

## Trizane functionalized inverse vulcanized copolymer prepared using one-pot method

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**Keywords:** Heavy Metal Removal, Trizane, Inverse Vulcanized Copolymers, Sulfur Enriched Polymers

**Abstract.** Inverse vulcanized copolymers have emerged as a promising adsorbent for mercury remediation due the presence of S-S chain in their structure. However, these adsorbents are still suffering from low selectivity, adsorption capacity due to their hydrophobic nature and less functionality. Herein we reported the synthesis of Trizane functionalized inverse vulcanized copolymer using one-pot method by reacting sulfur and 2,4,6-triallyl-1,3,5-trizane and DIB (crosslinker) at 163 °C. Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) were used to characterize the resultant copolymers. FTIR spectra of all copolymers shows the absence of C=C bond and C-C=C as there were no peak observed at 1660 and 3005 cm<sup>-1</sup>. TGA revealed that the produced copolymers are thermally stable and only started to degrade at 200 °C. It can be concluded here that TAC and DIB can react successfully with sulfur to form trizane containing copolymer.

### Introduction

Water scarcity is alarming as it is essential for living organism. Although 72 % earth is covered with water but only >1 % is available as freshwater. Freshwater is being contaminated by discarding waste in various water bodies in form of oil spill, industrial effluent, and marine dumping [1,2]. Diverse range of pollutant are found in water, but heavy metals are considered as the most lethal pollutants due to their persistent nature, bioaccumulation, toxicity, neurotoxicity, great solubility in water and mobility [3]. Fossil fuels combustion, artisanal gold mining, incineration of medical and municipal waste are major sources of mercury contamination which accounts to almost 90% of the total mercury pollution [4]. Coal combustion alone contributes about 50% of the total anthropogenic mercury contamination in ecosystem [2]. It is estimated by the UN environment agency that around 2000-2500 tons of mercury have already been released in the atmosphere in the 21<sup>st</sup> century so far, which is almost 30% of the total atmospheric emissions [1].

To overcome the mercury contamination, diverse range of methods have already been developed such as ion exchange, chemical precipitation, coagulation-flocculation, flotation, membrane filtration and adsorption [5]. Nevertheless, these technologies suffer from high operational cost, limited removal efficacy and generation of secondary pollutants. Owing to simplicity, high efficiency, availability of diverse range of adsorbents, easy operation, high reliability, promising reversibility, and low cost; adsorption is the widely considered method amidst all removal technologies [6–8]. To date various adsorbents have been utilized for the removal of heavy metals from waste water which includes geopolymers [9] activated coke [10],

biochar, low dimensional carbon [11], carbon composite and polymers [2], metal-organic frameworks [2], fly ash [12], metal oxides, natural zeolites [13], biomaterials, and nanomaterials [14,15]. Nevertheless, these adsorbents are still suffering from low selectivity, high operational cost, low surface area, instable pores, and low reversibility.

Inverse vulcanized copolymers are a new class of sulfur enriched polymers prepared using facile method invented by Pyun et al. [16]. These copolymers have attracted a lot of attention and have been utilized in many applications such as slow-release fertilizers [17–22], IR materials [23], boron removal [24] and mercury remediation [25–27]. The sulfur backbone of these copolymers makes them as potential mercury adsorbents and previous studies have shown promising results for example Limjuco et al. prepared a mercury adsorbent from inverse vulcanized copolymer obtained by reacting sulfur and 2-carboxyethyl acrylate (CEA) which showed an adsorption capacity of 835 mg/g which is very high as compared to other adsorbents [25]. Diverse range of monomers have already been utilized to produce the mercury adsorbents by utilizing hydrocarbons and aromatic enriched co-monomers, but these monomers produce hydrophobic polymers making them incapable of forming hydrogen bond with aqueous feed. Moreover, these copolymers do not have appropriate functional groups to bind mercury and to functionalize these copolymers, lengthy procedure of functionalization are adopted which increases the overall cost of the copolymers [24].

Herein, we reported the synthesis of triazine functionalized inverse vulcanized copolymer by reacting sulfur with 2,4,6-triallyloxy-1,3,5-triazine (TAC) at 163 °C using diisopropenyl benzene as a crosslinker. The resultant copolymer was then characterized using Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) to confirm the formation of copolymer and to determine its thermal stability.

## Materials

2,4,6-triallyloxy-1,3,5-triazine (TAC) and sulfur were procured from Merck, Malaysia.

## Methods

**Synthesis of copolymer.** 3 g of sulfur was added in 30 ml glass vial and heated at 163 °C to initiate the ring-opening process which was accompanied with a color change. Upon completion of ring-opening process which was indicated by orange color of the melted sulfur, 1.5 g of TAC and 1.5 g of DIB was added and was allowed to react for 1 hour under continuous stirring. After completion of reaction, the polymer was then extracted from glass vial, into a petri dish and was allowed to cool to room temperature [18,19,28].

