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An efficient ring-opening copolymerization of elemental sulfur with various olefinic compounds to produce thermoplastic polymeric sulfur: Synthesis and Characterization

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Abstract

Inverse vulcanization reaction is a copolymerization process that involves the interaction of elemental sulfur with alkenes at high temperatures to yield highly distinctive materials having high percentage content of sulfur. In this study, new polymeric sulfur compounds were synthesized via inverse vulcanization reaction in which elemental sulfur interacts with two different types of materials including thermoplastic polymers like amorphous Poly Alfa-Olefin (APAO) copolymer, and Ethylene-vinyl-acetate copolymer (EVA), while the second kind was thermoplastic rubber like styrene-butadiene-styrene copolymer (SBS), and rubber waste from MAC Carpet. The reaction occurred at 180 oC in the presence of bitumen as dissolving media. The polymeric sulfur products were chemically characterized by FTIR and XRD. Changes in the morphology of surfaces were examined by SEM. Thermal stability was also examined through DSC and TGA. Finally, dynamic mechanical properties were investigated using DMA. The result approved that all prepared polymeric sulfur have high stiffness, and the polymeric sulfur based on alfa olefin, and SBS have higher storage modulus than EVA, and Mac waste materials. Also, glass transition temperatures Tg of prepared polymerics sulfur were around 58 °C to 63 °C that confirms their high thermal resistance. Consequently selected synthesized materials succeeded as good elasticators for sulfur polymerization.

Keywords: styrene-butadiene-styrene, olefins, Industrial waste materials, inverse vulcanization, Polymeric sulfur

1. Introduction

Nowadays sulfur is produced with megatons as byproducts from oil and gas refinery processes through the removal of poisonous and corrosive hydrogen sulfide and carbon dioxide gases to prevent the pollution of the environment and corrosion of the metals [1]. This process leads to the availability of sulfur in large quantities with the anniversary overall production that ranged about 70 Mm3 ton which makes it one of the cheapest materials on Earth [2]. The sulfur element is mainly employed for producing sulfuric acid, cosmetics, fertilizers, and crosslinking agents for rubbers. However, these applications are considered limited due to the huge surplus of the sulfur element, which sometimes reaches mega tons per year [3]. Furthermore, for almost a century, polymeric sulfur and polymers containing sulfur have attracted scientific interest. However, obstacles in the chemistry of elemental sulfur have made it difficult

to produce sulfur-based polymeric compounds in substantial quantities. In the end, the straightforward production of distinctive polymers and composites directly from elemental sulfur offers an alluring new avenue in chemistry, the science of materials, and chemical engineering to produce inventive materials from an unusual chemical source. Incorporating a high content of S-S bonds into polymers provides beneficial features to substances since these groups are redox active, strongly polarizable, and display dynamic covalent nature [4]. It is well known that the vulcanizing process is one of the most important dependent reactions in the world of rubber manufacturing, which depends on the reaction of the double bond in polymer units with a little sulfur content at high temperatures that were found out by Charles Goodyear since 1844 as illustrated in *Scheme (1a)* [5]. This reaction yields the most famous cross-linked rubbers in our life now, where

