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Evaluation of the dynamic mechanical analysis, water absorption and chemical resistance properties of sulfur/epoxy composites

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Abstract

Modified epoxy composites have become attractive materials for various applications including coatings, polymer concrete, and with asphalt as steel bridge pavement material. In such applications, it is important to maintain high chemical and mechanical resistance to avoid load cracking and corrosion resulted from chemicals exposures. The purpose of this study is to produce sulfur/epoxy composites with excellent mechanical and chemical properties and able to be applied easily in a wide range of applications. The epoxy resin was mechanically mixed with different percentages of sulfur and linseed oil to form sulfur/epoxy composites. Where sulfur is well incorporated into the epoxy matrix. The prepared composites were characterized by dynamic mechanical analysis including storage modulus, loss modulus, and tan delta. In addition, the chemical and water absorption resistance was tested including two hours boiling water absorption resistance and long-term water absorption resistance. The results showed enhanced storage modulus, glass transition temperature, chemicals, and water absorption resistance. Also, it is observed that as the concentration of sulfur increases, the mechanical and chemical resistance properties increase.

Keywords: additives**;** adhesion**;** blends**;** coatings**;** plastics.

1. Introduction

Epoxy networks are one of the most important thermoset materials. Due to their excellent properties, such as low shrinkage during curing, high strength and stiffness, good adhesion, resistance to chemicals, and creep and good thermal characteristics, They are widely used for coatings, structural adhesives, and composites applications, as well as electrical and electronic materials. [1] Epoxy resin contains two or more epoxide groups per monomer. During the polymerization process, the hardener opens the C—O—C rings, and the bonds are rearranged to form a three-dimensional network of cross-linked chains. For certain types of epoxy resins, The cure reaction occurs rapidly at room temperature, although many of the high-strength epoxies used in aircraft need to be cured at high temperature (120–180 °C) [2].

Regarding the importance of epoxy resins, many researches endeavors were performed to modify epoxy resins to enhance their properties to be applied in a wide range. This includes incorporating nanomaterials into the epoxy matrix and reinforced epoxy resins with different fibers. Mehrzad Mortezaei and et al [3] modified epoxy resin with three types of nanosilica particles with different averages particle diameters (12, 20, and 40 nm). Where the nanosilica particles show a positive effect

on increasing the modulus and fracture toughness of the modified epoxies. However, they did not affect the glass transition temperature. Göksenin Kurt Çömlekçi and S. Ulutan [4]modified an epoxy resin by incorporating microcapsules containing either linseed oil or linseed oil-alkyed to produce self-healing coating. This incorporation changes the water vapor permeability as decreasing for the linseed oil-alkyed microcapsules while slightly increasing for linseed oil microcapsules. The adhesion strength on the metal surface was decreased due to the formation of low adhesion spots. Corrosion resistance was improved and the thermal properties did not affect negatively. Engin Sarikaya and et al [5] reinforced epoxy resin with different natural fibers; birch, palm, and eucalyptus fibers. eucalyptus fiber-reinforced composites gave the highest tensile strength and bending stress and palm fiber-reinforced composite had the highest impact energy.

Elemental sulfur, which usually occurs in the form of eight-member rings, is a solid at ambient temperatures and insoluble in water and most other liquids. Most of the sulfur used in the industry comes as a by-product of fossil fuel desulfurization[6].
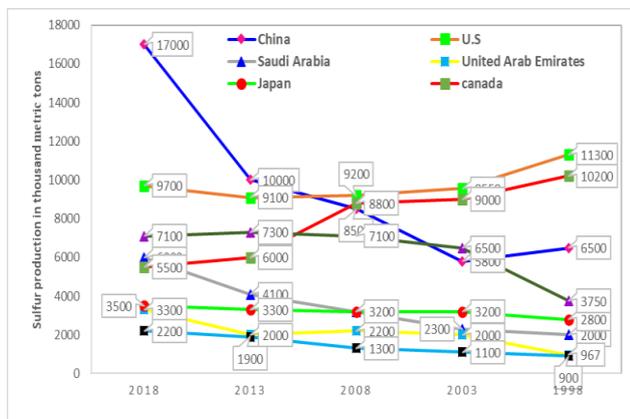

Figure 1. The top sulfur-producing countries from 1998 to 2018[7]

