

Urea particle coating for controlled release by using DCPD modified sulfur

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Abstract

The shell of sulfur coated urea was easily cracked due to sulfur being friable. Sulfur was modified with dicyclopentadiene (DCPD) to increase its strength and abrasion resistance. SEM images showed that the micro-structure of modified sulfur was denser and more uniform than pure sulfur. The strength of modified sulfur increased with the DCPD/S ratio. Experiments of urea particle coating with sulfur and modified sulfur were carried out in a fluidized bed coater. The shell of coated urea particles with modified sulfur was more compact than that with pure sulfur. The modification retarded the sulfur phase transformation from monoclinic to orthorhombic, avoiding the crack formation in the coating shell of sulfur. The modified sulfur coated urea particles can be produced with thinner shell and higher strength, and had better controlled release properties. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

Sulfur coated urea (SCU) has been produced for about 40 years. Many works have reported the improvement of the coating quality [1,2]. Due to that sulfur is friable, the coated shell cracks easily, and the shell is even peeled from the particle surface during transportation, stockpile storage, and fertilization. Wax and wax-like materials were usually coated on the outer surface of the sulfur coated urea to seal the flaws to reduce the release rate. However, these have a high cost, and the wax coating made the product adhesive so that additional treatments have to be set in the flowsheet for improving the fluidity of SCU particles.

Sulfur was plasticized by adding modifiers in sulfur containing composites for road repair, road-making material and concrete in building construction [3–6]. Most modifiers reported in literature were polymeric polysulfides or, alternatively, substances which react with sulfur, such as mercaptan and unsaturated hydrocarbon, to give *in situ* formation of polymeric polysulfides. Blight et al. [7] studied modifying sulfur with dicyclopentadiene (DCPD) and styrene, and showed that the modifiers can stop or reduce sulfur embrittlement. Bordoloi and Pearce [8] researched the viscosity of sulfur-DCPD solutions varied with reaction time and compositions, and showed that the viscosity increased exponentially as the

time and DCPD quantity increased. A kind of sulfur-plasticizing reagent with the formula $A-R-S_x-R-A$ was reported [9], where each R is a hydrocarbon radical having up to about 10 carbon atoms, at least one A is hydroxyl or carboxyl and x is an integer from 2 to 5. This polysulfide modifier was prepared by the reaction of sulfur with a mercapto compound selected from mercapto acids and mercapto alcohol in the presence of basic catalysts such as amines and ammonia. The viscosity of modified sulfur could be reduced by adding persulfides with $A-R-S_x-R-A$ structure. In addition, a slow release particulate fertilizer product in which the fertilizer particles were encapsulated with a plasticized sulfur coating, where the plasticized sulfur was prepared by adding a certain amount of a substituted symmetrical dialkyl polysulfide plasticizer to sulfur has been reported [10].

In this paper, DCPD, a product from petroleum cracking, was used as the modifier to prepare modified sulfur as the coating material for producing controlled release urea. The properties of the modified sulfur and the sulfur coated urea particles were investigated.

2. Experimental

2.1. Materials

Commercial urea particles with size in the range of 2~4 mm and 1335 kg/m³ in density were used in the experiments, which were produced by the Ningxia Petrochemical Company of

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PetroChina Co. Ltd. Dicyclopentadiene was a commercial product with purity 94.0% from the Hangzhou Yangli Petrochemical Co. Ltd. Sulfur was a commercial product with purity 99.9%.

2.2. Sulfur modification

A known amount of DCPD and commercial sulfur were mixed uniformly in a beaker at 145 °C controlled with an oil bath. After a specified time of reaction, the modified sulfur was obtained. The reaction time is in the range of 1–6 h.

Experiments showed that the viscosity of the molten modified sulfur significantly increased with the DCPD fraction and the reaction time. Bordoloi and Pearce proposed a viscosity expression for modified sulfur with DCPD at 140 °C [8],

$$\eta = 19.46 \exp(11.33X^{1.78}t), [X = 0 - 0.4] \quad (1)$$

where η is the viscosity of molten modified sulfur, cP; X is the mole fraction of DCPD; t is the reaction time, h. Considering that too high a viscosity is not suitable for the spraying coating process, therefore, based on the exploratory experiments, the DCPD fraction was set in the range of 0–10% sulfur by weight.