most car tires are made. However, they introduced a mechanism of inverse vulcanization referring to the method at which the high content of sulfur is cross-linked by certain olefins in contrast to the usual vulcanization process as shown in *Scheme 1(b)*. This approach was demonstrated in 2013. This mechanism can be able to obtain various polymers with high content of sulfur from various olefins to be applied for different industries [6–8]. Several research efforts were carried out for using S8 to prepare thermoplastic polymeric sulfur with high content of sulfur [9–11]. The mechanism of these attempts was depending on the ring-opening polymerization (ROP) reaction [12–14]. Where at temperatures higher than 159 °C, S8 of octameric ring S8 is opened and diradicals are generated which attack another one of S8 molecules and so on until the S-S bond backbone of linear polymer is obtained [15]. Unfortunately, the prepared polymers in this way are not stable because the terminal free radicals orient themselves to a cyclic sulfur form and depolymerization is done [16]. So, the free radicals must be blocked to stabilize the polymeric sulfur through the reaction with certain dienes. Many dienes can be utilized for this process, including; synthetic dienes such as styrene [17], 1,4-diphenyl-butadiene [18], 1,3-di-isopropenyl-benzene (DIB)[19], 1,3,5-tri-isopropenyl-benzene [20], methylated styrene [21], fractional distillates of C5 [22, 23], natural di-enes as cardinol benzox-azines [24], limon-ene [25], myrc-ene [13], the oil of canola [26], epoxy resin [27], terpenoids, triglycerides, fatty acids, sorbitan esters, amino acid derivatives, and guaiacol derivatives.
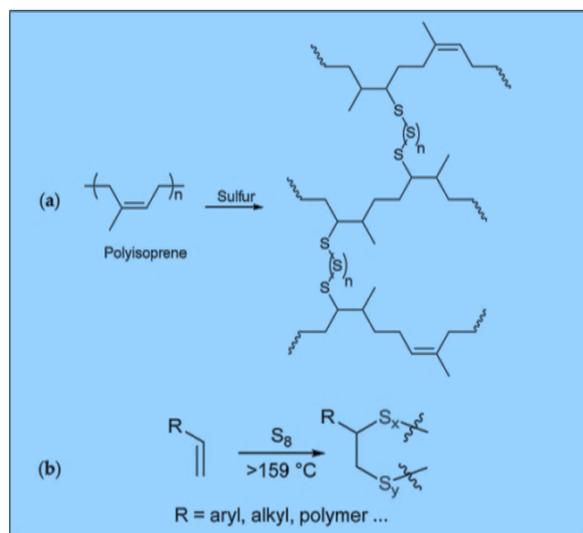
***Scheme* 1: (a) vulcanization and (b) inverse vulcanization processes [28].**

In this manuscript, two types of material including aliphatic thermoplastic polymers such as (Ethylene-vinyl acetate-copolymer (EVA), Amorphous poly alfa-olefin (APAO) copolymer), and aromatic

thermoplastic rubber-like (styrene-butadiene-styrene copolymer (SBS), and styrene rubber waste from industrial MAC Carpet company that were examined as plasticizing agents (elasticators) for elemental sulfur. Polymeric sulfur is chemically characterized by FTIR and XRD. Also, the surface morphology was scanned with SEM. Moreover, thermal stability was examined through DSC and TGA. Finally, the dynamic mechanical characteristics of prepared polymers were studied using DMA.

2. Materials and Methodology
2.1. Materials:
Sulfur element, Styrene butadiene styrene (SBS) copolymer purchased from KIMIA, amorphous poly alfa-olefin (APAO) copolymer Evonic industries. Germany, Tertiary amine, Ethylene Vinyl Acetate (EVA) copolymer purchased from Exxon-Mobil, and rubber waste from MAC Carpet Co.

2.2. Methods of preparation
Different high sulfur content polymers were prepared with different copolymers including; SBS, amorphous alfa olefin, EVA, and MAC residue. Firstly; 10 gm from each olefinic copolymer were individually dissolved in bitumen at 180 ºC which acts as dissolving media then 100gm of sulfur was added dropwise for each mixture, with continuous stirring for 2 hrs. The prepared polymeric sulfurs were allowed to cool at ambient temperatures. The general strategy for inverse vulcanization in this study is the direct dissolution of olefinic monomers into asphalt at 180 ºC followed by heating the molten state liquid sulfur above the floor temperature (Tf =159 ºC) for the ring opening polymerization (ROP) of S8, which enabled free-radical copolymerization to take place without the need for additional initiators or organic solvents at 180 ºC.

2.2.1 Copolymerization conditions and requirements
For the preparation of polymeric sulfur copolymers via inverse vulcanization, the copolymerization of different feedstock olefinic copolymers in liquid sulfur was conducted at 180 ºC to promote efficient ROP of S8 and afford chemically stable copolymers that did not readily depolymerize (*Scheme 2*). Bulk copolymerization in liquid sulfur at 180 ºC was conducted to ensure a sufficiently high concentration of sulfur diradicals generated from homolytic cleavage of S8 to promote the efficient initiation of the polymerization, as well as efficient propagation to S8 sulfur diradicals.