The largest consumer of sulfur is the fertilizer industry, which accounts for approximately 60% of the sulfur market [8]. However, due to the increase in the production of sulfur up to 80 million metric tons per year. This may cause environmental pollution results from the accumulation of a large amount of unused sulfur. So, to avoid this problem we must increase the application fields of sulfur. Soo-Jin Park and coworkers[9] modified epoxy resin with

polysulfone (a sulfur-containing compound). The modified epoxy showed a fracture toughness improvement with no thermal stability change occurred. Seunggun Yu and etal[10] fabricated sulfur through the polymerization reaction with a high content of oligomeric DCPD (60%weight). The resulted liquid state sulfur polymer was mixed with epoxy and asphalt for the production of LSP/epoxy asphalt (LSPA) which employed as repairing asphalt pavement materials. LSPA showed an increase in marshall stability and indirect tensile strength. Moreover, LSPA showed a decrease in repairing time by rapid hardening (< 1h) and excellent adhesion strength of approximately 1.95 MPa.

Herein, we applied sulfur in the epoxy industry to produce a safe and useful sulfur/epoxy composites. Where sulfur acts as a toughening agent and reinforcement material.

2. Expermental

2.1 Materials

Elemental sulfur produced by Egyptian refining company (ERC) as a byproduct from petroleum oil refining, commercial linseed oil produced by Tanta flax and oil company, El Gharbia, Egypt with the specifications showed in Table 1, commercial epoxy resin (Kempoxy150) part A, and its hardener part B supplied by Chemicals for Modern Building International Company (CMB) with the technical properties in Table 2 and Hydrochloric acid, Sulfuric acid, Acetic acid, Benzene, and Sodium hydroxide which are purchased from Sigma Aldrich USA. All chemicals were of AR grade and were used without further purifications.

Table 1. Specifications of linseed oil

Appearance	Yellow to brown liquid
Freezing point	-23.9 °C
Boiling point	> 315.6 °C
Flashpoint	206.1 °C
Relative density	0.925-0.935 kg/l

Table 2. Technical properties of (Kempoxy 150)

Color	Transparent
Solid content (by weight)	100 %
Density	1.11 ±0.02 kg/l
Mixing ratio, A: B by weight	2: 1
Full hardness	7 days

2.2 Methods

Regarding Table 3, elemental sulfur was melted in a thermostatic oil bath at 160-170 °C, linseed oil was added and mechanically mixed (1000 rpm) for 20 minutes then the appropriate amount of epoxy (part A) was added with continuous stirring and temperature keeping at 150 °C for about 2 hours. Finally, the produced composites (component A) were handily mixed at room temperature with the curing agent (part B) and lifted for full curing after 7 days.

Table 3. Sulfur/epoxy composites

		SO	SAA	SAB	SME	SMO
Component A (%)	Epoxy (part A)	100	90	80	70	60
	Sulfur	-	7	14	21	28
	Oil	-	3	6	9	12
Curing mixing ratio (Epoxy part A: hardner part B) is 2:1 according to the supplier						

2.3 Characterization

2.3.1 Fourier transform infrared spectroscopy

FTIR spectra were recorded using Nicolet IS-10 FTIR spectrophotometer (Thermo Fisher Scientific). The specimens were finely grinded and mixed with KBr, then these mixtures were compressed into pellet forms. FTIR spectral analysis was performed within the wavenumber range of 400–4000cm-1.

2.3.2 Dynamic mechanical analysis (DMA)

The dynamic mechanical analysis was performed by Triton Technology-TTDMA. Dynamic mechanical analysis is a useful technique for the experimental characterization of the small-strain

viscoelastic properties of polymers [11]. it refers to the response of a certain material to cyclic or dynamic forces which can be expressed in the form of storage modulus (elastic modulus, G'), loss modulus(viscous modulus, G'') and tan δ (damping coefficient, G''/G'). Results are usually represented as a graphical plot of G', G'', and tan δ as a function of temperature, frequency, or time.   Disk-formed specimens with a diameter of 10 mm and a thickness of 3 mm were tested using three-point bending mode and 1Hz frequency. The storage modulus is a measure of the elastic behavior of a sample which often associated with stiffness and it is conceptually related to Young's modulus, however, they are not identical. It is proportional to the maximum energy stored during a loading cycle. Loss modulus for a material is the dissipation of energy for that material under cyclic loading also known as damping and measured as the ratio between the loss modulus and the storage modulus [12].

