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Study of Morphology and Thermal Behavior of Newly Prepared Plasticized Sulfurs

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The morphology of plasticized sulfur with styrene (STY) and dicyclopentadiene (DCPD) was studied using scanning electron microscopy, to investigate the influence of type of additive and time on the rate of conversion of β- to α-structure. The results revealed that major part of plasticized sulfur with STY converted to α-phase after 30 days. While the DCPD-plasticized sulfur mostly possessed a β-structure and only a minor part was converted to α-structure with the elapse of time. The thermal behavior of sulfur, molten sulfur, and the plasticized sulfur samples were studied by thermogravimetry (TG) and differential scanning calorimetry (DSC), 522 days after their preparation. The results clearly revealed that, among different samples studied, the DCPD-plasticized sulfur possesses the highest thermal stability. The effect of addition of micro- and nanosilica, as modifiers, on the morphology and thermal behavior of the STY-plasticized sulfur was also studied. It was found that the presence of the above fillers to the matrix of STY-plasticized sulfur not only caused the creation of some cracks in the sample, but also could not block the conversation of β- to α-structure.

Keywords: Sulfur, Plasticized sulfur, Morphology, Thermal stability, β- to α-conversion

INTRODUCTION

Extremely large quantities of sulfur are obtained as a by-product of the petroleum and gas refining processes, coal processing and refining of copper in the mining sector, so that the development of new applications for sulfur are environmentally and economically of critical importance [1,2]. The unique properties of elemental sulfur make it a desirable base for a wide range of applications, especially in the field of civil engineering (coatings and construction) [3-5]. However, the commercial use of sulfur in these applications has been limited because of its brittleness, lack of resistance to thermal shock and poor weather ability [5].

In fact, sulfur exists in different allotropic forms which differ in their physical and chemical properties [1]. The principal allotropes are orthorhombic (S_α), monoclinic (S_β), and polymeric sulfur (S_w). The S_α and S_β allotropes are both crystalline materials consisting of S_8 rings, while S_w consists of chains of up to 106 sulfur atoms. Under ordinary conditions of temperature and pressure, S_α is the only stable allotrope of sulfur. The sulfur melt below 159 °C (S_λ) consists mainly of S_8 rings while, above 159 °C, the sulfur melt (SM) consists essentially of an equilibrium mixture of S_8 rings and polymeric sulfur. On rapid cooling from the melt above 159 °C, plastic sulfur is obtained, which is a mixture of polymeric sulfur and "non-crystalline" S_8 and possesses plastic properties. However, these properties rapidly disappear under ordinary conditions of temperature and pressure, and the material becomes brittle.

Thus, it has been necessary to modify sulfur with additives

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designed to stop the brittleness which occurs in pure elemental sulfur. The term plasticized- or modified-sulfur refers to the reaction product of sulfur with a plasticizer. The addition of plasticizers to sulfur results in lowering its melting point and increasing its crystallization time [6-8]. In contrast to elemental pure sulfur, the plasticized-sulfur is a composition that possess interesting characteristics and properties such as increased corrosion resistance and high mechanical strength [1,2].

Many additives such as phenolic derivates [8], olefins hydrocarbons [9], unsaturated hydrocarbons [10] and polysulfides [8,11] have been proposed for the modification of elemental sulfur. A number of research works cover the use of styrene and dicyclopentadiene as plasticizers to improve the sulfur properties [12-17], among which there is only one report about the study of the reaction product by scanning electron microscopy (SEM) [17].

In this paper, we studied microscopically the non-plasticized versus plasticized sulfur in order to determine which of the additives styrene (STY) and dicyclopentadiene (DCPD) is more appropriate in increasing crystallization time and reducing time of S_β to S_α transition. Since the presence of inorganic fillers in plasticized sulfur is known to have an important role in decreasing rate of transformation of S_β to S_α, we also evaluated the influence of nano- and micro-sized SiO_2 particles as conventional fillers on the morphology and thermal behavior of the plasticized sulfur.

EXPERIMENTAL

Reagents

Reagent grade sulfur, styrene (STY), dicyclopentadiene (DCPD) and N,N,N,N´-tetramethylenediamine (TMDA), as a catalyst, were obtained from Merck Chemical Company. Microsilica (325 mesh, 45 µm) was obtained from Beton Chimie Co. (Tehran, Iran). Silica nanoparticles (AEROSIL®200, around 12 nm average primary particle size) were purchased from Degussa Co. (Germany).

Apparatus

The SEM images were taken on a Philips XL30-SEM (Netherlands). A Thermo Gravimetric Analyzer (Polymer Laboratories TGA-1500) and a Differential Scanning Calorimeter Polymer Laboratories DSC-PL TGA were used to study the thermal behavior of the prepared plasticized sulfurs, 522 days after their preparation.

Plasticization of Sulfur with STY and DCDP

The plasticized sulfur samples (as shown in Table 1 and Fig. 1) were prepared by charging the indicated amount of sulfur, by weight, to a 1-l four-neck flask, equipped with a reflux condenser, a thermometer, a funnel decanter, an inlet for nitrogen purge and a magnetic stirrer. The sulfur was heated until molten at a temperature of about 120 °C and then the temperature increased to 140 °C and maintained at this temperature. Then, the other indicated ingredients were added to the stirred molten sulfur and the resulting mixture was heated until being homogeneous for 3 h (MS and PS1-PS4 samples). At the end of this period of time, the plasticized sulfur was cooled and then fastened on a sample rock with carbon glue and coated with a gold layer for improved SEM images.