2.3 Evaluation of polymeric sulfur
The high-content polymeric sulfur was chemically evaluated via different techniques including: - FTIR (Fourier Transform Infrared Spectroscopy) using

NICOLETIS-10 (Thermo Fisher Scientific). Sulfur element and modified sulfur were taken as thin film and mixed with KBr powder to make the pellets for IR analysis, X-ray diffractometer (XRD) based on a Brucker D_8 advanced X-ray diffractogram with Ni filter, Cu-Kα radiation (λ=1.542 Å) at 40 KV, 30 mA and the speed of scanning is 0.02° / S, The morphology was scanned using Scanning electron microscope SEM Model ZEISS (EVO10) with 500X magnification power, and 20 kv of electron high tension (EHT) which is used for characterizing the microstructure and the morphology of polymeric sulfur, Thermal properties were evaluated using DSC and TGA through Universal TA instrument. (Perkin ElmercDSC7), Dynamic mechanical characteristics were examined by a micro-scale technique using TTDMA (Triton Technology)- according to (ASTM 4065, ASTM 4440, and ASTM 5279).
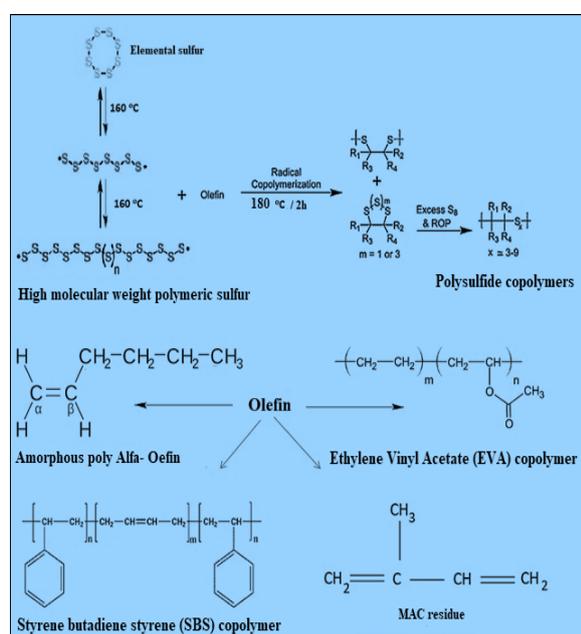
Scheme 2. The preparation of different types of high content polymeric sulfur copolymers by reaction of elemental sulfur with different kinds of an olefinic compounds such as (Styrene butadiene styrene (SBS), amorphous poly alfa-olefin (APAO), Ethylene Vinyl Acetate (EVA), (MAC residue) using one-pot inverse vulcanization

3. Results and Discussion
3.1 Structure elucidation of the prepared compounds

The chemical reaction between bitumen and sulfur can be classified into three kinds. Primary kind, sulfur dissolved into different segments of bitumen thus resulting in a solution. Another kind, sulfur interacts with bitumen and substitutes hydrogen to form hydrogen sulfide. The last kind, sulfur

crystallizes into micrometer-sized structures that perform as filler elements and residues in suspension form [29]. Bitumen can absorb as much as twenty percent (by weight of binder) or greater sulfur into its liquid form at representative mixing temperatures [30]. Sulfur performs as a binder and forms polysulfide at temperatures higher than 160ºC. The creation of polysulfide is important for cross-linking the bitumen with the organic molecules. In other words, sulfur chains (with hydrogen or alkyl group) perform as the linker between adjacent organic molecule chains, thereby bringing stiffness and strength. Bitumen's variable character and composition allow for varying levels of sulfur solubility. When the media is returned to room temperature, some of the dissolved sulfur may re-crystallize. Noted that additional mixing can avoid such re-crystallization [31].

