

Synthesis and Properties of Plasticized Sulfur-Montmorillonite Nanocomposites by Melt-Blending

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ABSTRACT: Plasticized sulfur/montmorillonite nanocomposites were prepared by the melt-blending method and the dispersion of montmorillonite (MMT) and the mechanical properties of the nanocomposites were studied. Natural sodium montmorillonite (NaMMT) and organically modified montmorillonite (OMMT) were used as filler. Scanning electron microscope (SEM), X-Ray powder Diffraction (XRD) and Transmission Electron Microscopy (TEM) indicated that OMMT is dispersed effectively in the plasticized sulfur matrix. The effect of varying amounts of natural sodium montmorillonite (NaMMT) and organically modified montmorillonite (OMMT) on the mechanical properties of the prepared nanocomposites were studied. The compressive, tensile, and flexural strengths of the plasticized sulfur nanocomposites containing OMMT compared to that containing NaMMT were, in general, greatly improved. Best MMT dispersion observed at 1.6 wt. %.

KEYWORDS: Sulfur, Plasticized sulfur, Sodium montmorillonite (NaMMT), Organically modified montmorillonite (OMMT), Nanocomposites, Mechanical properties

INTRODUCTION

Composite materials are now in wide use for numerous applications. The possibilities of producing materials with improved physical properties at low cost could result in interesting applications ranging from resistance coatings, adsorbents, industrial equipment and several others [1-8]. The major difference between research activities in this field is the type of matrix and its functional goal. Synthesis and modification of polymer composites using Low volume additions (1-5%) of nanoscale fillers, such as layered silicates [1],

nano silica [3], metal and metal oxide nanopowder [4] or carbon nanomaterials like graphene oxide [5] has been of increasing interest, that provide property enhancements that are comparable to those achieved by conventional loadings of traditional fillers. Nanocomposites based on montmorillonite (MMT) and layered silicates have been studied widely compared to others because of these materials are easily available and also their intercalation chemistry has been investigated for a long time [1]. The incorporation of layered silicates in polymers

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was first reported about forty years ago [2]. MMT is a well-known layered silicate which is most frequently used in nanocomposite materials. This is due to MMT's high excellent swelling ability, cation exchange capacity, high aspect ratio, ease of modification and its potential to exfoliate in the polymer matrix. These properties result in better stiffness, strength, and dimensional stability of the composites [9]. The layered structure of MMT that is a kind of crystal lattice of 2:1 layered silicates (or 2:1 phyllosilicates) consists of two-dimensional layers. In this structure a central octahedral sheet of alumina is fused on two external silica tetrahedral sheets by the tip, so that the oxygen ions of the octahedral sheet also belong to the tetrahedral sheets [10]. In recent years, many polymer/montmorillonite nanocomposites have been studied because adding just a small amount of nano montmorillonite to the polymer matrix could improve the mechanical and thermal properties of the polymers and reduce their flammability [11]. To enhance the interaction between the nano montmorillonite and polymer, the montmorillonite must be modified by strong interactions between the polymer and the layered silicate in the polymer. Nano montmorillonite composites caused the organic and inorganic phases to be well dispersed at the nanometer level and, hence, lead to their strong mechanical and thermal properties [10]. There are many research projects which have shown that modification of nano montmorillonite enhances the compatibility between MMT and polymer and results in improved thermal and mechanical properties of polymer montmorillonite nanocomposites [12-18]. Sulfur-based composites are generally used as salt- protective or acid-resistance coatings and construction materials [19, 20]. Many plasticizers, fillers, reinforcing agents and other modifiers have been used to modify and increase mechanical properties of elemental sulfur and develop the desirable properties of sulfur. Plasticizers used in this respect include for example styrene and dicyclopentadiene [21], DCPD and dipentene or DCPD and vinyl toluene and dipentene [22], olefin hydrocarbon polymers [23], polyethylene [24], polyethylene and acrylic acid [25] and many other additives. The sulfur used in such products is typically modified or plasticized in order to prevent allotropic transformation of the solid sulfur.

A well-known category of sulfur modifiers is olefinic compounds such as dicyclopentadiene, limonene, styrene,

or naphthalene that copolymerize with sulfur [26]. Plasticized or modified sulfur may be used in the form of a so-called plasticized sulfur matrix, which can be mixed at the temperature above the melting point of sulfur with filler and solidify. These sulfur-based composites usually contain fillers such as mica [27], asbestos [28], glass fiber [29], limestone and silica [14] and etc. However, to the best of our knowledge, there is no literature report on dispersing nano-sized montmorillonite clay in the plasticized sulfur matrix.