Preparation of Micro- and Nanoparticles Modified/ Plasticized-Sulfur

In an oil bath, the indicated amount of silica particles (Table 1) was added to melt STY-plasticized sulfur sample in the heated mixing reactor and stirred at 140 °C. The temperature was maintained at about 135-140 °C during the mixing process, and lasted for about 45-60 min. The progress of the reaction was monitored by the degree of homogeneity of the mixture *via* careful observation of the temperature and viscosity of the reacting mixture.

RESULTS AND DISCUSSIN

Morphology Studies of Sulfur and Plasticized-Sulfur Samples

If pure elemental sulfur is heated to 140 °C, monoclinic sulfur is instantaneously formed which, after cooling to ambient temperature, undergoes a transition to orthorhombic sulfur, as the stable form of sulfur at ambient temperature. This transformation is relatively rapid and generally occurs in less than 24 h. Since S_α is denser than S_β, a high stress is induced in the materials by solid sulfur shrinkage. Thus, the sulfur binders can become highly stressed and fail prematurely

Table 1. Ingredients Used in the Experiments (g)

Sample[a]	Ingredient (g)					
	Sulfur	Styrene[b]	DCDP[b]	Microsilica	Nanosilica	Catalyst
MS	50	-	-	-	-	-
PS1	50	7.5	-	-	-	-
PS2	50	7.5	-	1.6	-	-
PS3	50	7.5	-	-	0.8	-
PS4	50	-	7.5	-	-	0.1

[a](PS: Plasticized sulfur). [b](15 wt% of sulfur).

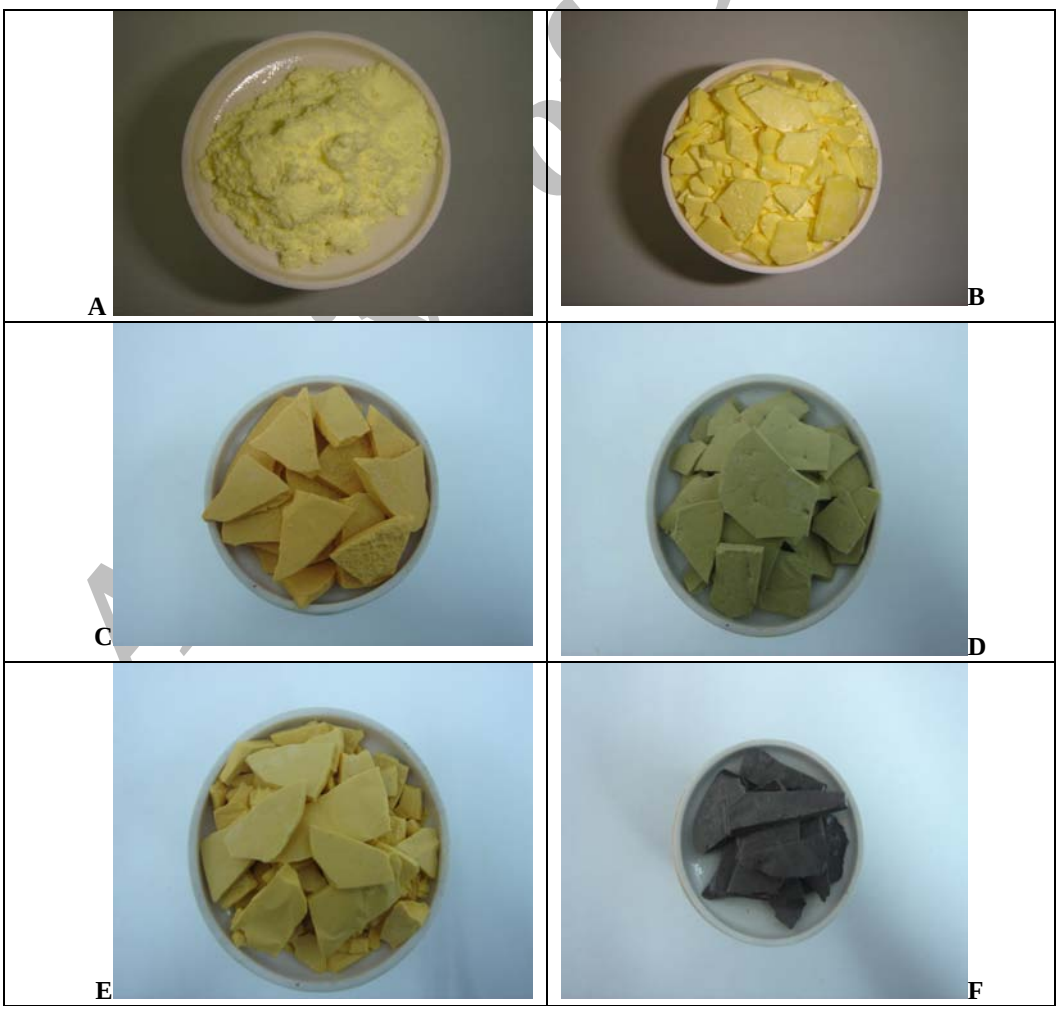

Fig. 1. Sulfur and plasticized sulfur samples: (A) sulfur powder, (B) MS, (C) PS1, (D) PS2, (E) PS3, (F) PS4.

