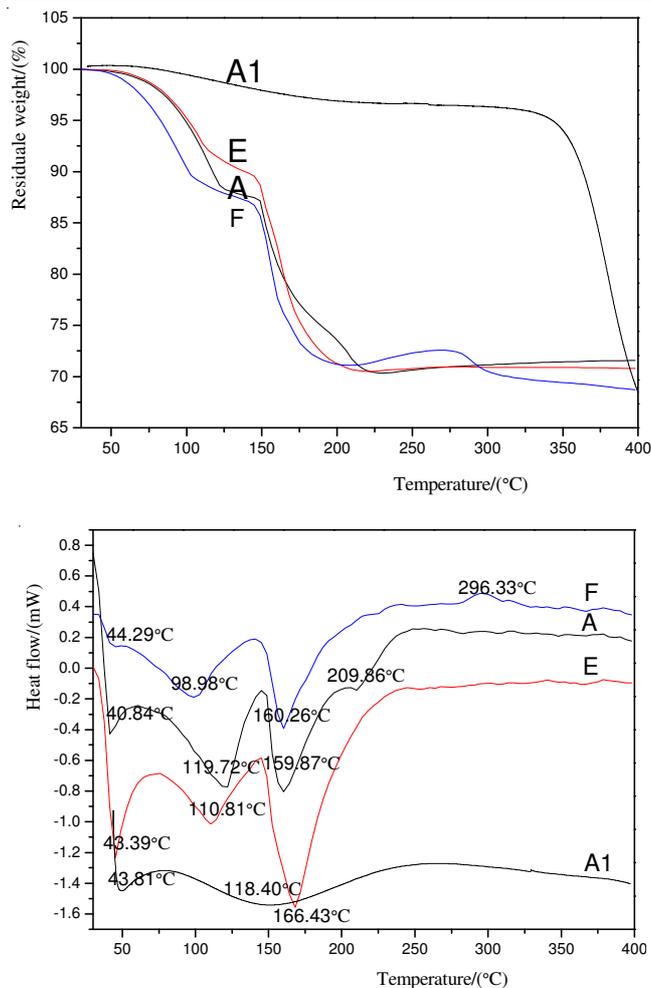


Fig. 6. TG and DTA thermographs of uncoated and optimum coated of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ particles at the heating rate of $10\text{ }^\circ\text{C}/\text{min}$ in an N_2 atmosphere

of which the first endothermic peak occurs at $40.84\text{ }^\circ\text{C}$ and is *ca.* 3.28 % related to the removal of physically absorbed water, meanwhile, it corresponds to the calcium nitrate crystal endothermic generation melting solution. The second stage of weight loss occurs at $119.72\text{ }^\circ\text{C}$ with a 13.15 wt % loss and is attributed to one molecule crystal water lost from $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ turned into $\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. The third endothermic peak is at $159.87\text{ }^\circ\text{C}$ and corresponds to the $\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ crystal decomposition formation of $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$. The last endothermic peak temperature is $209.86\text{ }^\circ\text{C}$ and corresponds to the $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ crystal further decomposition into $\text{Ca}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$. In addition, there is a broad exothermic peak at about $118.40\text{ }^\circ\text{C}$ and after $320\text{ }^\circ\text{C}$, a fast weight loss process is occurred with about 70 wt % loss of curing epoxy resins in Fig. 6(A1). Then, a weight loss period of the sample tends to be constant, that means a relatively stable material formed. In contrast to curves (Fig. 6), it is found that relative to the calcium nitrate crystal melting exothermic peak temperature, it is increased by 2.55 and $3.45\text{ }^\circ\text{C}$ when the best adding contents of epoxy resins coatings are 5 and 7 wt % of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals, respectively. The second endothermic peak temperature values of all coated specimens are so closed, but the third and fourth endothermic peak temperatures of all the coating samples are higher than calcium

nitrate original shape. It is implied that the surface coated of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals by epoxy resins could result in an improvement in thermal stability. After $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals coated, the method, not only can effectively suppress deliquescent of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals and control release rate of fertilizer under normal temperature conditions, but also can improve the chemical compatibility between $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals and substrate materials in energy storage materials.

Conclusion

This work describes an effective approach to improve surface properties of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystal granules with epoxy resin-based coating by mechanical dry method. The curing parameters of epoxy resin coating formation was studied and the results indicated that the optimum coating formation was composed of epoxy resin, ethanol and diethylenetriamine with mass ratios of 7:1:1.05. Based on the optimum coating formation experiment, it was discovered that the best effective encapsulated white dispersive particles were obtained by using the ca. 5-7 wt % of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals of coating materials to treat samples. In addition, through optical microscopy, moisture absorption test, FTIR and TG/DTA analysis, it was proved that the surface of each $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystal particles have been successfully coated by epoxy resins and the thermal stability of all coated of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals was enhanced. This method has a deep-seated significance for the application and development of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals in industry and agriculture.

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