In this work, preparation, characterization, and properties of plasticized sulfur-natural sodium montmorillonite (NaMMT) and organically modified montmorillonite (OMMT) nanocomposites were studied. Dispersion of NaMMT and OMMT in plasticized sulfur was expected to result in improved materials properties in several areas. At the first step, sulfur was plasticized with methyl styrene. Then, to investigate the effects of NaMMT and OMMT level on mechanical properties of the resulting composites, different amounts of nano-sized NaMMT and OMMT were added to the composition of plasticized sulfur by "direct-mixing" (melt blending) process.

EXPERIMENTAL SECTION

Materials

Granules of sulfur with purity of 99.5% were obtained from Razi Petrochemical Co. (RPC, Iran). Methyl styrene (55% 3-methyl styrene, and 45% 4-methyl styrene) was obtained from Merck, Germany. Natural sodium montmorillonite (NaMMT) (95-98%, mean diameter 25×1000 nm, X-ray d001 1.2 nm) and organically modified montmorillonite (OMMT) (95-98%, mean diameter 25×1000 nm, X-ray d001 3.5 nm) modified with dimethyl dehydrogenated tallow ammonium chloride (DDAC 40%) and dicumyl peroxide (DCP) were purchased from FCC, China. Home-made flexural strength testing molds (Cubic rectangular dimensions $4 \times 10 \times 80$ mm), compressive strength testing molds (cylindrical 25.4 mm length and 12.7 mm diameter) and tensile strength testing molds were constructed according to the ASTM - D-790, ASTM-D-695, and ASTM- D-638-96, respectively.

Synthesis of plasticized sulfur montmorillonite nanocomposites

The synthesis reactor (Fig. 1) consists of a five neck glass reactor with one liter capacity which is equipped with reflux condenser, thermometer, dropping funnel,



Fig. 1: Experimental set-up for nanocomposite preparation.

a mechanical stirrer, and stainless steel anchor device placed in an oil bath. Nitrogen was used as blanket gas and connected to the reactor. Nitrogen gas was transferred from two traps: the first trap containing pyrogallol solution was used for the adsorption of oxygen gas and the second trap containing CaCl_2 and glass wool was adopted for moisture absorption. The required amount of sulfur was heated to 140°C , and then methyl styrene (15% by weight of initial sulfur) was added dropwise. The mixture was stirred at the rate of 300 rpm for 3 h. Then, different amounts of NaMMT or OMMT equivalent to 0.5, 1.6, 2 and 3 weight % of initial sulfur was added to the reactor and mixed for 15 min. Finally, the prepared material was removed from the reactor and poured into the flexural, tensile and compressive molds that were warmed and greased.

Characterization

FT-IR analysis

FT-IR spectroscopy investigation was used to identify the qualitative composition of plasticized sulfur. KBr was extensively dehydrated by heating at 105°C about 8 h. 1 mg of plasticized-sulfur and 50 mg KBr were mixed and pressed using a pellet mold until a homogeneous pellet was obtained. The FT-IR spectra of plasticized-sulfur were obtained in the transmission mode with a Baker Vertex 70 instrument using 32 scans and 4 cm^{-1} resolution. Spectral range was from 400 to 4000 cm^{-1} .

Morphology studies

The structures of plasticized sulfur montmorillonite composites were characterized by Scanning Electron

Microscopy (SEM), X-Ray Diffraction (XRD) and Transmission Electron Microscopy (TEM).

A Phillips XL30 scanning electron microscope with accelerating voltage 17 kV was used to probe the morphology of samples. The samples were mounted rigidly on a specimen holder called a specimen stub and the fracture surface was coated with an ultrathin coating of the gold layer by vacuum sputtering.

The XRD measurements of the two montmorillonite nanocomposites, namely plasticized sulfur/NaMMT (PS/NaMMT) and plasticized sulfur/OMMT (PS/OMMT) were carried out on a Philips PW1800 X-ray diffractometer equipped with a Ni-filtered monochromatic $\text{Cu-K}\alpha$ radiation ($k=1.5418\text{Å}$, 40 kV, 30 mA). Measurements were made to examine the interlayer activity in the composite as prepared. Bragg's Law ($n\lambda = 2d \sin \theta$) was used to calculate the crystallographic spacing. The diffractograms were scanned from 4° to 14° in the 2θ range in the step size of 0.04° with the scanning speed $0.016^\circ/\text{s}$ and a slit width of 4° . The samples were chosen at random.

The ultra-thin TEM specimens from the powder of plasticized sulfur/OMMT nanocomposites were immersed in alcohol and dispersed by an ultrasonic probe. The solution was dripped on copper grids (200 meshes) to be viewed with a Philips CM10 HD electron microscope at an accelerating voltage of 100 kV.