3.1.1. FTIR Explanation
The initial formation of polymeric sulfur has been characterized by FT-IR spectra which depict the clear interaction of SBS, amorphous alfa olefin, EVA, and MAC olefinic with elemental sulfur. *Figures 1(from A to D)* illustrate FTIR curves for all polymeric sulfur and their corresponding elasticators, where *Figure 1(A)* represented the FTIR of pure EVA and its corresponding polymer (modified EVA), but *Figure 1(B)* displayed the FTIR of pure SBS and its corresponded polymer (modified SBS), while *Figure 1(C)* exposed FTIR of Pure MAC olefinic residue and its corresponded polymer (modified MAC olefinic residue), and *Figure 1(D)* showed FTIR of pure amorphous alfa olefin and its corresponded polymer (modified alfa olefin). By studying all curves, it was noticed the vanish of signals at 3040, 3010, and 1650 cm^{-1}, corresponded to the symmetric and symmetric stretching vibrations of C=C-H and stretching vibration of C=C respectively [32] which confirmed that the olefin moieties had been consumed in the reaction, as considered by loss of the olefinic C-H bending at 920 cm^{-1}, in addition to the appearance of a new peak at 966 cm^{-1} which corresponded to C-S bond vibration which resulted from free radical polymerization. Also, The lowering in peak intensity of the signal at 700 cm^{-1}, which is correlating to the C-H bending of cis di-substituted alkene [12], which considered as another proof of the polymerization reaction
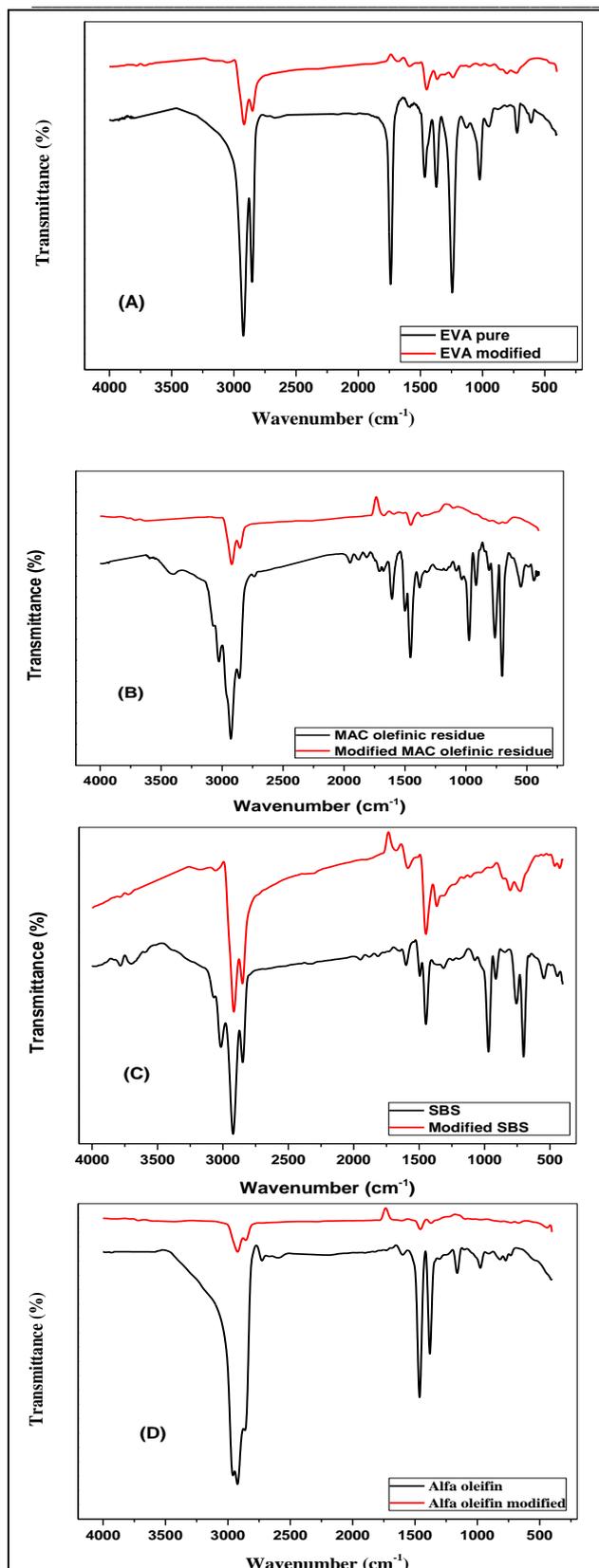
Figure (1) FTIR of elemental sulfur and polymeric sulfur based on different modifying agents