**FTIR.** FTIR Spectroscopy (PerkinElmer frontier model) is used to identify and characterize the synthesized copolymer via inverse vulcanization of sulfur and 2,4,6-triallyloxy-1,3,5-triazine (TAC). This model is equipped with the attenuated total reflectance (ATR) at the resolution of 4  $\text{cm}^{-1}$  and scanning range of 500 to 4000  $\text{cm}^{-1}$  frequency. The sample is scanned for 8 times to have a precise result on the formation of the synthesized copolymer.

**TGA.** TGA (PerkinElmer STA 6000) is used to determine the thermal stability of the synthesized sulfur-based copolymer. The temperature range of this instrument is 30 to 800 °C and a heating rate of 10 °C/min under a nitrogenic atmosphere.

## Results and Discussion

**FTIR.** The FTIR spectra of all copolymers synthesized, pure TAC and pure DIB are shown in Figure 1. Based on the infrared spectroscopy absorption table, the spectrum of TAC showed a high intensity peak associated with C-H stretching vibration for the alkane functional group at 2890  $\text{cm}^{-1}$  [19]. The intensity of the peaks for the synthesized copolymers reduces as compared to TAC. It can be deduced that the TAC was consumed during the synthesis as the decrease in the intensity of the peaks was resulted by the decrease in the amount of the functional groups in the sample. The copolymer synthesized with 50 wt% sulfur shows the lowest intensity peak at 2890  $\text{cm}^{-1}$ , indicating that the highest amount of TAC was converted in this copolymer. The spectra

of the synthesized copolymer also showed less intense peaks for C-H stretching at  $3005\text{ cm}^{-1}$  [7], [20], [21]. A peak shift was observed from  $3290\text{ cm}^{-1}$  for DIB spectrum to  $3305\text{ cm}^{-1}$  for the synthesized copolymers' spectra. This indicates that structural changes occurred within the molecule during synthesis [22]. The synthesized copolymers had introduced a new broad peak at  $2275\text{ cm}^{-1}$ , which is the isocyanate with  $\text{N}=\text{C}=\text{O}$  stretching. This peak was not found in both spectra for TAC and DIB and therefore, it can be deduced that a new material had been formed via the inverse vulcanization method.

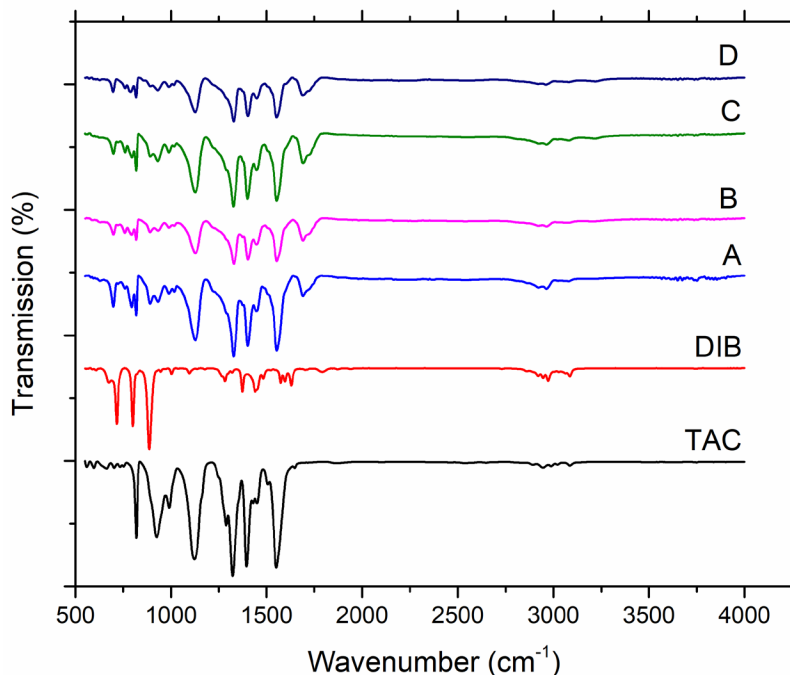


Fig. 1: FTIR Spectra of TAC, DIB, and Copolymer with (A) 50 wt% S, (B) 60 wt% S, (B) 70 wt% S (C) 80 wt% S and (D) 90 wt% S.