Mechanical properties

The tensile, flexural and compressive tests were performed after seven days on a Gotech 20kN testing machines INC. model GT-TCS-2000 at standard condition of laboratory ($23 \pm 2^\circ\text{C}$ & $50 \pm 5\%$ humidity) in accordance with ASTM D-638-96 for tensile strength, ASTM D-695 for flexural strength and ASTM D-790 for compressive strengths. All of these were determined at a crosshead speed of 5 mm/min, and averages of 5 successive tests reported.

RESULTS AND DISCUSSION

Chemical structure of plasticized sulfur

The reaction pathways for the synthesis of plasticized sulfur are shown in Fig. 2. In general, olefinic compounds successfully co-polymerize with sulfur and form plasticized sulfur. The plasticized sulfur contains unreacted sulfur and polymeric sulfur (polysulfide).

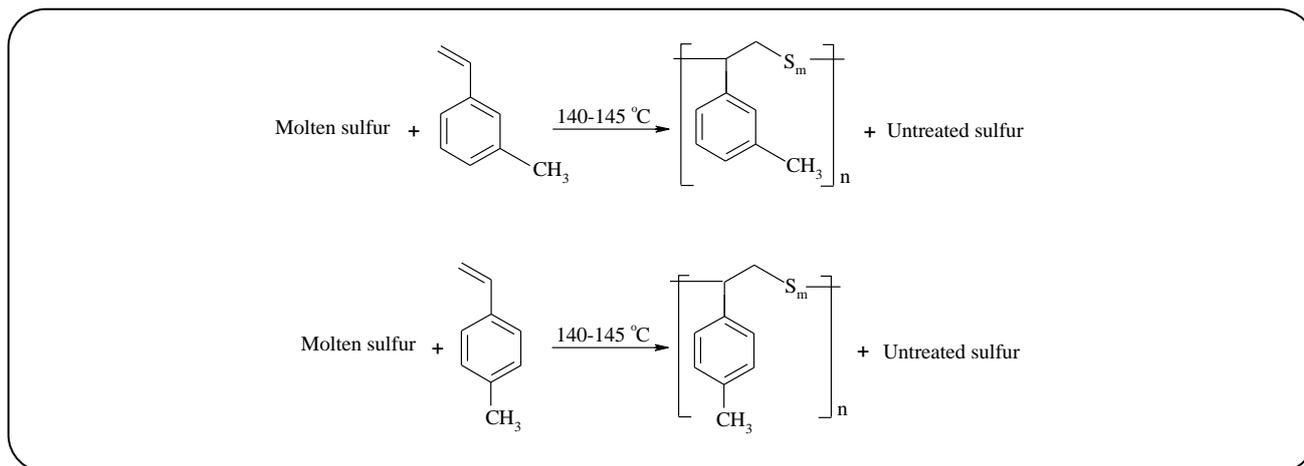


Fig. 2: Reaction scheme for the synthesis of plasticized sulfur.

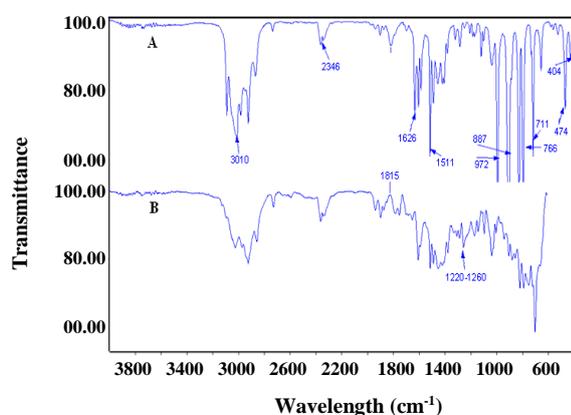


Fig. 3: FT-IR spectra of (A) methyl styrene and (B) plasticized sulfur with methyl styrene.

The FT-IR spectra of modifiers including methyl styrene and its reaction product with sulfur are shown in Fig. 3. The bands at $2000\text{--}1650\text{ cm}^{-1}$ and $1615\text{--}1500\text{ cm}^{-1}$ are characterizations of benzene group. The peak appearing in $3110\text{--}3000\text{ cm}^{-1}$ and $900\text{--}650\text{ cm}^{-1}$ are due to the C-H groups of aromatic compounds. Removal of C=C stretching band and stretching band C-H of the vinyl group at the spectral region of $900\text{ to }1000\text{ cm}^{-1}$ shows chemical reaction between monomers and formation of polymer. Observation of CH₂-S vibration in the region of $1220\text{ to }1270\text{ cm}^{-1}$ shows the presence of sulfur in the resulting polymeric chain

Morphological characterization

The structures of plasticized sulfur/layered silicate nanocomposites have typically been studied using

Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) analysis and Transmission Electron Microscopy (TEM).

