Influence of Micro and Nano Silica on Mechanical Properties of Plasticized Sulfur Composites

Shamsipur, Mojtaba*+
Department of Chemistry, Razi University, Kermanshah, I.R. IRAN

Bahrami Adeh, Narmin; Hajitarverdi, Mohammad Sadegh; Yazdimamaghani, Mostafa; Zarei, Fatemeh
Iranian Institute of Research and Development in Chemical Industries (IRDCI)-ACECR, Karaj, I.R. IRAN

ABSTRACT: *In this paper the influence of two different sizes of silica particles (micro-silica and nano-silica) was studied on mechanical properties of sulfur and sulfur composite. To improve the structural properties, sulfur was plasticized using dicyclopentadiene (DCPD) and methyl styrene (MSt). Plasticized sulfur composite was prepared by melt blending of plasticized sulfur and silica particles. The increment in compressive and flexural strengths revealed that the micro-particles enhance mechanical properties of sulfur while nano-particles improved mechanical properties of plasticized sulfur. Viscosity measurements indicated that mechanical properties of nano composites containing matrix with low viscosity (sulfur plasticized with methyl styrene) are improved with increasing mixer speed but increasing the mixer speed had negative effect on composites containing matrix with higher viscosity (sulfur plasticized with dicyclopentadiene).*

KEY WORDS: *Sulfur, Plasticized sulfur, Nanocomposites, Methyl syrene (MSt), Dicyclopentadiene (DCPD).*

INTRODUCTION

Sulfur has been known and used for several thousand years due to its unique characterization. Nowadays most chemists are aware of unusual molecular complexity of elemental sulfur and the fact that the physical-mechanical and chemical properties of solid sulfur depend on its temperature history and allotropic forms. These properties of sulfur made it useful to be used as composites matrix. Sulfur-based composites generally are used as protective salt or acid resistance coatings and construction materials [1-3].

The special characterization of elemental sulfur has limited the commercial use of sulfur-composites due to its brittleness, lack of resistance to thermal shock, and poor weather ability. So the plasticization of sulfur is necessary for better application. The term of plasticization refers to a chemical reaction (Fig.1) in which special materials or their mixtures are used to decrease the melting point and increase the crystallization time of sulfur [4,5]. Many additives have been proposed to modify elemental sulfur such as olefins hydrocarbons, unsaturated hydrocarbons, phenolic derivatives, and polysulfides. A number of researches cover the use of methyl styrene (MSt) and dicyclopentadiene (DCPD) as a plasticizer to improve sulfur properties. Two recent

* *To whom correspondence should be addressed.*
\+ *E-mail: mshamsipour@yahoo.com*
1021-9986/13/3/1 7/$/2.70

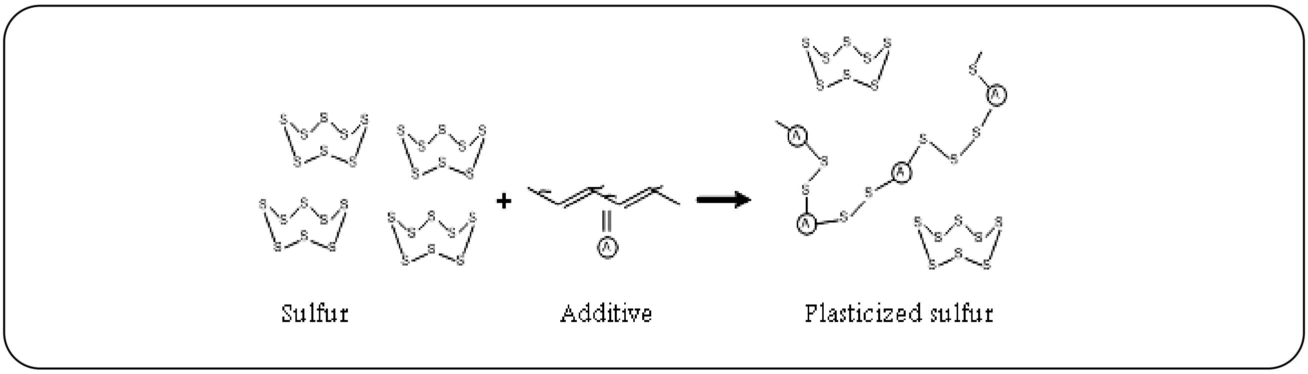

Fig. 1: Reaction mechanism of molten sulfur with plasticizer.

additives cause Sulfur polymerization and increment in available sites for chemical reaction that lead to polysulfide formation. In addition, the plasticized sulfur is more efficient in binding and strengthening than the other ingredients of the sulfur composition [6-7].