TGA. The TGA thermogram of elemental sulfur shows a single-phase degradation step and completely decomposes at around  $345\text{ }^{\circ}\text{C}$ . The thermogram reveals that the all the synthesized copolymers degraded in a two-step-degradation manner, except for copolymer with 40 wt% sulfur which underwent a one-step-degradation manner. The decomposition of all copolymers onset at around  $200\text{ }^{\circ}\text{C}$ , which is similar to the onsets decomposition temperature of elemental sulfur. For polymers that underwent the two-step-degradation manner, the loosely bonded sulfur chain decomposes mainly in the first step. The percentage of weight loss in the first step ( $200\text{ }^{\circ}\text{C}$  to  $355\text{ }^{\circ}\text{C}$ ) increases with the increase of sulfur weight percentage from 40 wt% to 70 wt%. The second step of degradation involves the decomposition of strongly bonded sulfur (C-S bond) in the sample. The copolymer with 40 wt% sulfur portrayed a single-phase degradation mainly due to the reduced sulfur content in the synthesized copolymer. It showed higher thermal stability as it retained the highest weight percentage during heating especially at temperature between  $400\text{ }^{\circ}\text{C}$  to  $700\text{ }^{\circ}\text{C}$ . In contrast, the copolymer with 70 wt% showed the most obvious manner for two-step-degradation. This is due to the highest sulfur content that is present in the synthesized copolymer. Copolymer with 70 wt% sulfur displayed the lowest thermal stability as it started to decompose at the lowest temperature, and retained the least weight percentage during heating, especially between temperature  $400\text{ }^{\circ}\text{C}$  to  $700\text{ }^{\circ}\text{C}$  [17,29–31]. Based on the TGA result, it can be concluded that the degradation of the copolymers takes place at similar degradation temperature of elemental sulfur, producing a polymeric material with high thermal stability. As can be seen from the TGA thermogram that even at  $800^{\circ}\text{C}$ , there is some char left and the pattern of the degradation is also different from monomers which confirms the successful structure formation of the polymer.

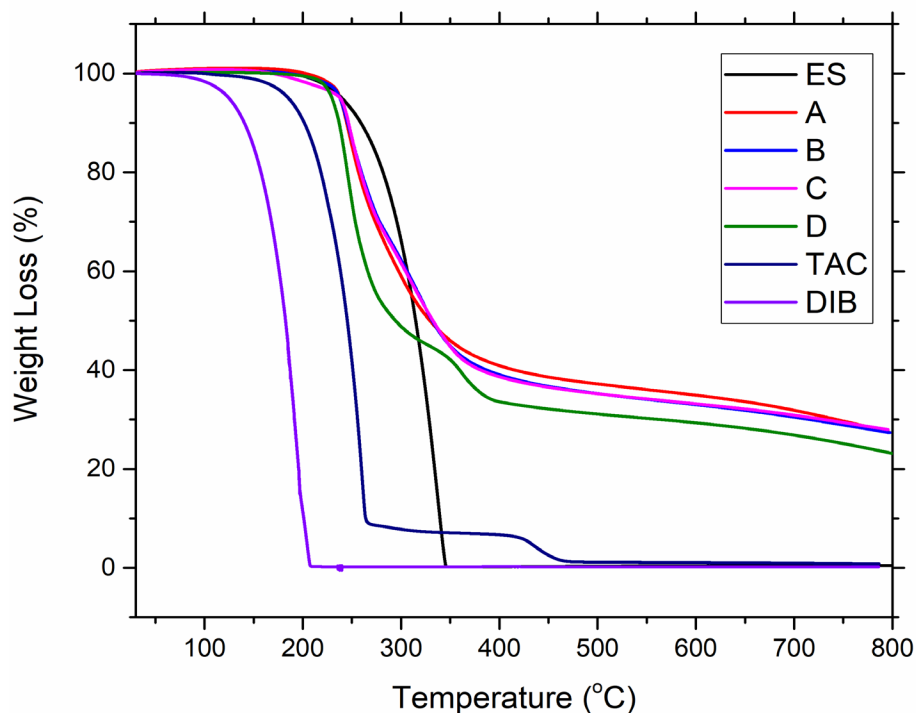


Fig. 2: TGA thermogram of TAC, DIB, and Copolymer with (A) 50 wt% S, (B) 60 wt% S, (B) 70 wt% S (C) 80 wt% S and (D) 90 wt% S.

## Conclusion

A novel trizane functionalized copolymer was synthesized using inverse vulcanization process by reacting sulfur and 2,4,6-triallyl-1,3,5-triazine at 163 °C and using DIB as crosslinker. FTIR confirmed the formation of a copolymer as there was no peak observed at 1660 and 3005  $\text{cm}^{-1}$  which indicates the utilization of C=C and C-C=C bonds for the formation of C-S bond. The TGA analysis demonstrated that the produced are thermally stable and onsets to degrade at 200 °C. TGA thermogram further confirmed the formation of polymer as char is left at 800 °C and the decomposition pattern is also different. This copolymer contains trizane as indicated by the FTIR, which makes this copolymer a potential adsorbent for mercury removal. In future this copolymer should be tested for mercury removal.

## Acknowledgement

The authors would like to acknowledge the funding supports from Ministry of Higher Education (MOHE) Malaysia through HICoE grant (Cost Centre 015MA0-052/015MA0-104/015MA0-136) to CBBR and Yayasan UTP (Cost Center 015C0-271).

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