2.3.3 Chemical Resistance

The chemical resistance of sulfur/epoxy composites against some chemicals such as 37% HCl, 30% H2SO4, 30% CH3COOH, 60% NaOH, and Benzene was evaluated according to ASTM D 543-06. Three specimens for each sample were weighed to the nearest 0.001 gm. The specimens were allowed to be immersed in the respective fresh chemical reagents for 7 days at room temperature. The reagents were stirred every 24 h by moderate manual rotation of the containers. After 7 days, the specimens were removed from the reagents, washed with running water, dried with a dry piece of cloth, and immediately weighed to the nearest 0.001 gm. The percent of weight gain was determined using Equation (1):

$$\text{Weight gain (\%)} = \frac{\text{Final weight} - \text{Initial weight}}{\text{Initial weight}} \times 100 \qquad (1)$$

2.3.4 Water Absorption Resistance

The relative rates of water absorption by the cured neat epoxy and sulfur/epoxy composites samples were determined according to ASTM D 570-98.

2.3.4.1 Two-Hours Boiling Water Immersion

The specimens were placed in a container of boiling distilled water. At the end of 120 ± 4 min, the specimens were removed from the water and were cooled in distilled water maintained at room temperature. After 15 ± 1 min, the specimens were removed from the distilled water, dried with a dry cloth, and weighed to the nearest 0.001 gm. The weight increase % was calculated as in Equation (2):

$$\text{Weight increase}(\%) = \frac{\text{wet weight} - \text{initial weight}}{\text{initial weight}} \times 100 \quad \textbf{(2)}$$

2.3.4.2 Long-Term Immersion

To determine the total water absorbance, the specimens were completely immersed in a container of distilled water maintained at room temperature and were weighed after 1st, 2nd, 3rd, 4th, 5th, 6th, and 7th week. For each week, the percentage of water absorbed was calculated by using Equation2.

3. Results and Discussion

3.1 FTIR

Figure 2. shows the FTIR spectra of linseed oil, epoxy resin, sulfur/epoxy composite, cured epoxy resin, and cured sulfur/epoxy composite. The major bands at 2926 cm^{-1} and 2853 cm^{-1} peaks are related to asymmetric stretching C-H of (CH$_3$ and CH$_2$) and the symmetric stretching of hydrogen (CH$_2$) in the hydrocarbon chain respectively [13]. The peaks at 1745 cm^{-1} are corresponding to the C=O stretching. The peaks at 1458 cm^{-1} result from the C-H bending vibration of the methylene group. Epoxy composites show significant peaks at 1605 cm^{-1} which are related to the C=C bond in benzene ring[14]. Epoxy composites show a signal at around 830 cm^{-1} which is related to C-H bending vibration mode of benzene ring. Linseed oil shows a significant peak at 3010 cm^{-1} and 1651 cm^{-1} which resulted from the stretching vibration of C-H (C=C) and C=C stretching vibration in the fatty acid chain. these peaks showed decreased intensities in epoxy composites. also, the peaks around 700 cm^{-1} are

related to C-H bending vibration of C=C bond [15]. This peak showed a decrease intensity in epoxy composites which represents another evidence of sulfur-free radicals attack and reaction on the double bond. The peaks appeared at 1246 cm^{-1} and 1035 cm^{-1} are related to C-O stretching vibration of epoxy aryl alky ether and C-OH bond respectively. These peaks tend to decrease intensities in the cured samples[16].

3.2 Dynamic mechanical analysis

Figure 3. shows the DMA plots of storage modulus versus temperature. Sulfur/epoxy composites give higher storage modulus than the neat epoxy. Where SME yielded an approximately 97% increase in storage modulus at 40 °C. this is an indication of the stiffness improvement of the prepared composites. The damping coefficient curves, tan δ, measured by DMA are shown in Figure 4. The peak height of tan δ decreased for sulfur/epoxy composites. However, the temperature determined from the peak height increased by 5 °C for SMO.

From the DMA study, the glass transition temperature can be calculated as (1) the temperature corresponding to the peak of the tan δ curve, (2) the peak temperature of the loss modulus curve G″.