[4,18]. As it is seen from in Figs. 2 and 3, pure molten sulfur crystallizes and form dense and large orthorhombic sulfur crystals (S_α).

There are two main methods for modifying sulfur, both of which try to control sulfur crystallization chemically or physically [2]. The first one tries to combine chemical substances to inhibit the transformation of the monoclinic sulfur to the orthorhombic structure, as a result of the chemical reaction with the substance. Several substances have been tried for this methodology, the most common of which being STY and DCPD [2]. The second method utilizes the modified sulfur by combining sulfur with olefin hydrocarbon polymers and a physical stabilizer such as fly ash or other fine substances [9].

The SEM image in Fig. 4 shows the product of reaction of sulfur with 7.5 g STY (15 wt% of sulfur content, PS1), obtained one day after synthesis of the STY-plasticized sulfur. Compared to elemental sulfur (Fig. 3), the STY-plasticized sulfur reveals a quite obvious different structure. This can be due to presence of β planes in the modified sulfur PS1, which have been formed besides the α-crystals in the composition.

In this matrix, the size and fraction of pores formed as a result of β to α transition is low. This fact suggests that, in PS1, sulfur cannot be completely modified with 7.5 g of STY (15% of sulfur). In other words, all sulfurs having the α-structure have not been transformed to their β form. The

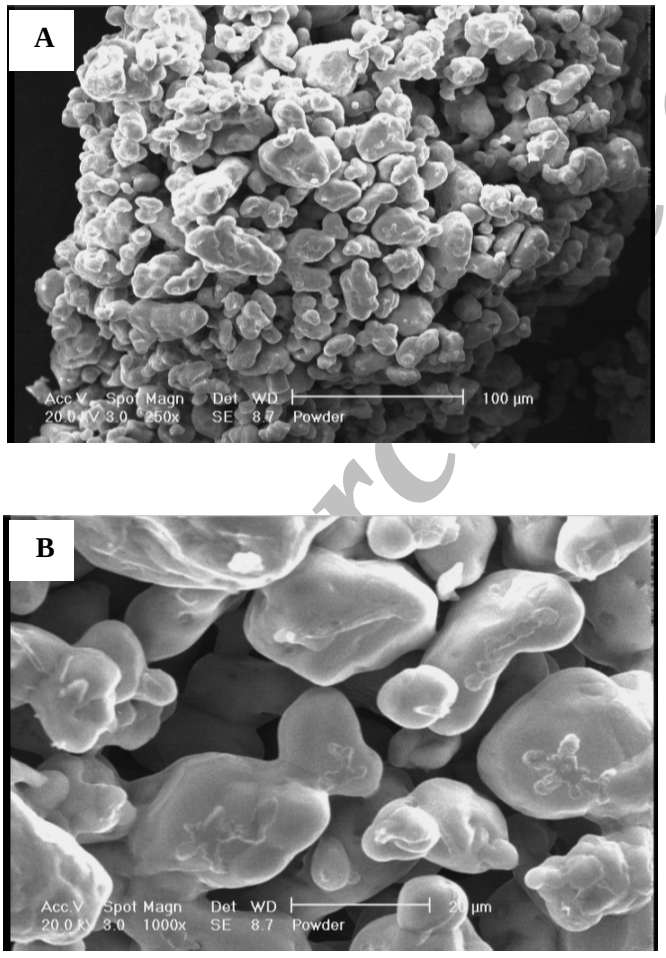

Fig. 2. SEM of sulfur powder.

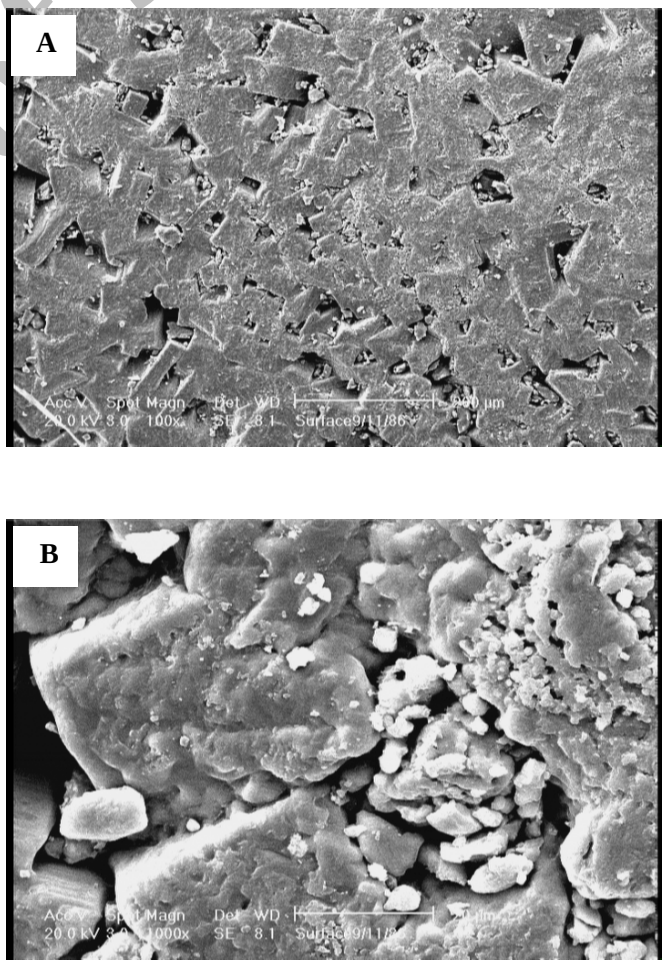

Fig. 3. SEM of molten sulfur MS after 30 days.