2.3. Fluidized bed coater and coating procedures

A fluidized bed coater, shown in the Fig. 1, was used for the coating of the urea particles. The fluidized bed was made of an organic glass column 150 mm in diameter and was widened in the upper section at 300 mm to restrict particle entrainment. A spraying nozzle of an air-atomized nozzle was centrally set above the fluidized bed.

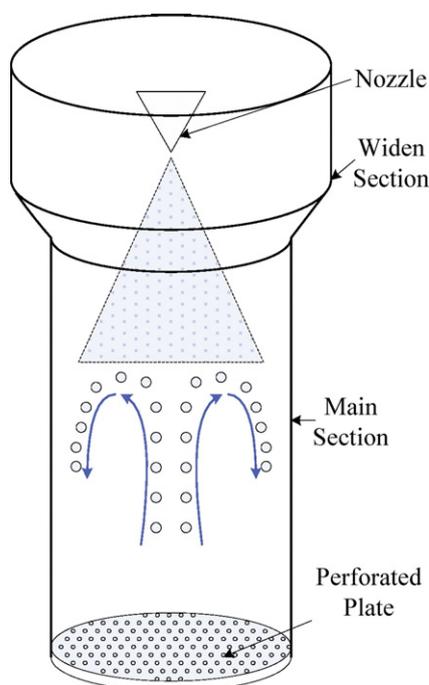


Fig. 1. Schematic diagram of the coating process in a fluidized bed.

Table 1
Operation parameters of coating process in a fluidized bed

Superficial gas velocity, m/s	Air pressure, MPa	Air flow rate, L/min	Molten sulfur flow rate, mL/min	Molten sulfur temperature, °C	Temperature in coater, °C
2	0.2	25	30	145	60

Urea particles of 1 kg in weight were put in the fluidized bed, and the bed was fluidized at a superficial gas velocity of 2.0 m/s. The molten coating material under a pressure of 0.2 MPa was atomized with compressed air, and sprayed onto the urea particles in the fluidized bed for coating. The operation parameters in the coating process were listed in Table 1. After spraying a set quantity of coating material, the particles were taken out for analysis.

2.4. Measurement of strength and abrasion resistance

In order to examine the properties of modified sulfur as a coating material, the compressive strength of the particles prepared with the modified sulfur was measured. Modified