Furthermore, to increase the mechanical and desirable properties of elemental sulfur, many different kinds of fillers have been employed. Sulfur-composites typically contains of fillers about from 1 to 15% by weight, based on the weight of total sulfur. Fillers acts as thickening agents and improve strength of sulfur-composite. Modification of the plasticized sulfur matrix with inorganic nanoparticles result in plasticized sulfur/inorganic nanoparticle composites with excellent performance due to the combination of higher rigidity, heat resistance of the inorganic fillers, good toughness and process ability of the polymer [8]. These exclusive particles have unique properties such as higher stability, long lasting and being safe which make them applicable in many fields such as self-cleaning, anti-bacterial agent, UV protecting agent, environmental purification, water and air purifier, gas sensors, and high efficient solar cells [9]. Usual sulfur composites fillers are particulate inorganic material with an average particle size 0.10 μm to 0.1mm [10-11]. Nano-silica has been added to polymer to increase strength, flexibility, and aging resistance. The low Coefficient of Thermal Expansions (CTE) of fused silica caused by the high Si-O bond energy, the silica fined composite to improve the mechanical properties and to reduce the CTE of polymer composite [14,15]. T he properties of polymer/silica nano-composites, however, are generally superior to the pure polymer matrix and polymer micro-composites. In particular, they commonly exhibit improved mechanical properties and thermal stability regardless of the preparative method [16]. In this work, plasticized sulfur-silica composites were prepared and the effect of silica nano/micro particles investigated. Moreover the influence of mixer speed on mechanical properties of plasticized sulfur was studied.

EXPERIMENTAL SECTION

Materials

Elemental sulfur (powder) with purity of 98% was obtained from natural gas, Iran. Dicyclopentadiene (98%), methyl styrene (55% 3-methyl styrene, and 45% 4-methyl styrene) N, N, N', N', Tetramethylethylenediamine (98%) were obtained from Merck, Germany. Silica powder (325 Mesh) was provided by Beton Shimi Company of Iran. Nano silica powder (99.5%, 12 nm) was purchased from FCC, China

Sample preparation

Preparation of plasticized sulfur

Reaction carried out in 1L five-neck, round bottom glass reactor, in oil bath, and equipped with reflux condenser, thermometer, dropping funnel, mechanical stirrer with a stainless steel anchor device and nitrogen gas inlet passed from two traps, First pyrogallol solution chamber for oxygen absorption and second, the mixture of $CaCl_2$ powder and glass wool for watert absorption. Initially, appropriate amount of sulfur was loaded into the reactor and heated up to 140 °C to be melt. Then 15% by weight of sulfur, hydrocarbon olefin (DCPD or MSt) was added drop wise and stirred for about 3 hours. Prepared samples were poured into the warmed and greased molds, Cubic rectangular dimensions 4 * 10 * 80 mm for flexural strength test and cylindrical (25.4 mm length and 12.7 diameter mm) for compressive strength test (Fig.2 a & b).