3.1.2. XRD Explanations

The copolymers produced from the inverse vulcanization process possess a natural amorphous structure with popular of them having cross-linked buildings and crystals of unreacted sulfur entrenched dependent on the content of sulfur and conditions of the vulcanization reaction [33]. The construction of the inverse vulcanized copolymer and the variation in the crystallite structure of pure sulfur before and after the vulcanization process were examined by X-ray diffraction. A representative example of pure sulfur compared with prepared polymeric sulfur (amorphous poly alfa-olefin (APAO), EVA modified, modified MAC olefinic residue, and modified styrene butadiene styrene) was presented in Figure 2. It was observed the Sulfur is crystalline; it showed sharp peaks at $2\theta = 23^{\circ}$, 27°, 28°, 53° and 56° (JCPSDNo. 08 024 7) [34, 35]. On contrary, the XRD pattern of the inverse vulcanized copolymer showed no crystalline peaks in other words the peaks of diffraction disappeared due to polymer formation [9].
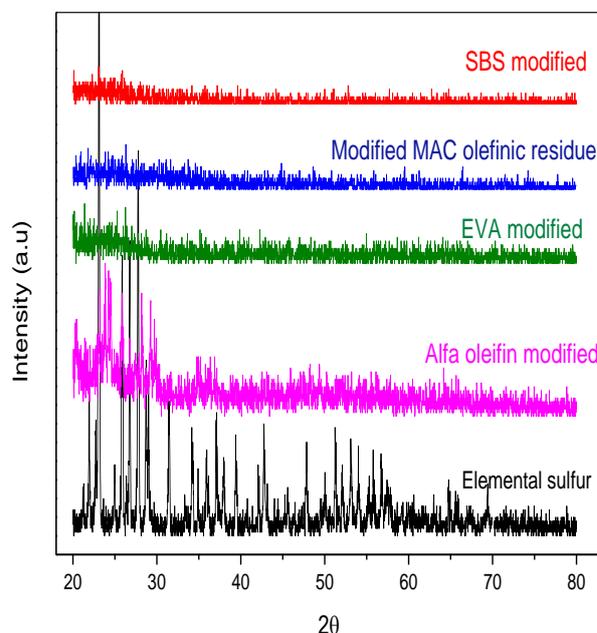

Figure (2) **XRD of elemental sulfur and polymeric sulfur based on different modifying agents**

3.1.3. Morphological study

The surface morphology of the sulfur before and after the vulcanization process with different olefinic compounds (amorphous poly alfa-olefin (APAO), EVA, MAC olefinic residue, and styrene butadiene styrene) was analyzed by scanning electron microscopy (SEM) *Figure 3(a-d)*

The surface morphology of pure sulfur is presented in *Figure 3a.* Showed particles with irregular shapes and it was noticed that the presence of high numbers of pores formed in the surface of

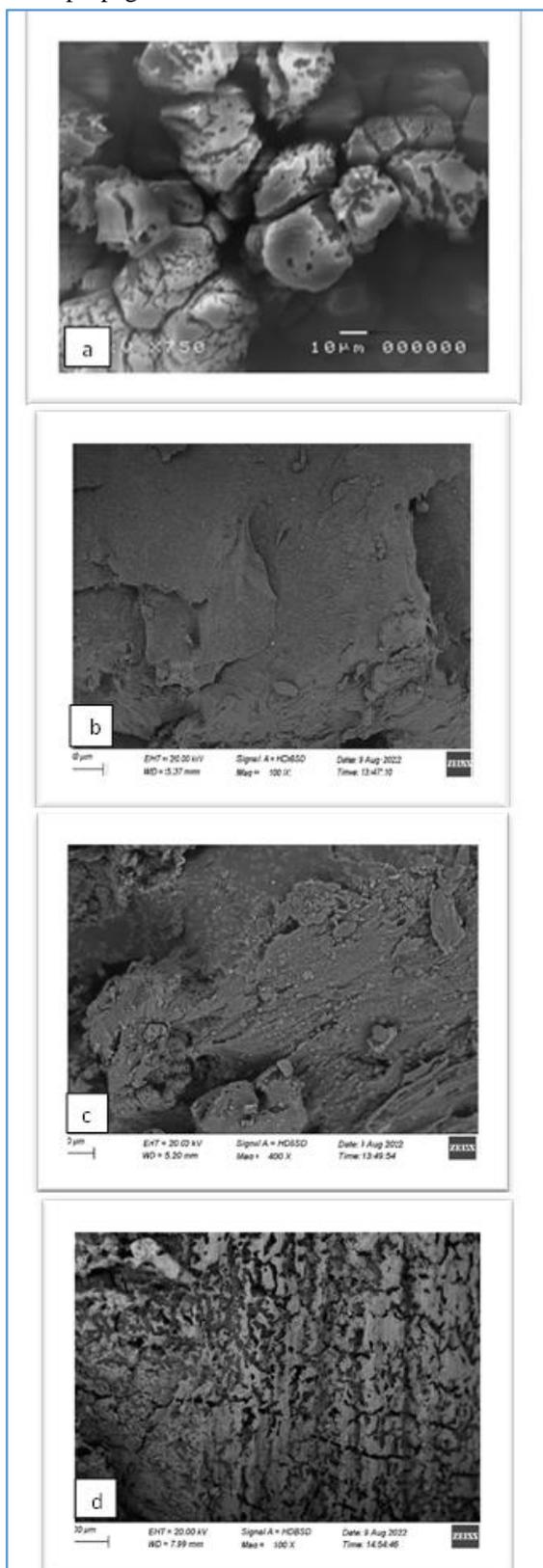pure sulfur due to β- to α- a transition which led to crack propagation in the surface.