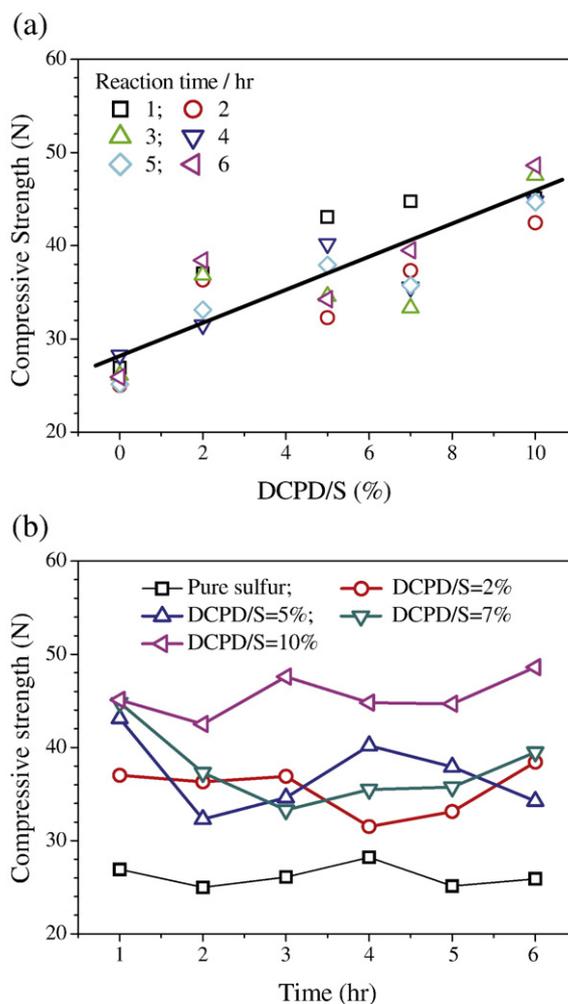


Fig. 2. Compressive strength of sulfur/modified sulfur granules versus DCPD/S ratio and reaction time.

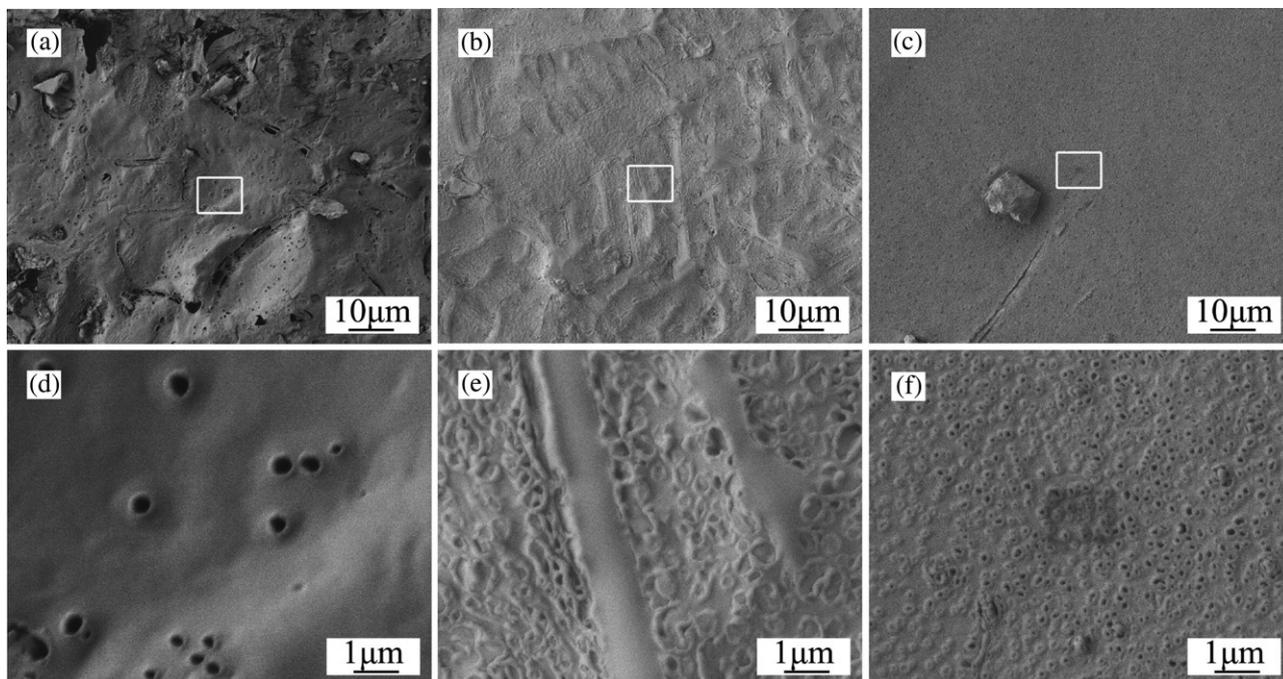


Fig. 3. Micro-structure of sulfur and modified sulfur DCPD/sulfur ratio: (a), (d): 0%; (b), (e): 5%; (c), (f): 10%.

sulfur in the molten state was dropped into a series of cylindrical molds, forming column particles 2 mm in diameter and 3 mm in height. The compressive strength of the particles was measured with a particle strength meter (KQ-3, Kunming, China). For each sample, an average value of 20 particle measurements was taken.