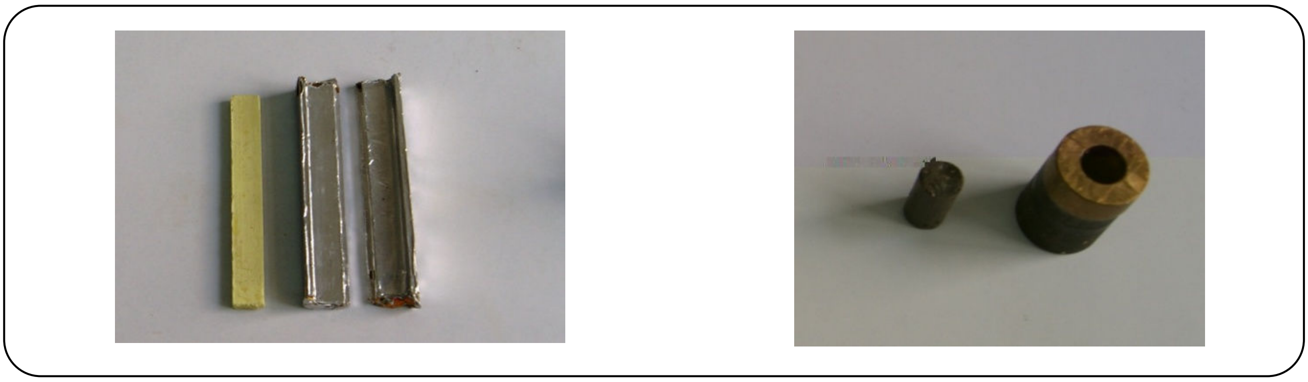

***Fig. 2:** Casting molds (a): flexural strength (b): compressive strength.*

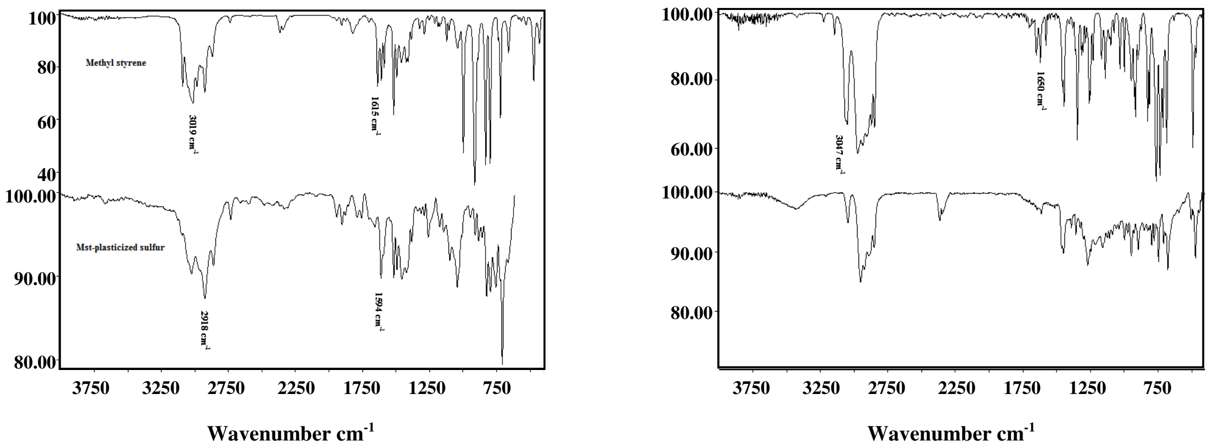

***Fig. 3:** FTIR spectra of plasticizers include MSt, DCPD and their reaction products with sulfur.*

Then the samples were separated from the molds after cooling and prepared for the next level.

Preparation of plasticized sulfur-silica composites

Plasticized sulfur was melted (140 °C) in heating reactor, in oil bath, and mixed with 1.6 % by weight of sulfur of silica powder (micro and nano) for about 15 minutes. Then the prepared composite was poured into the molds In order to further investigation on mechanical properties.

Characterization

FT-IR spectroscopy

The FT-IR spectra of plasticized-sulfur were obtained in the transmission mode in a Bruker Vertex 700 spectrophotometer.

Stress-strain measurements

The mechanical properties of the samples were investigated by a H10KS universal testing machine (Hounsfield, UK) according to ASTM D-695 for flexural strengths and ASTM-D-790 for compressive strengths.

Scanning Electron Microscopy (SEM)

Nano structure of composites was characterized by Scanning Electron Microscopy (SEM) Philips XL30 (Netherland).

RESULTS AND DISCUSSION

FT-IR spectroscopy

In, Fig. 3, the peaks at 2000-1650cm^{-1} and 1615-1500cm^{-1} clearly confirm the presence of benzene ring. Also peaks at 3110-3000 cm^{-1} and 900-650 cm^{-1} belong to the C-H group of aromatic compounds. Disappearing of C=C endocyclic stretching band at 1650-1550 cm $^{-1}$, stretching band of =CH vinyl at the area of 900 and 1000 cm^{-1} and C-H stretching near 3000 cm^{-1} for DCPD reaction product show chemical reaction between monomers and formation of polymeric chains. The CH_2-S

Table. 1: Viscosity of sulfur and plasticized sulfurs.

