Sulfur copolymers (SDIB) from inverse vulcanization of elemental sulfur (S₈) for polymer blend

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Abstract. Elemental sulfur (S₈) is largely available resource as by-product from petroleum refining process which is causing “excess sulfur problem” due to its limited usage. The utilization of sulfur as valuable material will not only address environmental concerns but provide cost-effective ways of consuming this huge amount of waste to develop new high-value, high-volume products. One facile synthetic method of utilizing sulfur directly as feedstock to produce polymeric material is inverse vulcanization. In this study, sulfur copolymers (SDIB) was synthesized via inverse vulcanization from S₈ and processed into polymer blend with component polymers, polybenzoxazine (PBz) and poly(methyl methacrylate) (PMMA) to show its potential processability into polymer blend. Initially, synthesis of SDIB with varying feed ratios of sulfur to comonomer 1,3-diisopropenylbenzene (DIB) was evaluated for its resulting properties. Spectroscopy showed copolymerization reactions occurred based on the change in characteristic absorption peaks (C=C-H, C=C, C-H) present in the spectra. Thermogravimetric analysis (TGA) indicated that SDIB is more thermally stable with the increase in onset temperature of degradation. Differential scanning calorimetry (DSC) profile exhibited new single glass transition temperature (Tg) that slightly increased with higher DIB ratio indicating evolution of microstructures of copolymers produced. The processability of SDIB into polymer blend was investigated by using SDIB (50 wt% S) with PBz and PMMA. Blending process using simple mixing technique with solvents was carried out for SDIB/PBz (10/10 wt%) and SDIB/PMMA (7.65/7.65 wt%) blend compositions. The results of this study demonstrated that polymer-copolymers interactions influenced the phase structure and behaviour with polymer blend of SDIB/PBz showing higher degree of miscibility with more homogeneous and transparent blend as compared to SDIB/PMMA blend. The suitability of polymer blend in electrospinning of nanofibers could provide variety of new applications for SDIB.

1. Introduction
Elemental sulfur (S₈) as an alternative feedstock has demonstrated its potential in developing new sulfur-based materials [1]. It represents a largely available untapped resource as by-product of petroleum refining process [2]. An estimated amount of more than 60 million tons of sulfur is generated annually from the hydrodesulfurization process of natural gas and oil to reduce sulfur dioxide emissions from these fuels [3]. However, the demands for sulfur usage is causing the generation of 7 million tons annually of surplus elemental sulfur which is causing the “excess sulfur problem” [3]. Current utilization
of sulfur is mostly used for the production of sulfuric acid and phosphates for fertilizers, synthetic rubber and cosmetics [4]. According to Griebel et al. [5], in order to utilize this huge amount of unutilized sulfur, it is necessary to develop new high-value, high-volume products and create facile synthetic methods for preparation of valuable materials.

The main limitation of S8 is its processability into melt or solution which is highly complicated, aside from the limited miscibility of molten sulfur with conventional organic reagents [5]. These issues coupled with the lack of synthetic and processing methods are the drawbacks for its direct utilization. In unravelling the chemistry behind the structure and conversion of S8 into molten phase, it became the key to the preparation conditions and requirements for its synthesis into polymeric material. Sulfur is most stable in the orthorhombic phase which is converted to monoclinic phase at 95 °C and polymerizes to form high molecular weight polymeric material when heated above its floor temperature of 159 °C [3]. However, the presence of active sulfur radicals in the chain terminal promotes depolymerization which was the major obstacle in producing a more stable material [6]. Termination of the active radicals by crosslinking with a comonomer was the critical aspect of stabilization of sulfur chains [7]. Stabilization of polymeric sulfur was achieved through a process known as inverse vulcanization [1]. Inverse vulcanization involved copolymerization process of sulfur as solventless medium with 1,3-disisopropenylbenzene (DIB) which promotes efficient ring-opening polymerization (ROP) of S8, enabling the preparation of copolymers, poly(sulfur-random-1,3-diisopropenylbenzene) (poly(S-r-DIB)) [3]. This synthesis method accomplished the goal of directly utilizing sulfur as feedstock in preparing valuable material.