The untreated sulfur was crystallized and formed large alpha sulfur crystals (S_{α}) with orthorhombic sulfur morphology (Fig. 4A). While the SEM image in Fig. 4B reveals the reaction product of sulfur with a plasticizer (methyl styrene). It was observed differences between structures of plasticized and elemental sulfur which was due to the presence of β planes, which were formed beside the α -crystals in the plasticized composition. Although the phase transformation from β to α can occur in the plasticized sulfur, the size and fraction of the pores which were formed are lower than that of the unmodified sulfur [30].

The SEM images of plasticized sulfur nanocomposites filled with 1.6% (by weight of initial sulfur) of OMMT (Fig. 5A) and NaMMT (Fig. 5B) were shown. The figures show that both nano-clay particles have dispersed well in the plasticized sulfur matrix. The SEM images also indicate that the plasticized sulfur/OMMT nanocomposite possesses fewer pores and a more uniform surface than plasticized sulfur/NaMMT nanocomposite. This is the result of proper interaction and better compatibility of OMMT nanoparticles with the sulfur matrix. In the cases of both nanocomposites, the observed pores with a diameter of about 100 nm may be the result of sulfur conversion from the "monoclinic" to the "orthorhombic" form.

In the plasticized sulfur nanocomposites, XRD (Fig. 6) shows that plasticized sulfur chains have intercalated and exfoliated the interlayers of OMMT. The role of

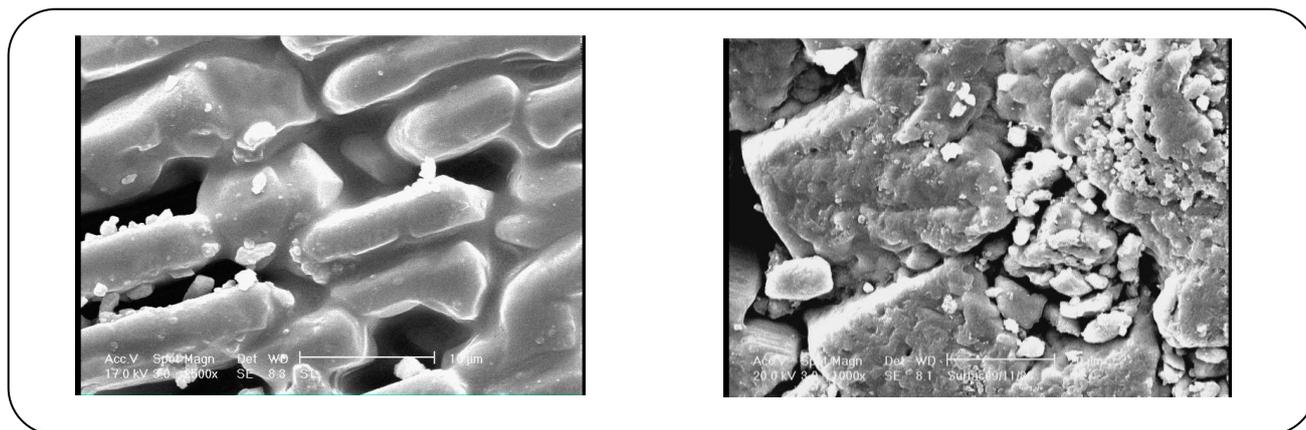


Fig. 4: SEM of (A) untreated sulfur and (B) unfilled plasticized sulfur.

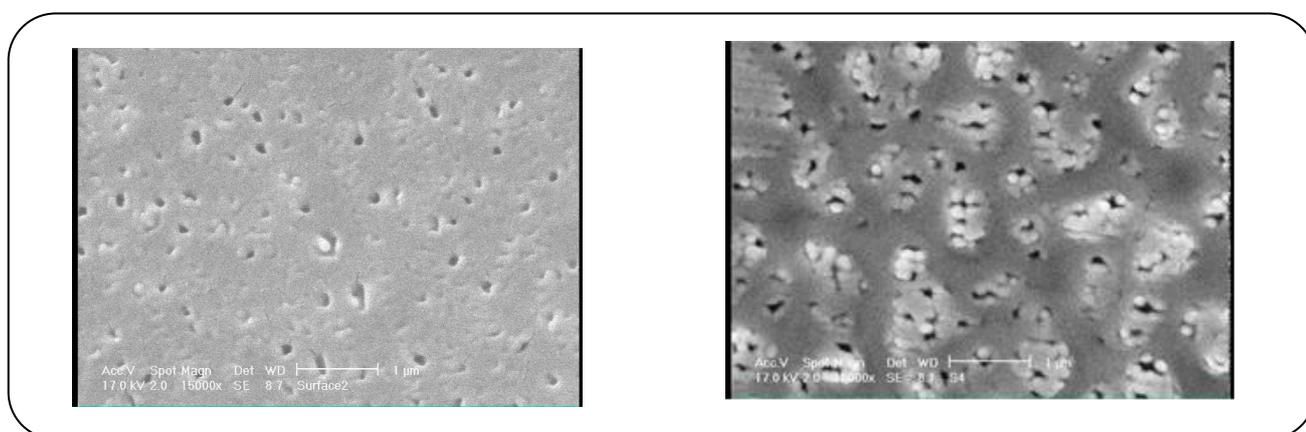


Fig. 5: SEM images of (A) plasticized sulfur/NaMMT composite and (B) plasticized sulfur/OMMT composite.