Table 4. Tg calculated from DMA

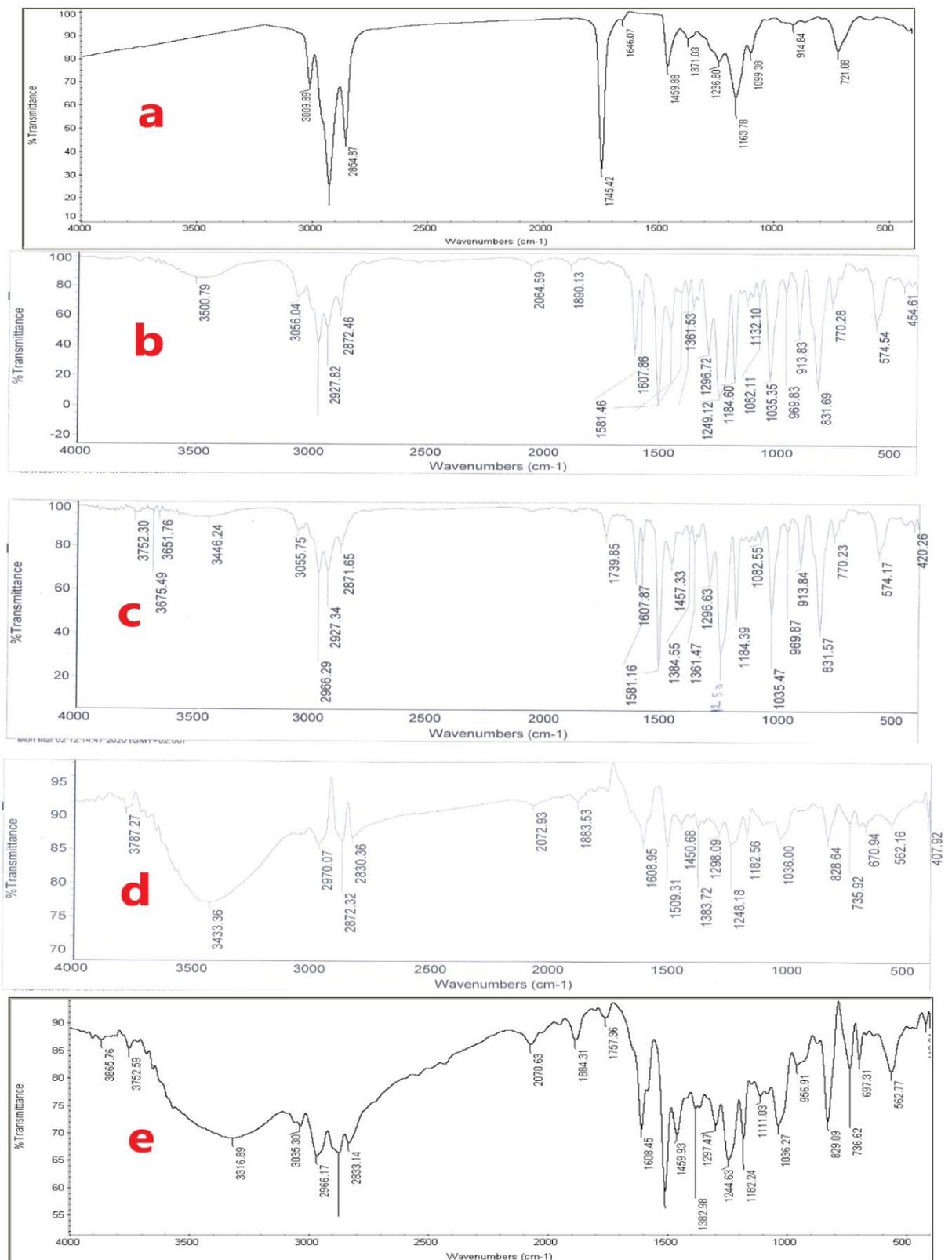| Sample	Tg (tan δ) (°C)	Tg (G″) (°C)	Difference (°C)
SO	58.4	49	9.4
SAA	59.2	50	9.2
SAB	61.5	50.7	10.8
SME	62.1	51.6	10.5
SMO	63.6	54.8	8.8

Figure. 2. FTIR spectra of   a) linseed oil.   b) epoxy resin.   c) sulfur/epoxy composite.
d) cured epoxy resin.   e) cured sulfur/epoxy composite.