Synthesis of sulfur copolymers (SDIB) from S8 and utilization as component polymer in developing new polymer blend were studied. According to Parker et al. [8], high sulfur content provides distinct properties to a polymeric material. Also, the sulfur copolymers produced from this method are chemically stable, processable polymeric material [1]. Another remarkable outcome obtained from the copolymers composition is its direct effect on electrochemical properties which paved the way for its development as active cathode material for performance improvement of lithium-sulfur (Li-S) batteries [9]. This was so far the most promising application of sulfur copolymers which led to exploring other applications. Advancement of potential applications of SDIB requires evaluation of structure-property relationships with the copolymers composition to give insights on its processability options. Thus, first part of the study showed the benefits of increasing the sulfur content in copolymerization reaction with comonomer DIB. SDIB were synthesized at mass ratios of 40, 50, 60 wt% to probe the S8/DIB compositions and its influence on structural evolution, thermal stability and thermal property in relation to the copolymers microstructures. Based on these results, the processing of SDIB was undertaken to show compatibility in polymer blending process. Polymer blending process is an easy and cost-effective method of developing new polymeric materials from mixing two polymers with properties that can be manipulated by the component polymers [10]. Compatible blends could result to synergistic properties from the component polymers [11]. Mixing two polymers together have shown to have properties somewhere between those of the unblended polymers [12]. This was the reason for undertaking different possible types of polymer blends in previous works, some of which were combination of poly(vinylidene fluoride) (PVDF) and poly(methyl methacrylate) (PMMA) [13], blends of two types of polyimide (PI) [14], and in the widely investigated design of proton exchange membrane by combining sulfonated polymer with non-conductive like sulfonated poly(ether ether ketone) (SPEEK) with poly(ether imide) (PEI), poly(ether sulfone) (PES) and poly(2,6-dimethyl phenylene oxide) (PPO) and sulfonated poly(ether ketone ketone) (SPEKK) with poly (ether sulfone) (PES) [15].

In this study, blending of SDIB was carried out using two component polymers, poly (methyl methacrylate) (PMMA) and polybenzoxazines (PBz). PMMA as carrier polymer of SDIB was previously studied in producing nanofibers [16]. But the combination of SDIB with PBz was not exploited yet in polymer blend. PBz, a thermoset material as component polymer of SDIB is a reasonable choice due to its superior properties. One major advantage of PBz is easy thermal curing that results to high mechanical and thermal properties [17]. The blending of SDIB with PMMA and PBz were examined for its physical behaviour and phase structure as indicator of compatibility of polymers in blends and suitability for further processing into electrospun nanofibers.
2. Experimental

2.1 Materials
The materials used in the synthesis of SDIB copolymers and polymer blending were summarized in table 1. All chemicals were used as received without any purification.

| Material                  | Chemical Symbol | Description/Manufacturer        |
|---------------------------|-----------------|---------------------------------|
| Sulfur                    | S₈              | powder, sublimed, Alfa Aesar 99.5% |
| 1,3-diisopropenylbenzene  | DIB             | TCI Chemicals, > 97.0%          |
| Polybenzoxazine           | PBz             | prepared based on the works of Li and Liu [18] |
| Poly(methyl methacrylate) | PMMA            | Aldrich, Ave MW ~ 120,000       |
| Dimethylsulfoxide         | DMSO            | ACS grade, Echo, 99.9%          |
| Tetrahydrofuran           | THF             | inhibitor free high purity, Tedia, 99.8% |
| Dimethylformamide         | DMF             | J.T. Baker, >= 99.8%            |

2.2 Synthesis of sulfur copolymers via inverse vulcanization
The synthesis of sulfur copolymers (SDIB) was undertaken using the procedure described in the works of Chung et al. [1]. The amount of sulfur used in the synthesis was varied from 40, 50, and 60 wt%. Sulfur powder inside a 25 mL glass vial equipped with a magnetic stir bar was heated to 185 °C in a thermostated oil bath for 5 mins until a clear orange colored molten phase was formed. DIB was then directly added to the molten sulfur in the glass vial. Then resulting mixture was continuously stirred for 8-10 minutes at 185 °C until vitrification was complete. Lastly, the product from the reaction after complete vitrification of the solution was cooled to room temperature.