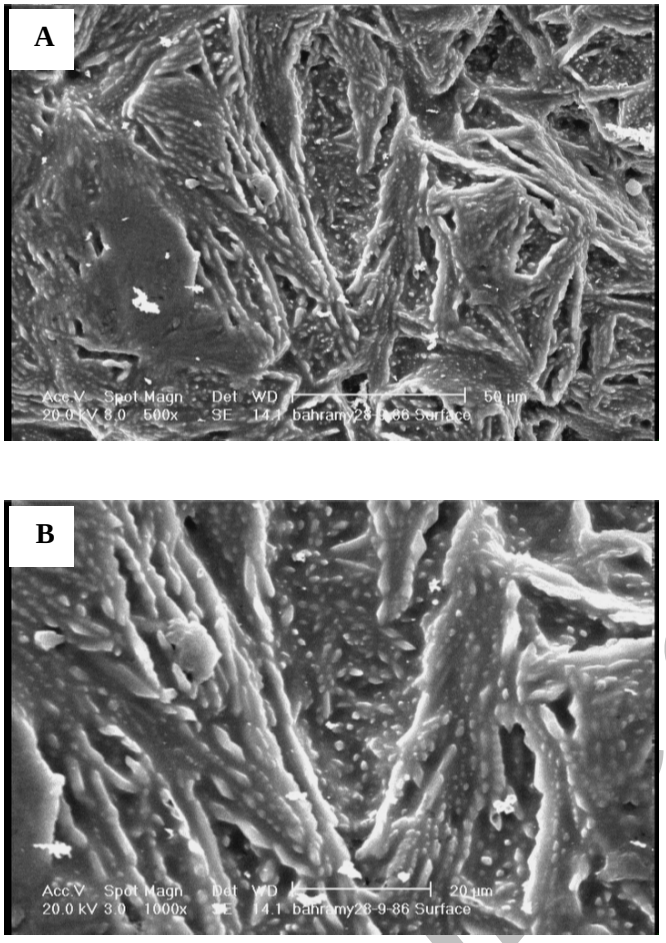

Fig. 4. SEM of styrene-plasticized sulfur (PS1) after one day.

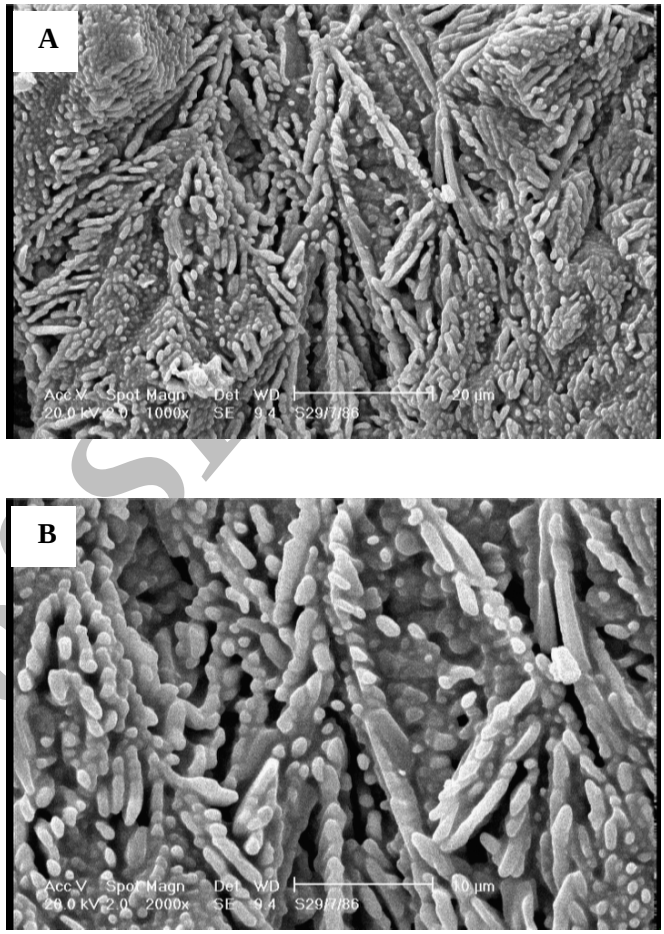

Fig. 5. SEM of styrene-plasticized sulfur (PS1) after 30 days.

following reasons can be accounted for this phenomenon: (i) styrene does not serve as a suitable modifier for sulfur, (ii) the weight fraction of styrene is insufficient for sulfur modification and (iii) the mixing *via* magnetic stirring is not appropriate.