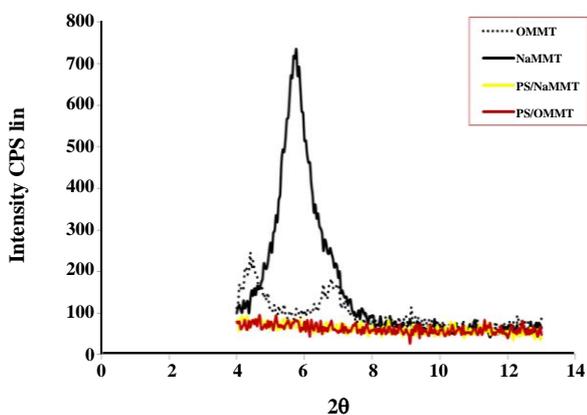


Fig. 6: X-ray diffraction patterns of MMT, OMMT, PS/NaMMT (1.6%) and PS/OMMT (1.6%) nanocomposites.

modifiers (dimethyl dehydrogenated tallow ammonium chloride (DDAC 40%) and dicumyl peroxide (DCP) in the organoclay are to lower the surface energy of the inorganic host and improve the wetting characteristics

with the plasticized sulfur. The disappearance of any coherent X-ray diffraction from the distributed silicate layers results in the extensive layer separation associated with the delamination of the original silicate layers in the polymer matrix.

TEM analysis was used to confirm the morphological information obtained from the XRD data about dispersion and distribution of nanoclay because morphology cannot be fully characterized only by XRD analysis. The absence of scattered intensity peaks in the XRD diagrams cannot always surely demonstrate achievement of the disordered intercalated or the exfoliated structures. Fig. 7 shows the TEM image for the plasticized sulfur system based on OMMT (1.6%) as a reinforcing agent. We suggest that the structure of OMMT plasticized sulfur nanocomposite has an exfoliated structure that is in good agreement with the XRD analysis. The dispersion of OMMT was very uniform that is due to the higher compatibility between

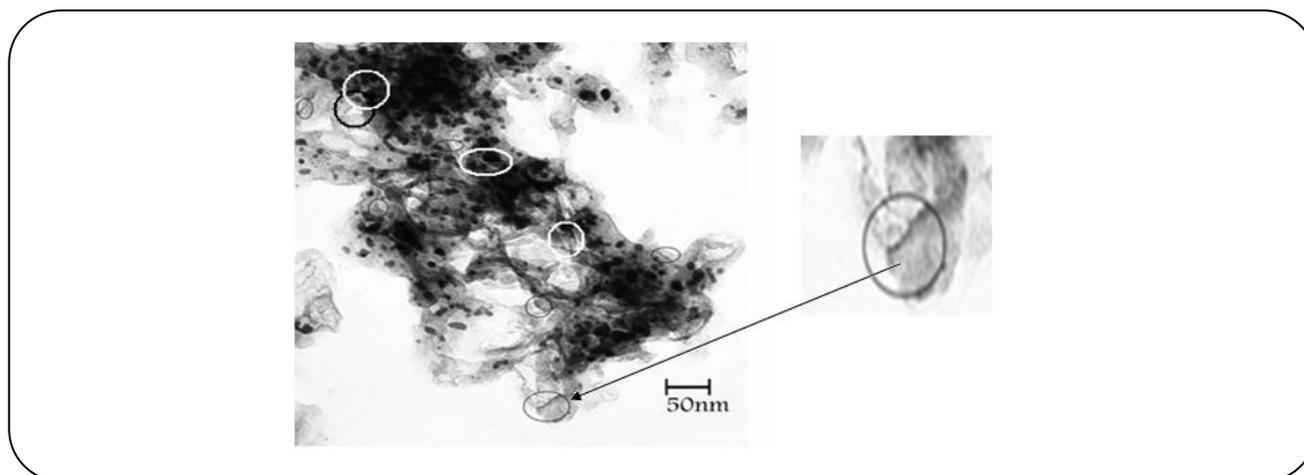


Fig. 7: TEM image of PS/OMMT (1.6%) nanocomposite.

the plasticized sulfur matrix and the modified montmorillonite. Unreacted sulfur was observed in the TEM image as black points.