Sample	Viscosity range (cp)	Temperature range (°C)
Sulfur	15-16	130-135
DCPD-plasticized sulfur	1084-1200	130-135
MSt-plasticized sulfur	33-35	130-135

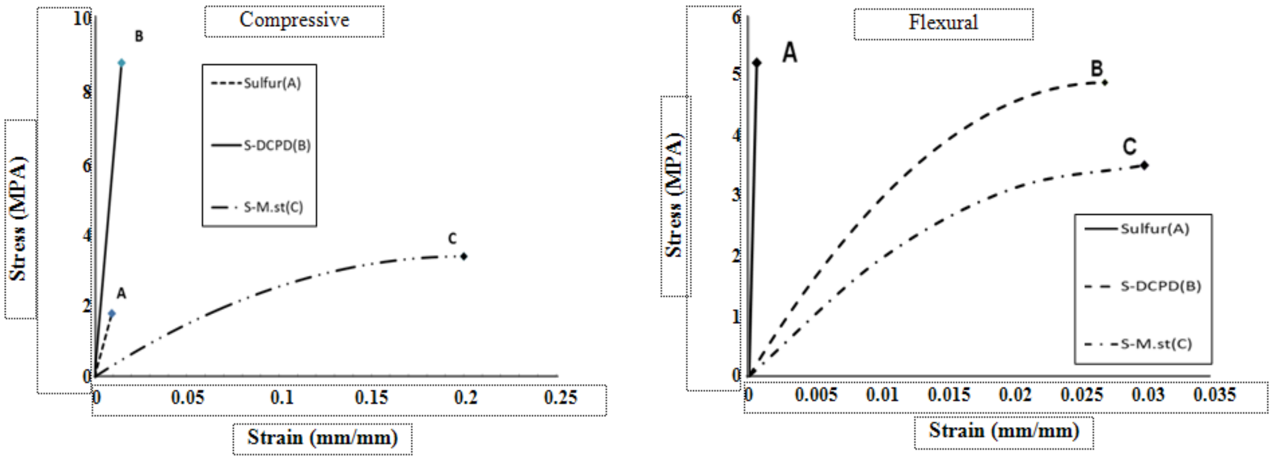

Fig. 4: Compressive and flexural Stress-Strain curve of plasticized sulfur.

stretching band in the area of 1220 cm^{-1} to 1270 cm^{-1} is a sign for the presence of sulfur in the polymer.

Viscosity studies

Viscosity of plasticized sulfur samples were measured by Brookfield Rotary viscometer model LV II according to ASTM C 1159 (See Table. 1). Results showed that viscosity of the plasticized sulfur treated by DCPD was higher than the other samples. The variation of viscosity with temperature was significant for DCPD from 130 °C to 135 °C, which was increased approximately 116 cp. In the samples treated with MSt the variation rate of viscosity is about 2cp and for sulfur is 1cp.

Stress-Strain measurements

Mechanical properties of Sulfur-composites were determined after 7 days and averaged with five repeatition. As can be seen in Fig. 4, the compressive strength of treated samples was increased. Among the samples, DCPD treated one had significant improvement. However these samples were became brittle compare to other samples prepared with MSt which are tough and had lower elasticity module. The results clearly explained that the MSt modifier is able to increase the rate of strain and makes the samples flexible. It is important to note that A and B samples were Broken at the end point, but C sample were yielded. The flexible samples are desirable for engineering application compared to brittle samples.

The mechanical properties of sulfur composites contain 1.6 wt. % of silica particles in nano and micro size showed increase in flexural and compressive strengths. Micro particles had a higher increment in compressive and flexural strength and lower modulus than nano particles due to the agglomeration of these particles which result in stress increament [see Fig. 5].

Figs. 6 and 7 shows the improvement in compressive and flexural strengths and strain at yield point of DCPD and MSt-plasticized sulfur caused by nano particles while micro particles reduced compressive and flexural strengths.

Mixer speed studies

Uniform distribution of particles in plasticized sulfur matrix is an important factor for development of mechanical properties. For this purpose, proper amount of nano and micro sized silica particles mixed with MSt and DCPD-plasticized sulfur with high shear rate of mixer, around 10,000 rpm using Homogenizer model PT 6100, and Compressive and flexible strengths test results were measured.