In order to more explore this subject, the same sample was studied by taking its SEM image after 30 days (Fig. 5). As can be clearly seen, the fraction of α-crystals has been significantly increased, in the expense of diminished amount of β-crystals, which support the fact that a high fraction of β-phase has been transformed to α-phase. Obviously, the size of pores formed as a result of this transition is larger than those formed after one day (Fig. 4). Meanwhile, the resulting stress, brought about from β- to α-transition, has led to crack propagation in the matrix. From the above observations, it can be concluded that time has a negative effect on the function of STY as plasticizer in softening of sulfur.

Since the presence of fillers usually cause an increase in mechanical strength of sulfur composite, in the next step, we examined the use of some 1.6 g (3.2 wt% of sulfur content) of fine microsilica particles (mesh 325, particle size 45 μm) for possible filling of the pores formed as a result of β- to α-transition in the STY-plasticized sulfur PS1. The presence of these filler particles may possibly prevent the β-structure from transforming back into its α-phase.

Thus, the sample PS2 was prepared according to Table 1 and its SEM image was taken after 30 days (Fig. 6), to compare with that of sample PS1, taken under similar

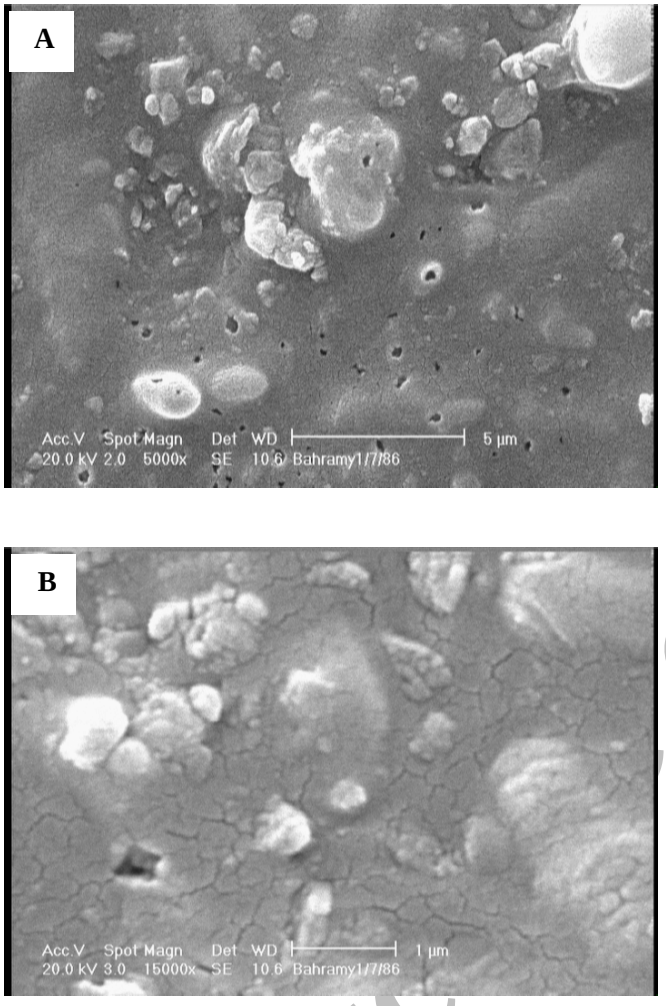

Fig. 6. SEM of styrene-plasticized sulfur with microsilica (PS2) after 30 days.

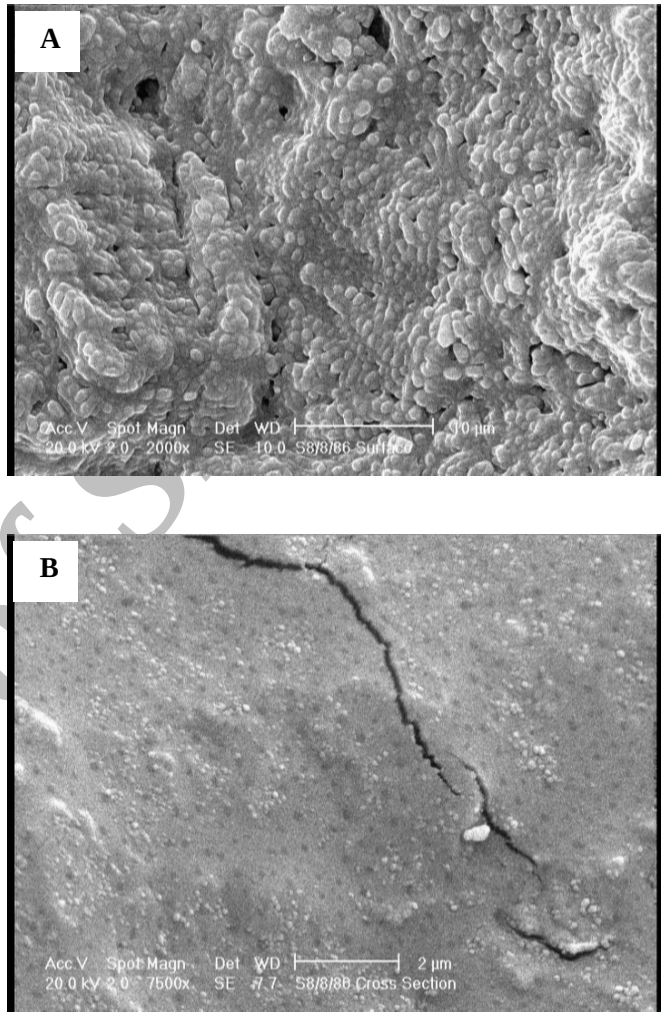

Fig. 7. SEM of styrene plasticized sulfur with nanosilica (PS3) after 30 days.