The abrasion resistance of sulfur or modified sulfur coated urea particles was examined in the fluidized bed by checking the weight loss versus abrasion time. For comparison, the abrasion resistance of urea particles is also measured. The collisions between particles and particle collision with the wall in the fluidized bed were used to simulate the abrasion environment in transportation, stockpiling, and fertilization. 200 g sieved particles of 3.2~4 mm was put into the fluidized bed at a superficial gas velocity of 1.4 m/s. The particles were fluidized and abraded in the bed. All the particles were taken out after an interval of 30 min and weighed. Then, all the particles were put back into the fluidized bed again to continue the abrasion test.

2.5. Measurement of release rate

The release rate of coated urea in water was measured. For each sample, 25 g coated particles were put into a beaker containing 500 ml deionized water. Each beaker was covered with a PE film to prevent water evaporation and kept at 25 °C in a constant temperature box. At certain time intervals, 5 mL of solution was sampled for nitrogen content, and 5 mL of water was added into the beaker to maintain the solution volume constant. The solution was agitated before sampling.

The nitrogen concentration was determined using alkaline potassium persulfate digestion and UV spectrophotometry according to the China Standard GB 11894-89 method. Potassium persulfate in aqueous solution decomposes to potas-

sium hydrogen sulfate and atomic oxygen when the temperature is higher than 60 °C, and potassium hydrogen sulfate dissociates to H^+ completely under alkaline conditions. The atomic oxygen produced at 120~124 °C converts the compound containing nitrogen to a nitrate. The nitrate concentration can be determined by measuring the absorbency with a UV spectrophotometer.

3. Results and discussion

3.1. Strength of modified sulfur

The particle strength of sulfur/modified sulfur was measured. The strength of modified sulfur change with the DCPD/sulfur ratio and different reaction time is shown in Fig. 2. The strength of the modified sulfur increased markedly as the DCPD/sulfur ratio increased, as shown in Fig. 2(a), but the strength change with the reaction time did not show a clear trend, as shown in Fig. 2(b).

3.2. Micro-structure of sulfur and modified sulfur

In order to observe the micro-structure of sulfur and modified sulfur, samples were prepared according to the following

Table 2
Coating material composition

No.	Composition	Coating quantities, %
1	S	22.6
2	S	32.1
3	S+2% DCPD (wt)	16.1
4	S+2% DCPD (wt)	18.6
5	S+5% DCPD (wt)	26.5

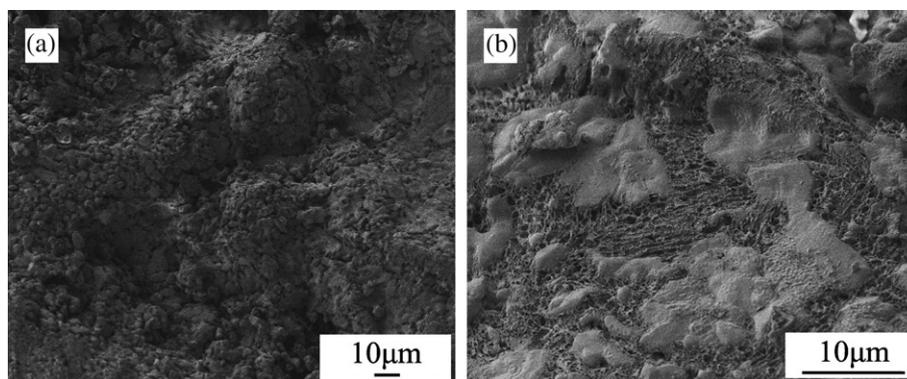


Fig. 4. The surface of sulfur coated urea particles (SEM, sample 2[#]).

procedures. Molten modified sulfur after 2 h reaction was poured into a mold comprising a stainless steel ring 5 mm in height and 30 mm in diameter on a steel plate for cooling, to form a “cake.” The sulfur sample was similarly prepared. After solidification, the cake of pure sulfur has a bright yellow color, and the cake of modified sulfur at a ratio of 5% DCPD/sulfur had a brown chocolate color and black chocolate color at a ratio of 10% DCPD/sulfur.