Mechanical testing techniques

The effect of NaMMT and OMMT contents on the mechanical properties of composites are graphically shown in Fig. 8. Mechanical properties of composites depend on many factors like the ratio of filler and degree of dispersion of the filler in the matrix. As is shown in Fig. 8 A and B, mechanical properties such as the compressive and flexural strength of the plasticized sulfur/NaMMT (PS/NaMMT) prepared by direct-mixing method show a tendency to decrease and then increase with increasing NaMMT content and show the maximum value at the 1.6% of the NaMMT content. This phenomenon confirms that composite has been destroyed before critical value (1.6%) and at the higher concentration some aggregates were happened but generally, there is not a good compatibility between NaMMT and plasticised sulfur.

Fig. 8 C shows the tensile strength of the plasticized sulfur/NaMMT (PS/NaMMT) prepared by the direct-mixing method. This Fig. shows a tendency to decrease and then increase at the 3.0 %Wt. of NaMMT. Mechanical properties of the plasticized sulfur/OMMT (PS/OMMT) are considerable compared to plasticized sulfur/NaMMT (PS/NaMMT). Plasticized sulfur nanocomposite containing %1.6 of OMMT showed the highest tensile and compressive strength equal to 24.23 and 4.07 Mpa, which was about 7 and 3 times higher than unfilled plasticized sulfur respectively.

The maximum flexural strength (Fig. 8 B) of plasticized sulfur nanocomposite containing 1.0% of OMMT was equal to 7.08 Mpa, which was about 2 times higher than NaMMT plasticized sulfur. The improvement of the mechanical properties is a result of stronger interaction between OMMT and plasticized sulfur and OMMT in this concentration, possesses higher stress bearing capability and efficiency. Addition of more OMMT decreased the mechanical properties and at the higher concentration, some aggregates happened. The obtained results are in accordance with other results that generally mechanical properties of OMMT polymer composites were better than NaMMT polymer composites [6-19].

The effect of nanocomposite formation on the elongation at break has not been widely investigated yet. The elongation at break of plasticized sulfur nanocomposites is shown as a function of clay loading in Fig. 9 This Fig. 9 shows that OMMT reduced elongation properties of the sulfur nanocomposite. In contrast, NaMMT improved elongation properties of the sulfur nanocomposite. In OMMT sulfur nanocomposite, exfoliated phenomena caused improving rigidity of the composite and meanwhile decreasing the elongation. The elongation at break for almost all nanocomposites was lower than that of the original matrix. A reduction in elongation is characteristic of most of the filled polymer composites because the additive effectively reduces the cross-section of the polymer resisting deformation. The polymer-filler interface often acts as a point of weakness and thus induces premature break.

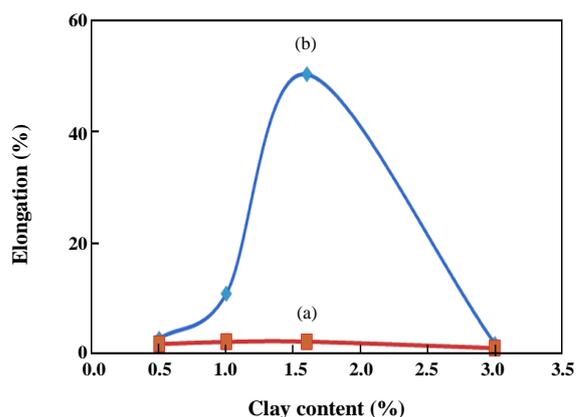
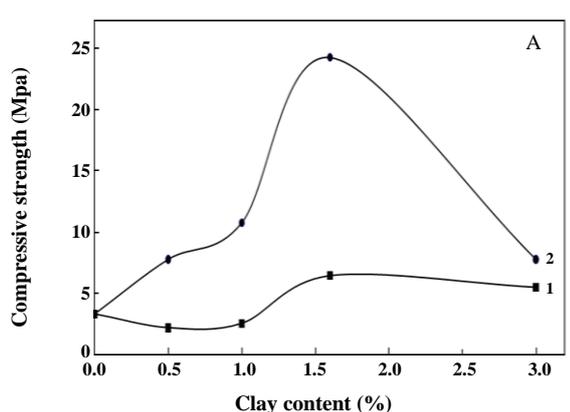


Fig. 9: Elongation percent of (a) PS/OMMT and (b) PS/NaMMT nanocomposites.