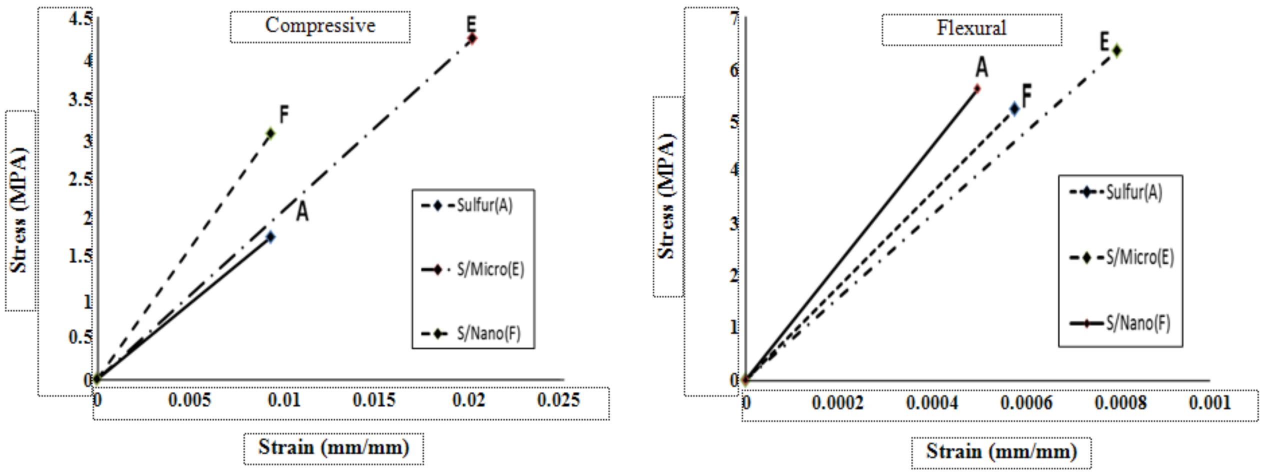

Fig. 5: Compressive and flexural Stress-Strain curve of sulfur/silica composites.

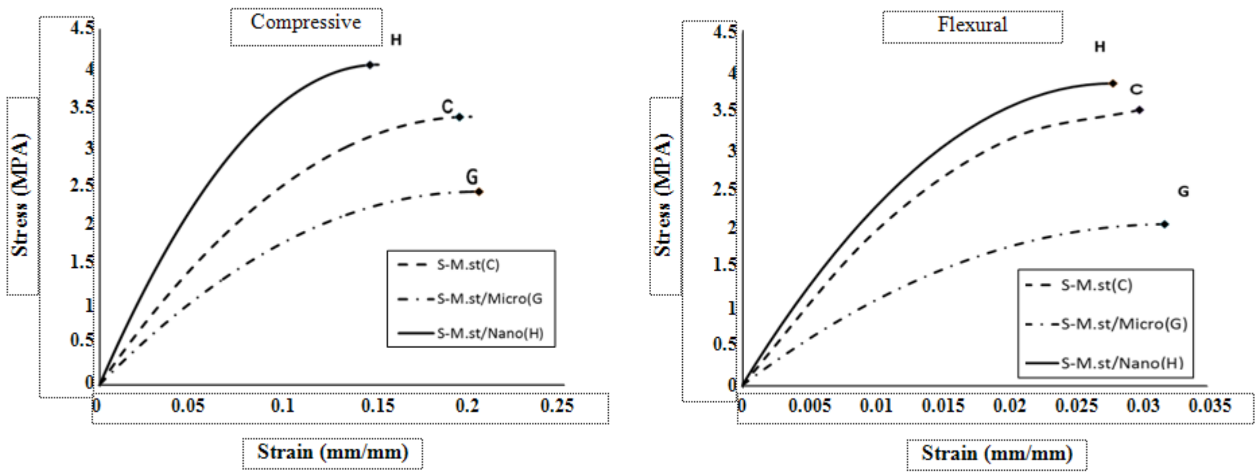

Fig. 6: Compressive and flexural Stress-Strain curve of MSt- plasticized sulfur/silica composites.