Samples were taken from the inner part of a broken cake. The micro-structure of the sample was observed by a scanning electron microscope (SEM, JSM-7401F, JEOL, Japan). Fig. 3 shows the micro-structure of sulfur and modified sulfur. Fig. 3 (a), (b), (c) corresponds to the DCPD/sulfur ratio at 0, 5%, 10% respectively, and Fig. 3(d), (e), (f) are the corresponding images at higher magnification. It is seen that the surface of modified sulfur was more uniform and smoother as the DCPD/sulfur ratio increased. Fig. 3(d), (e), (f) shows the “pore-like” morphology. The “pores” were denser and smaller as the DCPD/sulfur ratio increased.

The pore-like structures are pore or cavity can be qualitatively distinguished from the measured BET value. After grinding to micron size, the modified sulfur powder was characterized with a BET adsorption apparatus. The specific surface area of each sample was very low ($<0.5 \text{ m}^2/\text{g}$), which indicated that the “pores” in the sulfur and modified sulfur were not connected but sealed or isolated. So the “pores” observed by SEM should be shallow cavities.

3.3. The structure of the coating shell

Urea particle coating was carried out in a fluidized bed using sulfur and modified sulfur as the coating materials. The coating material composition and coating quantities are shown in Table 2.

The surface texture of pure sulfur coated urea particles (sample 2[#]) is shown as Fig. 4. It is seen that the exterior surfaces are uneven, coarse, and look like many small droplets stuck together, shown as Fig. 4(a). SEM examination of the surface at higher magnification showed a mosaic texture of net structure and island-like structure, shown in Fig. 4(b).

The surface texture of the modified sulfur coated particles (sample 5[#]) is shown as Fig. 5. This is different from Fig. 4 with some fine particles stuck to the coating shell, as shown in Fig. 5 (a), and the surface is denser than the surface of sulfur shell. The image at higher magnification for the surface of the modified sulfur coated urea particles is shown as Fig. 5(b). Although the surface of the modified sulfur shell was not perfectly uniform, visible defects like cracks and holes were not found.

By cutting SCU particles with a sharp knife, the cross section of the coating shell can be observed. The SEM images of the cross section of sulfur and modified sulfur coated urea are shown in Fig. 6. It is seen that there are some cracks in the sulfur coating shell, which are marked in Fig. 6(a). The modified sulfur coating shell had no cracks, but had some isolated cavities which do not connect with each other. The modified

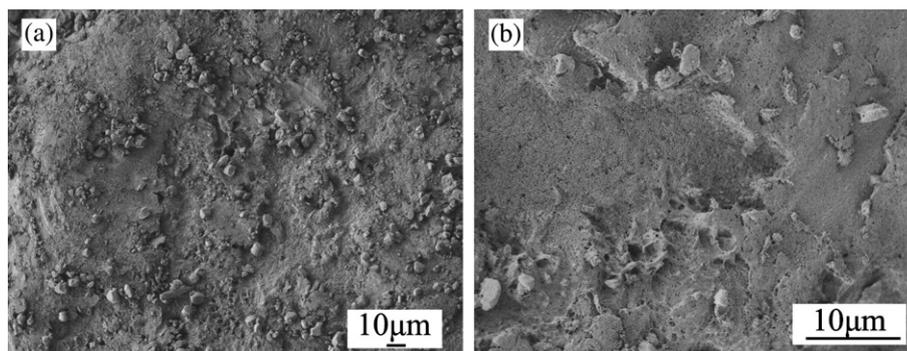


Fig. 5. The surface of modified sulfur coated urea particles (SEM, sample 5[#]).