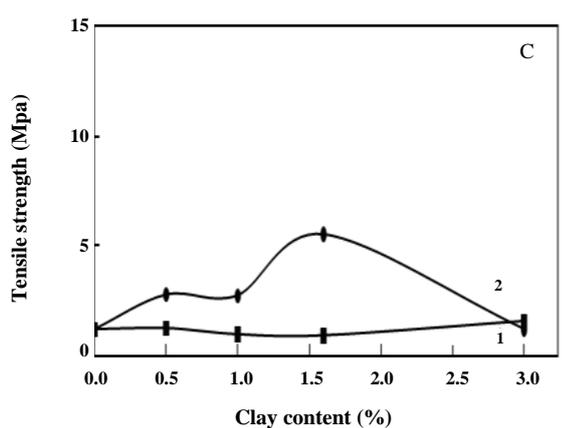
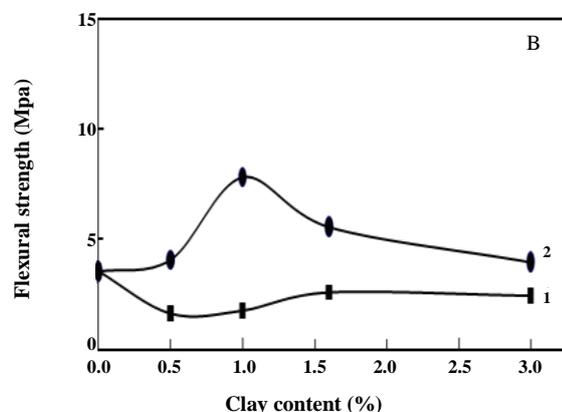


Fig. 8: Effect of NaMMT (1) and OMMT (2) on (A) compressive, (B) flexural and (C) tensile properties of PS/NaMMT and PS/OMMT nanocomposites.

CONCLUSIONS

Plasticized sulfur nanocomposites were prepared by reinforcing plasticized sulfur matrix with 1.6 % of modified montmorillonite and showed the proper interaction between matrix and the inorganic components. TEM

and X-ray observations suggested the possibility of formation of exfoliated structures in plasticized sulfur OMMT nanocomposite containing 1.6 % of OMMT. The mechanical properties of plasticized sulfur nanocomposites containing OMMT compared to plasticized sulfur nanocomposites containing NaMMT were in general greatly improved; this improvement was related to the stronger interaction between OMMT and plasticized sulfur and possible exfoliation of silicates layers in the plasticized sulfur. Study of mechanical properties showed that tensile and compressive strength increased up to an OMMT content of 1.6 % and flexural strength increased up to an OMMT content of 1.0 %. Therefore, OMMT acts as reinforcing agent. In the other way, OMMT contents above 1.6 % decreased the mechanical properties. This behavior attributed to the formation of some OMMT agglomerates.