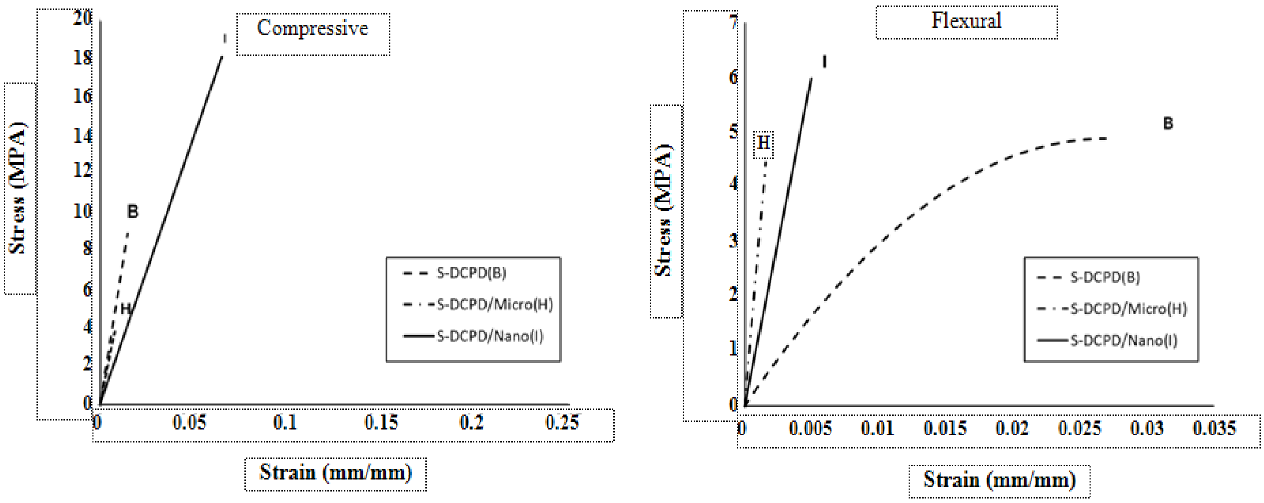

Fig. 7: Compressive and flexural Stress-Strain curve of DCPD-plasticized sulfur/silica composites.

Table. 2: Compressive and flexural Strenght for plasticized/nanosilica composites.

sample	Mixing rate (rpm)	Compressive yield strength (MPA)	Compressive strength (MPA)	Modulus of elasticity (MPA)
MSt-plasticized sulfur composite	200	4.067		838
MSt-plasticized sulfur composite	10000	8.24		641
DCPD-plasticized sulfur composite	200		18.03	286
DCPD -plasticized sulfur composite	10000		8.11	511

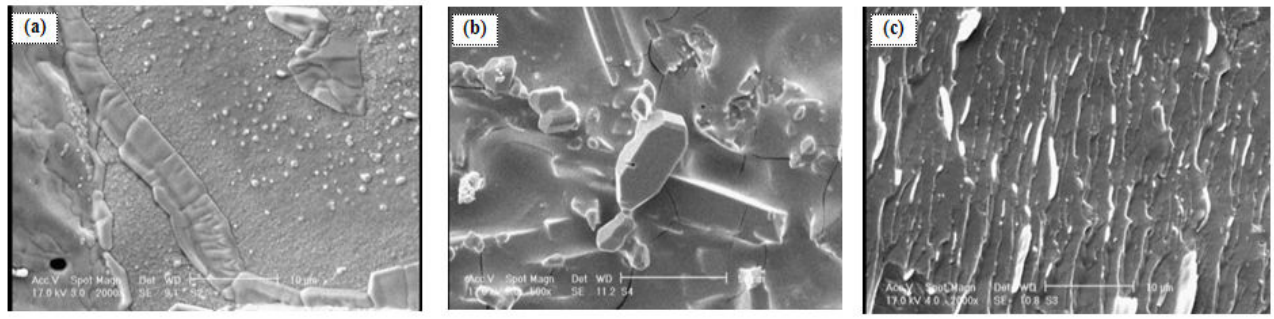

Fig. 8: SEM fraction section of sulfur/ nanosilica (a), MSt -plasticized sulfur/nanosilica(b) and DCPD-plasticized sulfur/nanosilica composites (c).