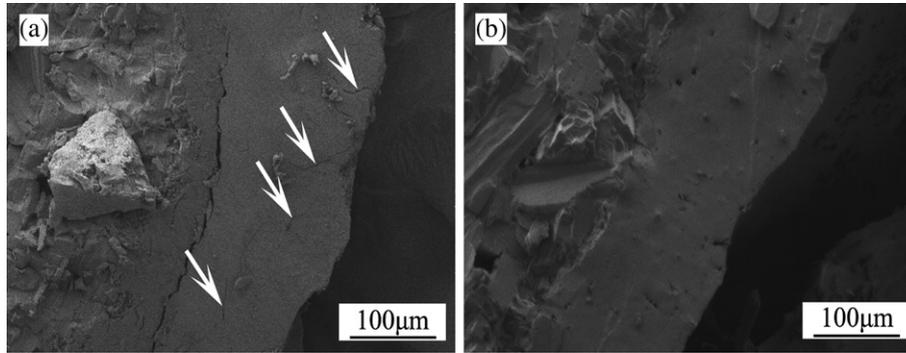


Fig. 6. Cross section of coated urea particles (SEM) (a) sulfur coated, (b) modified sulfur coated.

sulfur coating shell contact to the urea was tight. Thus, the brittleness of the modified sulfur shell decreased and the plasticity increased.

Therefore, a uniform and compact shell can be achieved by using the modified sulfur as coating material.

3.4. Abrasion resistance of coated urea particles

The abrasion resistance of sulfur and modified sulfur coated urea particles were tested in the fluidized bed. The abrasion resistance of urea particles is also given for reference. Fig. 7 shows the curves of the weight of samples versus abrasion time. Comparing with the urea particles, the sulfur shell is more friable. The weight loss of pure sulfur coated particles is clearly higher than that of the modified sulfur. This shows that the modified sulfur had higher abrasion resistance than pure sulfur.

3.5. Release behavior of coated urea particles

The release process of coated urea in water can be described as the following process [11]. Water penetrates through the coating shell and dissolves the urea, then the dissolved urea diffuses into the water medium through the coating shell. Fig. 8 shows the cumulative released quantity versus time from sulfur and modified sulfur coated urea particles for different coating quantities. This shows that the coated urea was released at a

constant rate in the initial stage, and then released slowly till the end. The modified sulfur coated urea released urea slower than the sulfur coated urea. The sulfur coated urea particle (sample 2[#]) release was 82.9% at 7days and 87.8% at 28days, while the modified sulfur coated urea particle (sample 5[#]) release was 53.5% at 7days and 62.5% at 28days. The coating quantity of the modified sulfur (sample 5[#], 26.5%) was less than that of sulfur (sample 2[#], 32.1%). The release rate of sample 1[#], coated with 22.6% sulfur, was close to that of samples 3[#] and 4[#] which were coated with 18.6% and 16.1% modified sulfur, respectively. Therefore, the same or better release behavior can be achieved using less modified sulfur for the coated urea particles.

3.6. Analysis on modification process

Sulfur reacts with DCPD to form polymeric polysulfide at 145 °C. The modified sulfur is a mixture of polysulfides and unreacted sulfur. In the pure sulfur coating process, molten sulfur at 145 °C is quickly cooled down to ambient temperature, and forms monoclinic sulfur (S_{β}) that converts to orthorhombic sulfur (S_{α}) over a period of time [7,8]. The phase transformation causes cracks on the shell due to the volume change resulting from the density difference of S_{α} (2070kg/m³) and S_{β} (1960kg/m³), shown in Fig. 6.

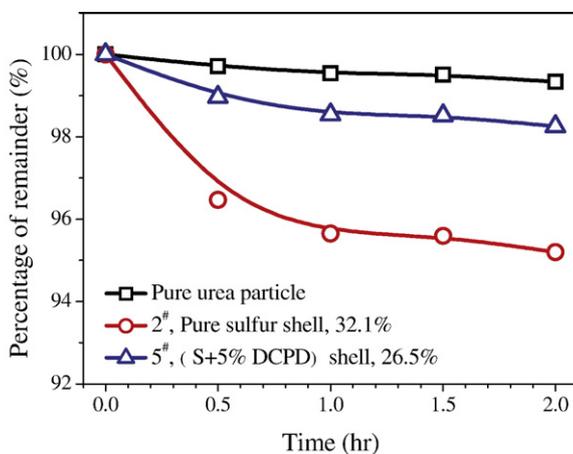


Fig. 7. Weight of coated urea particles versus abrasion time (3.2~4 mm).