Figure (3) SEM micrograph of Sulfur (a) and prepared polymeric sulfur (b,c,d)

On the other side, the surface of polymeric sulfur **Figure 3(c-d)** showed smooth surfaces with the absence of phase separation and crystals because during inverse vulcanization reaction, cross-linking destroyed the crystalline arrangements of sulfur and it turned into a uniform amorphous polymer [37], which indicates the successful conversion of the crystalline sulfur to amorphous copolymers. The results reveal graphically how the polymer controls the crystallization of sulfur, preventing the growth of macro crystals, and thereby imparting durability. This result was compatible with the XRD data.

3.2 Thermal studies

3.2.1. DSC analysis

In general, there are numerous crystalline types of elemental sulfur. From 116°C to 160°C as a liquid, Sulfur's structural form can be divided into two general groups. The first type was intra-molecular allotropes, in which sulfur atoms create molecules through chemical bonds. While the second kind is inter-molecular allotropes where lattice structures form through the arrangement of molecules [38]. Sulfur can create both rings and chains, giving rise to a wide variety of intra-molecular allotrope combinations. Sulfur exists in two prevalent solid allotropes: orthorhombic (α) and monoclinic (β) [39]. These sulfur allotropes are made up of cyclic units with eight sulfur elements. The most prevalent and anisotropic form of sulfur is orthorhombic. Orthorhombic, (Sα) was stable at temperatures up to 95°C, While monoclinic (Sβ) is stable at temperatures ranging from 95°C to 120°C (melting point) [40]. However, it is crucial to remember that if the monoclinic sulfur form was quenched to a solid form at room temperature, it is probable to revert to its α form [41]. It is known that for pure sulfur, Sα→Sβ transition occurs at 105 °C, however, Sβ→Sγ transition occurs at 122 °C. The thermal properties of sulfur-based polymers were investigated using DSC. As shown in **Figure 4,** the DSC thermo-gram of the elemental sulfur was utilized as a control sample which displays two melting peaks at 109 ° C comparable to the melting transitions from the orthorhombic, and 119°C identical to melting transitions from monoclinic phases [42]. While the DSC thermo-grams of the inverse vulcanized copolymers showed a significant decrease in the height of the peaks compared with the corresponding one in pure sulfur and no melting peaks could be detected which demonstrates these copolymers are amorphous [33]. The DSC curves exposed that

mentioned elasticators have effectively prevented α → β transformation process which is responsible for sulfur depolymerization which is responsible for crack formation. Similar findings were observed from XRD analysis and scanning electron microscopy (SEM).
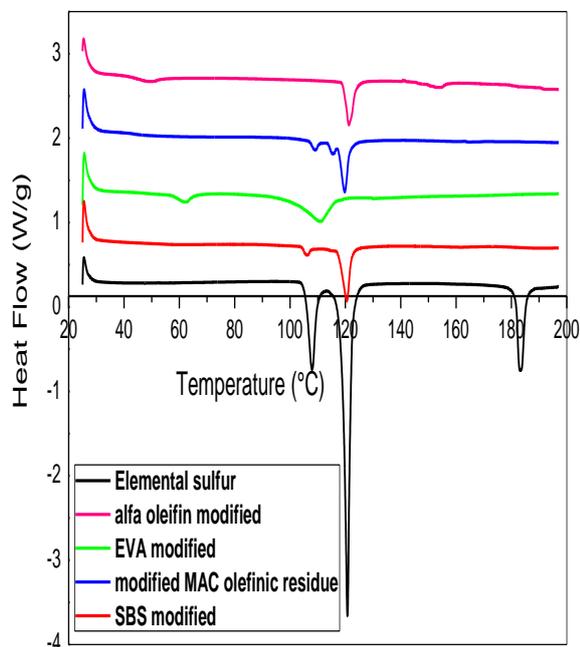