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REFERENCES

- [1] Pavlidou S., Papaspyrides C.D., [A Review on Polymer-Layered Silicate Nanocomposites](#), *Prog. Polym. Sci.*, **33**: 1119-1198 (2008).
- [2] Kiliaris P., Papaspyrides C.D., [Polymer/Layered Silicate \(Clay\) Nanocomposites: An Overview of Flame Retardancy](#), *Prog. Polym. Sci.*, **35**: 902-958 (2010).
- [3] Shamsipur M., Bahrami A., Hajitarverdi M.S., Yazdimamaghani M., Zarei F., [Influence of Micro and Nano Silica on Mechanical Properties of Plasticized Sulfur Composites](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **32**: 1-7 (2013)
- [4] Gupta V.K., Agarwal S., Pathania D., Kothiyal N.C., Sharma G., [Use of Pectin-Thorium \(IV\) Tungstomolybdate Nanocomposite for Photocatalytic Degradation of Methylene Blue](#), *Carbohydr. Polym.*, **96**(1): 277-83 (2013)
- [5] Manafi M.R., Manafi P., Agarwal S., Bharti A. K., Asif M., Gupta V. K., [Synthesis of Nanocomposites From Polyacrylamide and Graphene Oxide: Application as Flocculants for Water Purification](#), *J. Colloid Interface Sci.*, **490**: 505-510 (2017)
- [6] Saleh A. T., Gupta V.K., [Column with CNT/Magnesium Oxide Composite for Lead \(II\) Removal from Water](#), *Environ. Sci. Pollut. Res.*, **19**: 1224-1228 (2012)
- [7] Gupta V.K., Agarwal S., TA Saleh T.A., [Synthesis and Characterization of Alumina-Coated Carbon Nanotubes and Their Application for Lead Removal](#), *Journal of Hazardous Materials, Chem. Eng. J.*, **185**: 17-23 (2011)
- [8] Gupta V.K., Nayak A., [Cadmium Removal and Recovery From Aqueous Solutions by Novel Adsorbents Prepared From Orange Peel and Fe₂O₃ Nanoparticles](#), *Chem. Eng. J.*, **180**: 81-90
- [9] Xiong J., Liu Y., Yang X., Wang X., [Thermal and Mechanical Properties of Polyurethane/Montmorillonite Nanocomposites Based on a Novel Reactive Modifier](#), *Polym. Degrad. Stabil.*, **86**: 549-555 (2004).
- [10] Ray S.S., Okamoto M., [Polymer/Layered Silicate Nanocomposites: a Review From Preparation to Processing](#), *Prog. Polym. Sci.*, **28**: 1539-1641 (2003).
- [11] Zhao C., Qin H., Gong F., Feng M., Zhang S., Yang M., [Mechanical, Thermal and Flammability Properties of Polyethylene/Clay Nanocomposites](#), *Polym. Degrad. Stabil.*, **87**: 183-189 (2005).
- [12] Gârea S.A., Iovu H., Voicu G., [The Influence of Some New Montmorillonite Modifier Agents on the Epoxy-Montmorillonite Nanocomposites Structure](#), *Appl. Clay Sci.*, **50**: 469-475 (2010).
- [13] Gu Z., Song G., Liu W., Wang B., Li J., [Preparation and Properties of Organo-Montmorillonite/cis-1,4-Polybutadiene Rubber Nanocomposites by Solution Intercalation](#), *Appl. Clay Sci.*, **45**: 50-53 (2009).
- [14] Madaleno L., Schjdt-Thomsen J., Pinto J.C., [Morphology, Thermal and Mechanical Properties of PVC/MMT Nanocomposites Prepared by Solution Blending and Solution Blending + Melt Compounding](#), *Compos. Sci. Tech.*, **70**: 804-814 (2010).
- [15] Davarpanah Z., Keramat1 J., Hamdami N., Shahedi M., Behzad T., [Dispersion of Silicate Layers in Zein/Montmorillonite Composite Films Using Two Sonication Methods](#), *J. Agr. Sci. Tech.*, **18**: 1523-153 (2016).
- [16] Tajeddin B., [Preparation and Characterization \(Mechanical and Water Absorption Properties\) of CMC/PVA/Clay Nanocomposite Films](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **35**(3): 9-15 (2016)
- [17] Yuan X., Li X., Zhu, E., Hu J., Cao S., Sheng W., [Synthesis and Properties of Silicone/Montmorillonite Nanocomposites by In-Situ Intercalative Polymerization](#), *Carbohydr. Polym.*, **79**: 373-379 (2010).
- [18] Zhao F., Bao X., McLauchlin A.R., Gu J., Wan C., Kandasubramanian B., [Effect of POSS on Morphology and Mechanical Properties of Polyamide 12/Montmorillonite Nanocomposites](#), *Appl. Clay Sci.*, **47**: 249-256 (2010).
- [19] Paulson J.E., Simic M., Campbell R.W., [Sulfur Composites as Protective Coatings and Construction Materials](#), in: Bourne D.J., Ed., "New Uses of Sulfur", American Chemical Society, pp. 215-226 (1978).
- [20] Sullivan T.A., McBee W.C., and Blue D.D., [Sulfur in Coatings and Structural Materials](#), "New Uses of sulfur-II", American Chemical Society, 55-74 (1975).
- [21] McBee W.C., Sullivan A., [Structural Material](#), *US Patent, No. 4022626*, (1977).
- [22] Ludwig A.C., Dale J.M., Frazier H.F., [Sulfur Compounds and Method of Making Same](#), *US Patent, No. 4290816*, (1981).

- [23] Vroom A.H., Sulfur Cements, [Process for Making Same and Sulfur Concretes Made Therefrom](#), *US Patent NO. 4293463*, (1981).
- [24] O'Brien M.H., Erickson A., [Process and Material That Encapsulates Solid Hazardous Waste](#), *US patent, No. 5962630*, (1999).
- [25] Willis C.G., Miller B.R., [Plasticized Sulfur Compositons and Method of Manufacturing Same](#), *US Patent, No. 5304238*, (1994).
- [26] Marinus J.R., [Modified Sulphur and Product Comprising Modified Sulphur as Binder](#), *US Patent No. 2007/0068422 A1*, (2007).
- [27] Simic M., [Sulfur Composition with Mica](#), *US Patent No. 4026719*, (1977).
- [28] Simic M., [Plasticized Sulfur Compositon](#), *US Patent, No. 4164428*, (1979).
- [29] Schneider R.A., [Monoolefinic Plasticized Sulfur](#), *US Patent, No. 4282040*, (1981).
- [30] Bahrami-Adeh, N., Afghani T., Shamsipur M., [Study of Morphology and Thermal Behavior of Newly Prepared Plasticized Sulfur](#), *J. Iran. Chem. Soc.*, **8**:1063-1072 (2011).