conditions (Fig. 5). Figure 6 clearly shows the presence of filler particles in the plasticized sulfur matrix, although they are not homogeneously distributed throughout the sample, possibly due to insufficient mixing with magnetic stirrer. In addition, many fine cracks and pores of smaller sizes are still existed in the structure. This is due to the fact that many of the pores with smaller sizes than the filler particles are still remained unfilled in the structure; thus, it can be concluded that the presence of filler particles has reduced, only to some extent, the overall stress induced after β- to α-transition.

Therefore, based on the above mentioned observations, it was expected that utilizing finer fillers may possibly result in more homogeneous stress distribution in the system and gives better results. Thus, in further experiments, nanosilica particles with size of 12 nm were used as filler. In the first attempt, and for the sake of better comparison, a sample with composition of 50 g sulfur, 7.5 g STY and 1.6 g nanosilica was prepared according to the corresponding procedure. Unfortunately, in this case, the addition of 1.6 g nanosilica resulted in a large increase in the viscosity of reaction medium so that the reaction greatly suppressed. Therefore, the amount of nanosilica filler was decreased to 0.8 g and, according to

Table 1, the sample PS3 was prepared successfully.

Figure 7 shows the SEM micrograph of sample PS3, after 30 days. The SEM results reveal that nanosilica particles possess a much better homogeneous distribution than the case of microsilica (Fig. 6). Also it seems that in PS3 sample, the β- to α-transformation has occurred at a lower extent, compared to PS1 and PS2 samples. However, the observed crack in PS3 sample may suggest that the use of a magnetic stirrer is not appropriate for thorough mixing of the nanosilica particles in a viscous sulfur matrix; it may also be due to poor compatibility of the hydrophilic surfaces of nanosilica with the STY-plasticized sulfur.

From the results thus obtained it can be concluded that silica filler particles (micro- or nano-sized) have no significant effect on the rate of β- to α-sulfur transformation and could not lead to a suitable stress distribution in the system, so that it would led to sample cracking. It seems that the presence of filler may also cause the weakening of modification process (chemical reaction) and led to crack propagation in the sample.

In order to investigate the effect of modifier type on morphology of the plasticized sulfur, sample PS4 was prepared containing DCPD, as a potential plasticizer, according to Table 1. In this case, 0.1 g of N,N,N',N'-tetramethylethylenediamne was used as initiator together with 7.5 g of DCPD (PS4). The main function of the initiator is acceleration in formation of polymeric products with low molecular weight, necessary for sulfur modification.

Figure 8 shows the SEM image of PS4 sample after 30 days. The differences between the structures of this sample with those of samples modified with STY are quite evident from this figure. The plate-like crystals of sulfur having β-structure can be observed in most parts of the sample, while only a low fraction of the modified sulfur with β-structure has transformed back to α-structure after 30 days. The plate-like structure is well-known to help to resist cracking [2]. The results make it clear that DCPD is a superior modifier for elemental sulfur, in comparison with STY. It is mainly because of much lower rate of transformation of sulfur from β- to α-structure in the presence of DCPD.

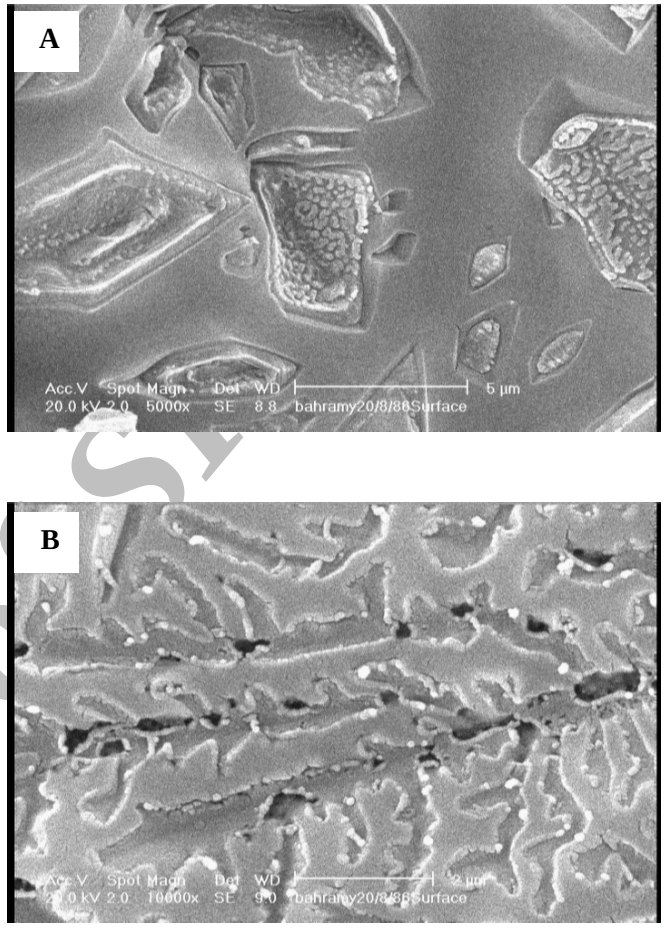

Fig. 8. SEM of dicyclopentadiene-plasticized sulfur (PS4) after 30 days.