Figure (4) DSC of pure and polymeric sulfur based on different modifying agents

3.2.2. TGA Analysis

Figure 9 shows the TGA curves for the sulfur element and prepared polymeric sulfur. All samples started to decompose at around 250 °C. Also, it is noticed that pure sulfur is completely decomposed at approximately 300 °C, with a weight loss of around 95%. However, other prepared polymeric sulfur was completely decomposed at around 500 °C, with weight loss ranging from 60 to 80 %. However, the thermal stability and decomposition tendency changed when sulfur was incorporated into a bulk copolymerization process with olefinic compounds. In this case, the inverted vulcanized copolymer decomposes in three stages, the first of which begins at about around 210 ºC released SO_2 gas due to sulfur degradation [43]. The weight loss in the first step increased with an increase in the sulfur content in the copolymers [44]. While the second decomposition step was due to the decomposition of the organic content of the copolymer which starts decomposing at temperatures ranging from (250 to 300ºC) depending on the type of co-monomer this step corresponds with releasing CO and CO_2 [3, 45]. The

third step occurred at a temperature above 300 ºC accompanied by released traces of CO and CO_2 beside SO_2 from the sulfur that is directly bonded to C-atoms [46]. By making a comparison, it is concluded that the inverse vulcanized copolymer is more thermally stable than sulfur, with an important portion of mass residual after heating to 500 ºC, indicating the creation of polymeric material. Additionally to this, the polymeric sulfur based on EVA, SBS, and Mac waste is the most thermally stable prepared polymers.
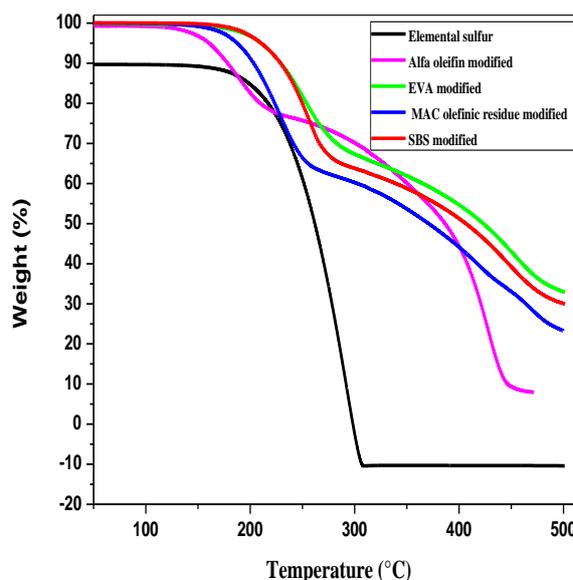

Figure (5) TGA of pure and polymeric sulfur based on different modifying agents

3.2.2. Dynamic Mechanical characteristics (DMA)

The variety of inverted vulcanized copolymer structures makes it difficult to characterize these copolymers. Since the copolymers produced by the reaction of sulfur and olefinic compounds take the form of thermosets with highly cross-linked structures, it is impossible to assess their rheological properties using rheometers, which needs re-melting of the copolymer [47]. DMA can be an effective substitute method provided that the standard protocols are followed. They involve first creating the pre-polymer, then molding it, and curing process it at the same creation temperature [48]. As well as, the DMA unlike the DSC thermogram which was established to be more sensitive and is valuable in determining the transition between the glassy states to rubbery states Tg of such copolymers, So, it is greatly recommended to use DMA as a main characterization method for these copolymers [28, 49]. *Figure (6)* **and** *Figure (7)* represent the study of

storage modulus and damping coefficient (tan δ) respectively using DMA is useful in determining the performance of the preparation of polymeric sulfur based on EVA, SBS, alfa olefin, and Mac waste residue under the stress at a temperature range between 20 to 100 °C. It is observed in *Figure (6)* that polymeric sulfur based on EVA, alfa olefin, and SBS have outstanding improvements in strength modulus than Mac waste residue, this can be attributed to the higher proportion of organic material in the polymeric sulfur based on EVA, alfa olefin, and SBS, which contains more double bonds and can stabilize the chains of sulfur crosslinking the material, the storage modulus rises as the weight percentage of sulfur in the composites declines [39, 42]. Although the increase in the cross-linking resultant of the existence of additional double bonds in Mac wastes residue molecule, the close nearness of cross-linkable sites leads to encouraging the intra-molecular cross-linking-based formation of some cyclic structures. Such intra-molecular crosslinks would increase the overall strength of the materials [7, 50]. As a result, Mac waste residue possesses a lower value of storage modulus. Also, the glass transition temperature (T_g) can be measured from the temperature corresponding to the highest peak for tan δ curves shown in *Figure (7)*. It was observed that the T_g of the prepared polymeric sulfur ranged from 58.4°C (alfa olefin) to 63.6°C (EVA). This confirms the high thermal resistance of polymeric sulfur samples, which is in agreement with the thermal study previously mentioned in section (3.2.2).
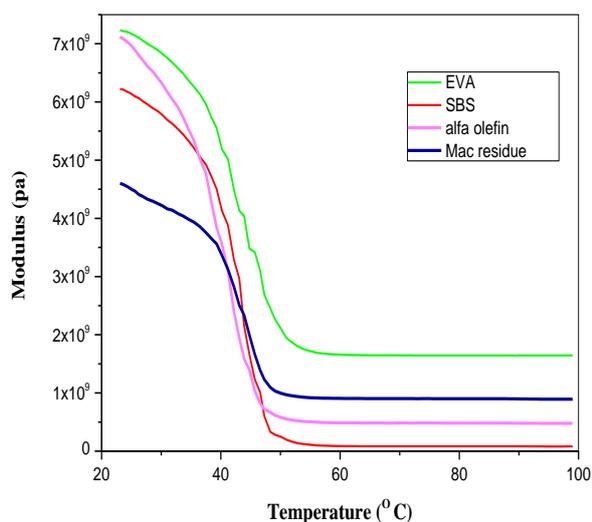