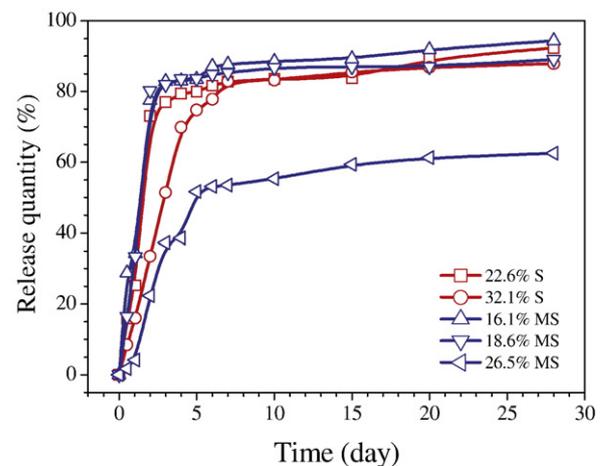


Fig. 8. Cumulative release quantity versus time for sulfur and modified sulfur coated urea particles.

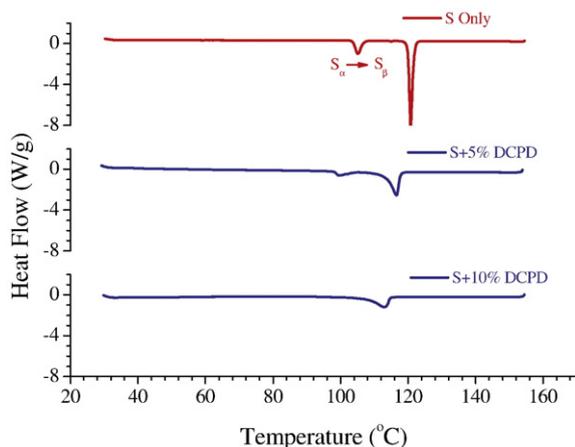


Fig. 9. DSC thermograms of sulfur and modified sulfur. (Reaction: 145 °C, 6 h; 5 month storage).

It was reported that the phase transformation occurs over 20 h [7] or longer, even several weeks [12]. Sulfur and modified sulfur samples prepared from the molten state and reacted for 6 h at 145 °C were analyzed with DSC after 5 months storage under ambient condition. The 5 months storage is to ensure enough time for the phase transformation from S_{β} to S_{α} to be complete.

The DSC curve is shown in Fig. 9. This shows that the pure sulfur showed an obvious peak of the transformation of S_{α} to S_{β} during temperature increase. However, the phase transformation signal from S_{α} to S_{β} became smaller for modified sulfur with DCPD/S=5%. With the DCPD/S=10% sample, no phase transformation appeared, that is, there is no solid to solid phase transformation and it showed only a phase transformation from solid to melt. Therefore, in practical coating process with modified sulfur, there is no crack formation due to phase transformation after spraying solidification.

Molten polysulfide retards the crystallization of unreacted sulfur in the modified sulfur, forming a compacted structure. Thus, the strength and abrasion resistance of the modified sulfur are improved. Meanwhile, the formation of high molecular weight polysulfides increases the viscosity of modified sulfur. However, a high viscosity is not suitable for the spraying coating process, so the DCPD quantity and reaction condition need to be optimized.

4. Conclusions

Sulfur was modified using DCPD as the modifier. Experimental results show that the strength of modified sulfur

increased with increased DCPD/sulfur ratio. The modified sulfur was denser and had smaller cavities than the pure sulfur. The abrasion resistance of urea particles coated with modified sulfur was improved markedly compared to pure sulfur. The coating shell of modified sulfur was denser and more uniform than the shell of pure sulfur, and had nearly no cracks. The same or better release behavior of SCU can be achieved by using less modified sulfur.

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