Thermal Behavior of Pure and Modified Sulfur Samples

Thermal properties of pure and modified sulfur samples were studied using TG and DSC analyses, 522 days after their preparation. The TG and DSC analyses were employed to monitor the weight changes and the heat flow in sample materials, respectively, as a function of temperature.

Figure 9 shows the TG curves for pure sulfur, molten sulfur and modified samples PS1-PS4. As it is seen from Fig. 9A, the maximum thermal effects for pure sulfur and molten sulfur are occurred between 213-370 °C, with some negligible differences; while, in the case of DCPD-plasticized sulfur (PS4), it can happen between 215-600 °C (Fig. 9B). Furthermore, in the case of PS4, 13% of modified sulfur was remained at 600 °C, whereas in case of pure and molten sulfur, most of material was decomposed at temperatures lower than

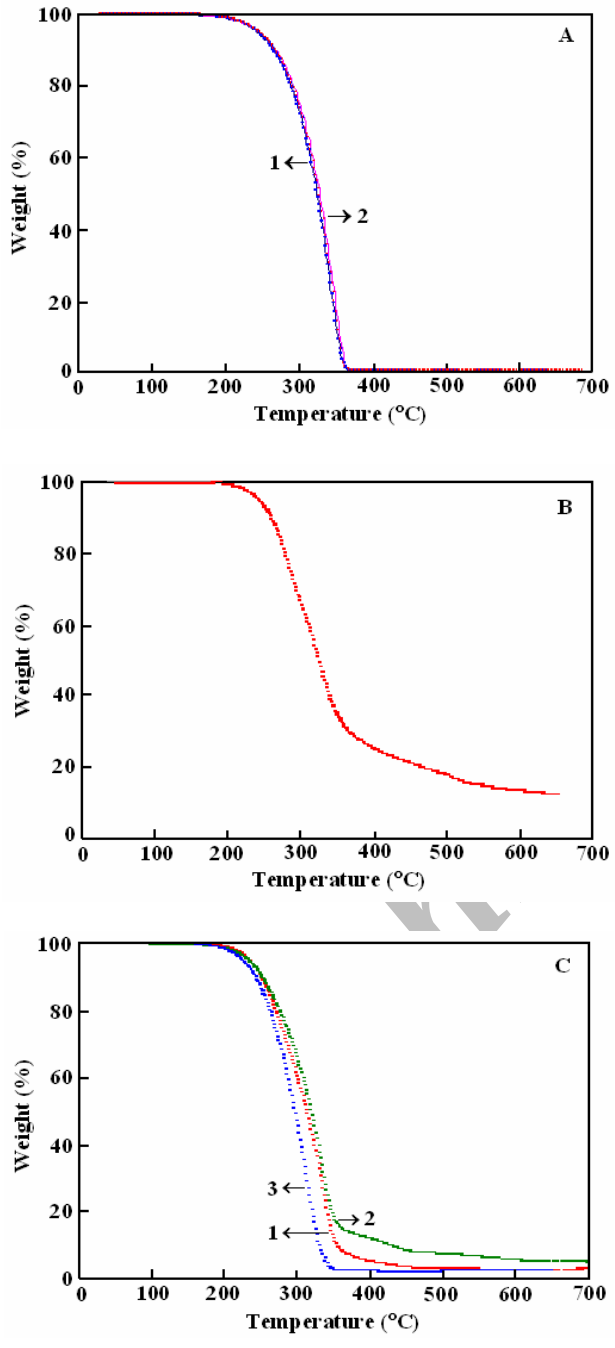

Fig. 9. Thermogravimetric analysis (TGA) curves for sulfur and modified sulfur at a heating rate of 20 deg min^{-1} in N_2 atmosphere. (A) pure sulfur, 1 and MS, 2; (B) PS4; (C) PS1, 1, PS2, 2 and PS3, 3.