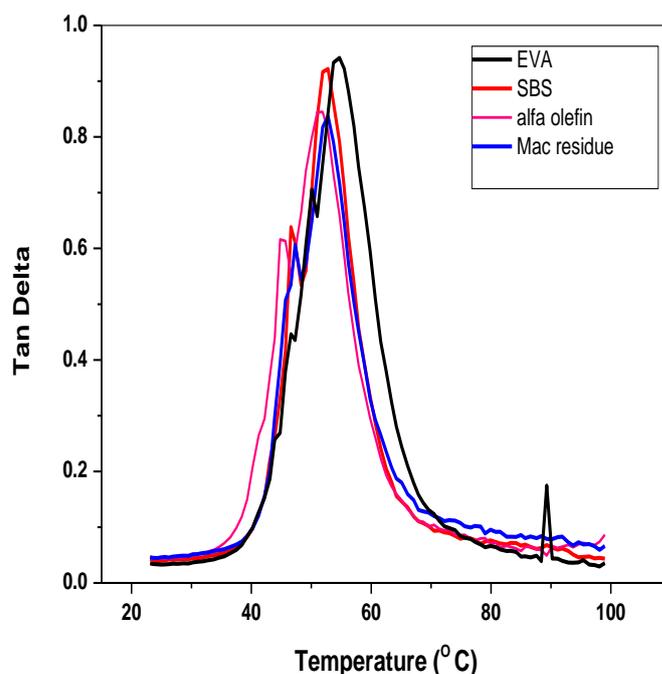*Figure (6)* **Modulus of polymeric sulfur based on EVA, SBS, alfa olefin, and Mac waste residue**

Figure (7) Tan delta of polymeric sulfur based on EVA, SBS, alfa olefin, and Mac waste residue

4-Conclusion

In this study, two types of materials were used as elasticators for sulfur polymerization including thermoplastic polymers (such as EVA, and APAO), and thermoplastic rubber (such as SBS, and rubber waste from the industrial MAC carpet). The inverse vulcanization process was chemically confirmed by FTIR spectra which approved the occurrence of a free radical polymerization reaction. The crystallographic structure was studied by an XRD spectrophotometer that showed a complete difference between diffraction peaks for pure sulfur and prepared polymeric sulfur. The scanning microscope showed an obvious distinction between the surface morphology of sulfur and prepared polymeric sulfur. The scanned surface for polymeric sulfur showed one phase surface with no pores that enable crack propagation. Differential scanning calorimetry study confirmed the reaction of the elasticators with sulfur able to prevent α → β transformation process which is responsible for sulfur depolymerization and followed by cracks formation. Also, a thermal gravimetric study conclude that polymeric sulfur based on EVA, SBS, and MAC waste rubber showed high thermal stability than polymeric sulfur based on APAO. Finally, the prepared polymeric sulfurs were exposed to a temperature sweep from 20 °C to 100 °C to study their dynamic mechanical properties including storage modulus and damping co-efficient

tan delta. The results confirmed that polymeric sulfur based on APAO, and SBS gave higher stiffness than EVA and MAC waste rubber. Also, glass transition temperatures T_g were around 58 °C to 63 °C that confirms their high thermal resistance.

4.   Acknowledgment

5. Declarations

The authors of the manuscripts confirm that there is no conflict of interest between this study with other studies

6. Data Availability Statement

All data and materials are included in the manuscript

7. References

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