From Table 4, we can observe that the glass transition temperatures obtained from G″ curve are lower than that obtained from the tan δ curve by approximately 9 to 11 °C. However, the maximum glass transition temperature in both cases corresponded to SMO which contains the highest sulfur percentage. The increase in the glass transition temperature is due to the restricted mobility of epoxy chains. This can occur as a result of the enhanced interaction between sulfur polymer and epoxy matrix and the increament of the cross-linking density of epoxy chains due to the presence of high molecular weight cross-linked sulfur polymer[17-19].
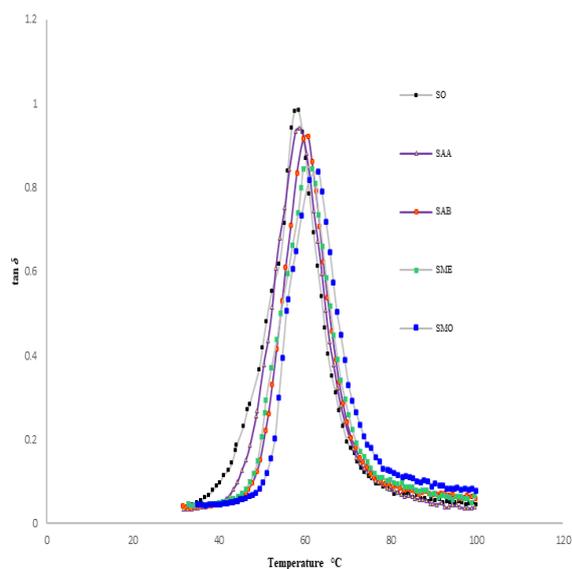
Figure 3. Storage modulus (GPa)

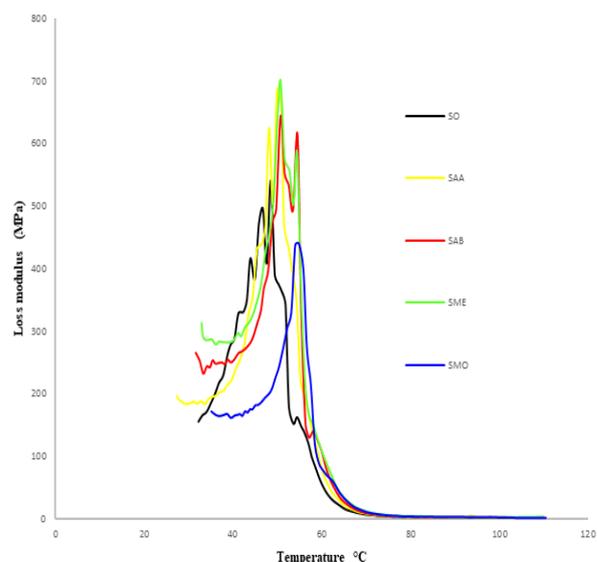**Figure 4. Damping coefficient (tan *δ*)**

Figure 5. Loss Modulus (MPa).

3.3 Chemical resistance test:

Figure 6. represents the chemical resistance of the cured neat epoxy and sulfur/epoxy composites against different chemicals. It was observed that the cured sulfur/epoxy composites showed a good chemical resistance against 37% HCl, 30% CH_3COOH, 60% NaOH, and Benzene. However, with 30% H_2SO_4, the results of weight increase % for the cured sulfur/epoxy composites are very close to that of cured neat epoxy. The modified composites still showed good chemical resistance after 7 days of immersion in 30% H_2SO_4 with gained weight less than 0.5%.