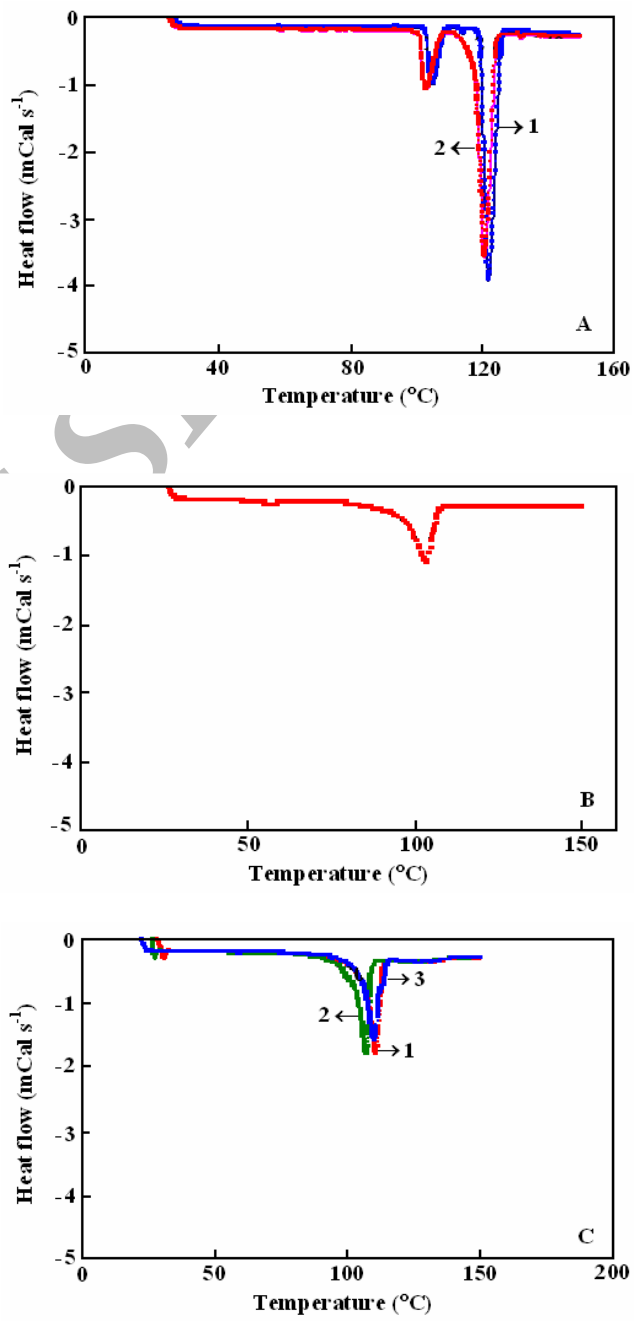

Fig. 10. Differential scanning calorimetric (DSC) curves for sulfur and modified sulfur at a heating rate of 5 deg min^{-1} in N_2 atmosphere. (A) pure sulfur, 1 and MS, 2; (B) PS4; (C) PS1, 1, PS2, 2 and PS3, 3.

370 °C and solely 0.7% of sample was remained. These results suggest that DCPD could suitably increase the thermal stability of sulfur.

The TG plots of PS1-PS3 samples (Fig. 9C) show that, in all three samples, only 2-5 wt% of materials was remained at temperatures higher than 580 °C. Comparison of these plots with TG curves of pure and molten sulfur shows that STY could significantly increase the thermal stability of samples. There is, however, some differences between PS1, PS2 and PS3, so that their stability decrease more or less in the order PS2 > PS1 > PS3, revealing the fact that the presence of silica nanoparticles as filler accelerates the thermal decomposition of STY-plasticized sulfur.

A comparison between TG curves of samples modified with DCPD (Fig. 9B) and STY (Figs. B and 9C) shows that, among the two modifiers, DCPD has been more effective in increasing the thermal stability of samples. These results are nicely in support of those obtained from the SEM studies.

The DSC curves of pure and molten sulfurs are shown in Fig. 10A. As seen, similar to the corresponding TGA curves (Fig. 9A), there is some negligible differences in the corresponding peak temperatures. In fact, the $S_\alpha \rightarrow S_\beta$ transition has been occurred at 105 °C and 103 °C for pure and molten sulfurs, respectively. Also the occurrence of $S_\beta \rightarrow S_\lambda$ transition can be seen at 122 and 120 °C for pure and molten sulfurs, respectively. The observation of some lower transition temperatures for molten sulfur, compared to the pure one, suggest that the melting of sulfur for 3 h at 140 °C resulted in modification and consequent softening of molten sulfur (MS), to some extent. This little change is more evident from DSC analysis, compared to TGA.

Figure 10B shows the DSC curves of the sulfur sample modified with DCPD (PS4). It reveals that the $S_\alpha \rightarrow S_\beta$ transition has disappeared, while the occurrence of $S_\beta \rightarrow S_\lambda$ is observed at 104 °C, much lower than that for pure and molten sulfurs, with a significantly decreased peak height, in comparison with the corresponding peaks in Fig. 10A. In support of the results concluded from SEM image of PS4 (Fig. 8), the observed DCS curve clearly revealed that the presence of DCPD as modifier has effectively prevented the $\alpha \rightarrow \beta$ transformation in PS4 sample.

The DSC curves of sulfur samples modified with styrene (PS1, PS2, and PS3), shown in Fig. 10C, revealed patterns similar to the DSC curve of PS4 (Fig. 10B), except that in these samples the corresponding DSC peaks have appeared at some higher temperatures of 107-112 °C. Thus, the observed DSC curves clearly support the facile modification of sulfur and effectiveness of styrene in the modification process. Meanwhile, the presence of micro- and nanosilica as fillers has no considerable effect in softening of sulfur, which is in close support of the above mentioned SEM and TGA results. Finally, the observed peak temperature differences in Figs. 10B and 10C clearly indicated the superiority of DCPD over STY in plasticization, which also is in accord with the results of SEM and TGA studies.

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