Table. 2 showes increasing effect of agitation on the mechanical properties of composites. Also increasing the mixer speed from 200 rpm to 10000 rpm improved the compressive strength and reduced the elasticity module of MSt plasticized sulfur composite compared with DCPD plasticized sulfur due to the lower viscosity of MSt treated sample and as a result, higher dispersion rate as continuous phase.

Morphology studies

The presence of β sulfur in prepared composites was confirmed by SEM fracture sections (Fig. 8). The pores and cracks and unreacted sulfur (α-sulfur) were seen in plasticized sulfur composites. MSt and DCPD plasticized sulfur composites represent lower crack and higher Plasticization comparing to nano silica particle treated sulfur composite, also the fractures of nano silica particle treated DCPD and MSt plasticized sulfur show considerably rougher surface than Sulfur/nano silica composite.

CONCLUSIONS

Sulfur and plasticized sulfur-silica composites were prepared via melt blending method. It can be concluded that nano silica particles (1.6 Wt. %) improved the mechanical properties of plasticized sulfur while micro particles (1.6 Wt. %) reduced. Nevertheless, micro particle improved the unreacted sulfur properties than nano particles. It seems that nano particles have high compatibility and dispersability in plasticized sulfur as polymeric matrix. Also the higher mixing rate followed by the improvement in mechanical properties of MSt plasticized sulfur composite might be due to lower viscosity of this sample compared to DCPD plasticized sulfur.

Received : Nov. 19, 2012 ; Accepted : Aug. 27, 2013

REFERENCES

[1] Paulson J.E., Simic M., Campbell R.W., Sulfur Composites as Protective Coatings and Construction Materials, in: “New uses of Sulfur”, ACS Publication, (1977).

[2] Sullivan T.A., Been W.C.M., Blue D.D., Sulfur in Coatings and Structural Materials, in: “New Uses of sulfur”, ACS Publication (1978).

[3] Sandrolini, F., Manzi, S., Andrucci, A., Sulfur-Polymer Matrix Composites from Particulate Wastes: A Sustainable Route to Advanced Materials, *Composites A.*, **37**, p. 695 (2006).

[4] Currell B.R., Williams A.J., Mooney A.J., Nash B.J., Plasticization of Sulfur, in: "New Uses of Sulfur", 1-17, ACS Publication (1978).

[5] Simic, M., Plasticized Sulfur Composition, *USP 4348233,* (1982).

[6] Shamsipur M., Bahrami Adeh N., Afghani T., The Study on Morphology and Thermal Behavior of Plasticized Sulfur, *J. Iran. Chem. Soc*., **8**, p. 1063 (2011)

[7] Bahrami Adeh N., Mohtadi Haghighi M., Mohammad Hosseini N., Preparation of Sulfur Mortar from Modified Sulfur, *Iran. J. Chem. Chem. Eng*., **27**(1), p. 123 (2008)

[8] Dastjerdi, R., Montazer, M., A Review on the Application of Inorganic Nano-Structured Materials in the Modification of Textiles: Focus on Anti-Microbial Properties, *Collis.& Surf. B*, **79**, p. 5 (2010).

[9] Nimer E.L., Campbell R.W., Sulfur Cement-Aggregate Compositions and Methods for Preparing, *USP 4496659,* (1985).

[10] McBee W.C., Patrick O.B., Sullivan T.A., Structural Material, *USP 4022626*, (1977).

[11] Schneider R,A., Simic M., Plasticized Sulfur Compositon, *USP 4308072*, (1981)

[12] Gar L., Woo T., Sulfur foam Process and Product, *USP 4219364*, (1980).

[13] Schnelder R.A., Monoolefinic Plasticized Sulfur, *USP 4282040*, (1981).

[14] Li G., Properties of High-Volume fly Ash Concrete Incorporationg Nano-SiO_2, *Cement and Concrete Research*, **34**, p. 1043 (2004).

[15] Simic M., Plasticized Sulfur Improved Thixotropy, *USP 4210458*, (1980).

[16] Zou H., Wu S., Shen J., Polymer/Silica Nanocomposites: Preparation, Characterization, Properties, and Applications, *Chem. Rev*., **108**, p. 3893 (2008).