3.4 Water Absorption Resistance:

The water absorption resistance of the cured sulfur/epoxy composites is showed in Figures 7&8., where the highest water absorption resistance belonged to SME and SMO. Since increasing the contribution of sulfur into the epoxy matrix increases the water absorption resistance, sulfur/epoxy composites would be good coating materials for applications related to a prolonged water immersion such as swimming pools, and applications that require high water absorption resistance such as Desalination plants.
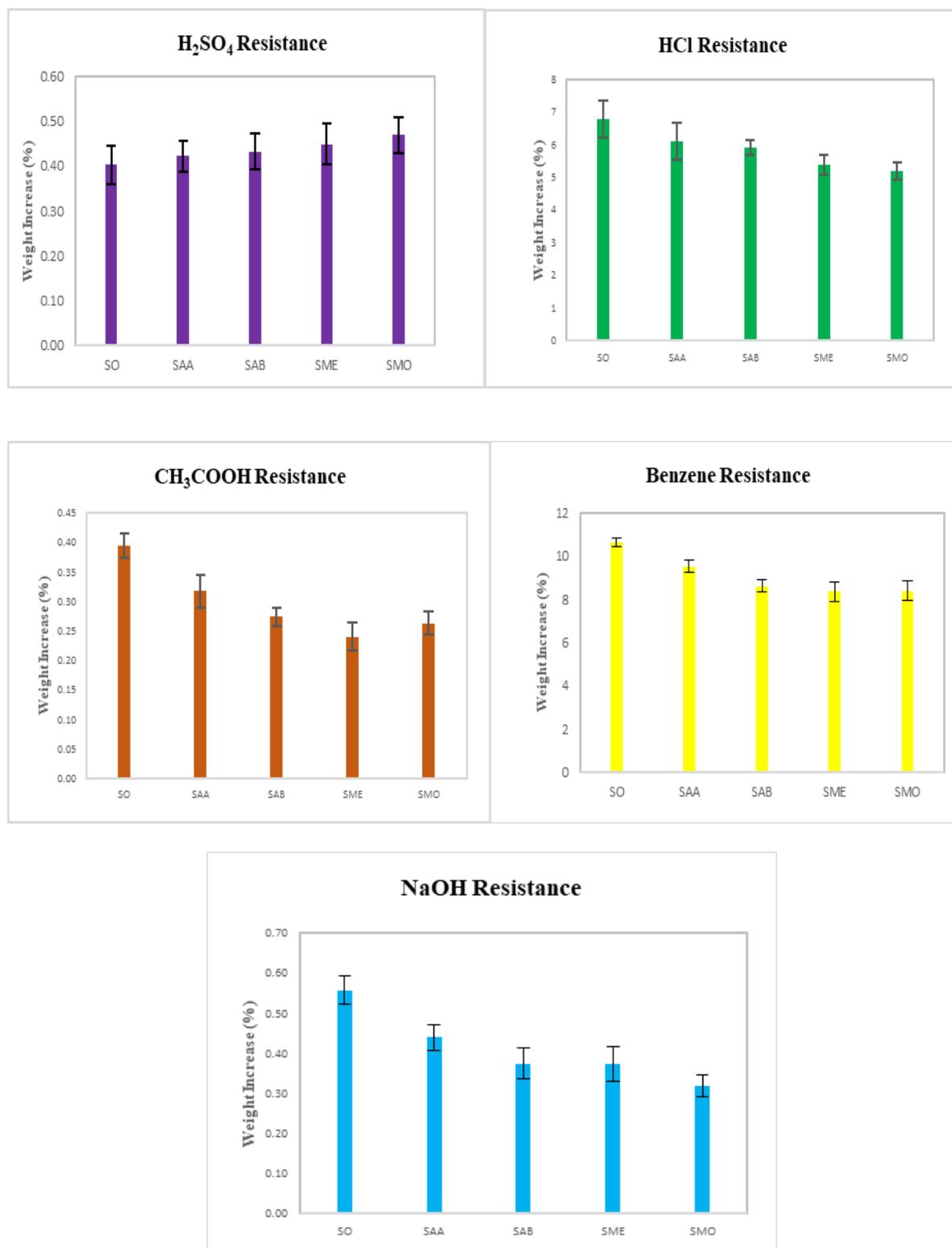
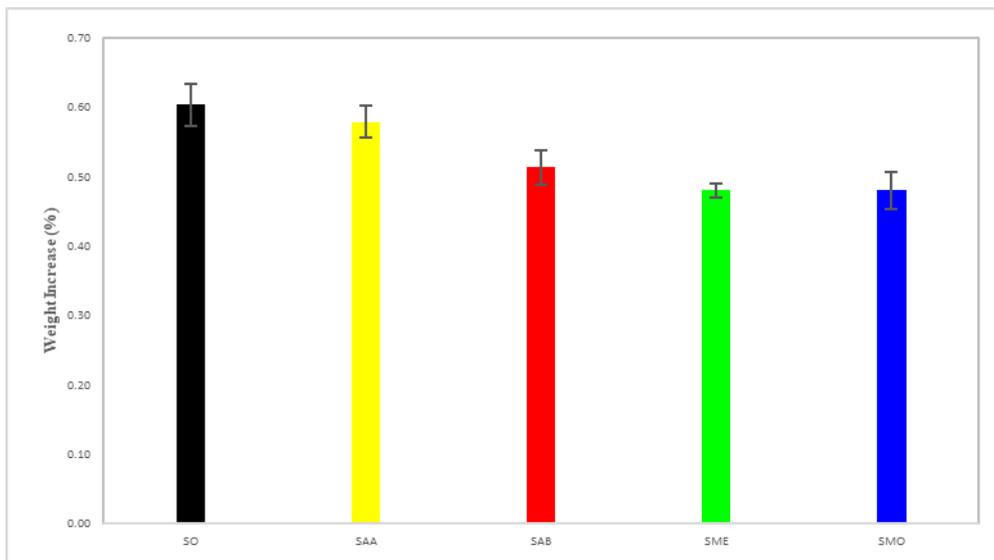**Figure 6. Chemical resistance against some chemicals**
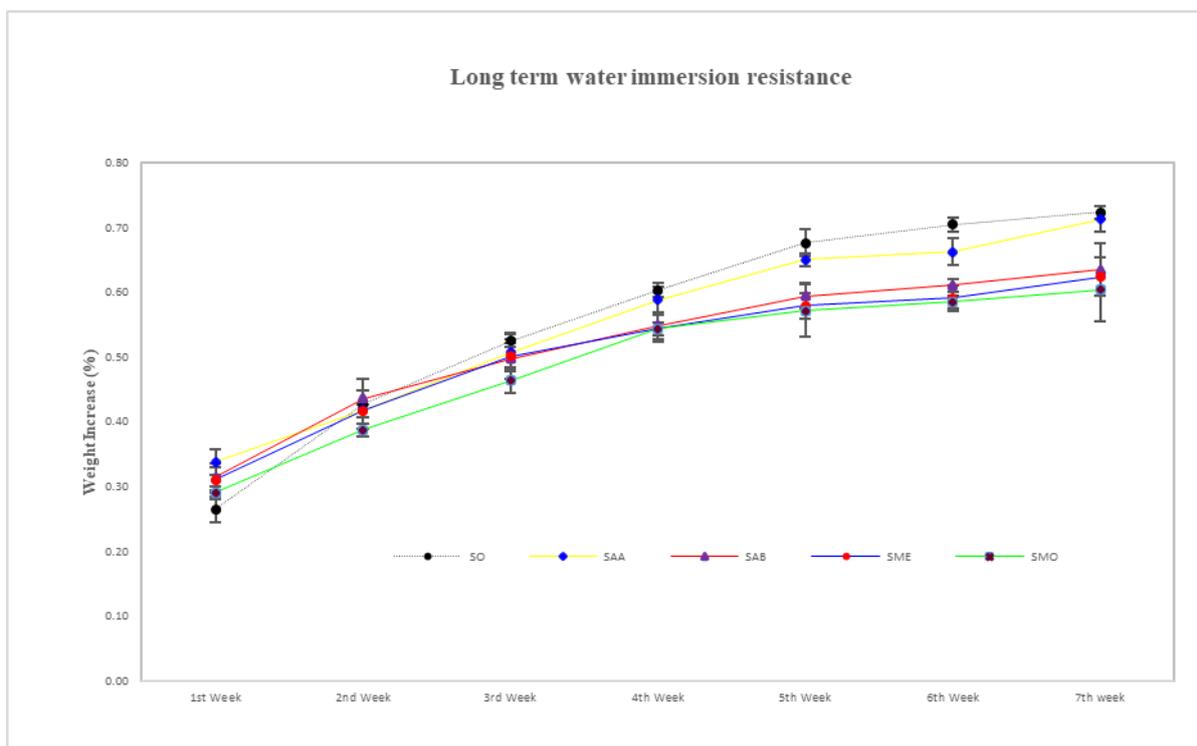
Figure 7. Two hours boiling water immersion resistance.

Figure 8. Long term water immersion resistance.

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4. Conclusion

We have prepared sulfur/epoxy composites through modification of a commercial epoxy (kempoxy 150) with sulfur and linseed oil. Since the oil enhances the compatibility between sulfur and epoxy as sulfur is immiscible with epoxy. The prepared composites are mechanically and chemically tested. The results demonstrate that the cured modified composites gave higher storage modulus and glass transition temperature than the neat epoxy. Moreover, they showed higher chemical and water immersion resistance. finally, we conclude the produced composites to be applicable in a wide range.

5. Acknowledgment

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