2.3 Characterization of sulfur copolymers
SDIB samples coded as SDIB-x where x represents the amount of sulfur (40, 50 and 60 wt%) were characterized to determine the influence of varying mass ratios of sulfur to DIB on its properties. Fourier-transform infrared spectroscopy (FTIR) was performed to know the structural evolution of SDIB using a Perkin Elmer Spectrometer between 400 cm⁻¹ to 4000 cm⁻¹. The samples were loaded in transmission after pressing into a KBr disc. Thermal stability was determined using Thermogravimetric analysis (TGA) which was carried out in platinum pans using a Q50 IR analyzer (TA Instrument) with an automated vertical overhead thermobalance. The samples were heated at 10 °C min⁻¹ to 800 °C under nitrogen gas. Differential scanning calorimetry (DSC) was conducted to confirm copolymerization reaction and thermal property using a Q20, TA instrument at heating rate of 10 °C/min in the temperature range between -50 °C and 200 °C under nitrogen environment.

2.4 Preparation of polymer blend
Polymer blending process was carried out using simple mixing technique by dissolving the polymers in separate mixture of solvents as described in the procedures in the work of Parreño et al. [19]. Different approaches were tested initially, to find suitable mixing strategy for different combinations of component polymers. Two polymer blends of SDIB/PMMA and SDIB/PBz were prepared at mass ratios of 7.65 wt% for both SDIB and PMMA based on previous works of Thiellke et al. [16] and 10 wt% for both SDIB and PBz based on previous preparation of pure PBz solution. For SDIB and PBz, the polymer blend was prepared using mixture of DMSO/THF 1:3 (v/v) solvents while SDIB and PMMA was prepared using mixture of THF/DMF 7:3 (w/w) solvents. The successful blending was carried out by preparing two separate solutions of component polymers (SDIB with PMMA and PBz) in mixture of solvents. After continuous stirring of the two solutions for at least 24h at room temperature and when both SDIB and component polymers were fully dissolved, the two solutions were mixed together to obtain the blended solution. The blend was stirred for at least 1h at room temperature to fully mix the polymers as final polymer blend for electrospinning process.
3. Results and Discussion

3.1 Synthesis of sulfur copolymers

The SDIB (SDIB-40, SDIB-50 and SDIB-60) synthesized from the copolymerization of sulfur with DIB are shown in figure 1. According to Chung et al. (2013), by merely changing the S to DIB mass ratio during inverse vulcanization process, the copolymer composition and thermomechanical properties can be controlled. This was evident in the SDIB copolymers obtained with the formation of polymeric material with different physical appearance as indicator of changing composition and structure of the polymeric material. Increasing the sulfur content (60 wt%) showed the formation of opaque polymeric material while increasing the DIB ratio (60 wt%) results to dark red transparent glass.

![Figure 1. Sulfur Copolymers (SDIB) with different sulfur content SDIB-60 (60 wt% S), SDIB-50 (50 wt% S) and SDIB-40 (40 wt % S).](image)

In addition, more brittle material was observed with higher DIB ratio which could be attributed to more amorphous structure as exhibited in the transparent, more glassy appearance. It was reported that for SDIB, semi-crystalline material was obtained at higher S$_8$ while wholly amorphous copolymers was prepared at higher DIB ratio [5]. Moreover, SDIB with higher sulfur content which have opaque appearance resulted to less brittle, more flexible material. According to Khawaja et al. [7], flexibility of the sulfur copolymers is inversely correlated with increased comonomer amount due to crosslinking of sulfur with DIB. As confirmed in the study of Griebel et al. [5], the variation in the S$_8$ to DIB ratios affects the copolymer microstructures which is shown in figure 2. The sulfur copolymers structural evolution involved branched to hyper branched as comonomer DIB increase. For SDIB with higher sulfur content (90 wt%), the copolymers structure comprised of longer polysulfide loops while higher DIB ratio (20-50 wt%) produced copolymers with hyper branched structure.

![Figure 2. Schematic representation of proposed sulfur polymer microstructure as a function of 1,3-diisopropenylbenzene (DIB) content. Reprinted from Progress in Polymer Science, 58, Jared J. Griebel, Richard S. Glass, Kookheon Char and Jeffrey Pyun, Polymerizations with elemental sulfur: A novel route to high sulfur content polymers for sustainability, energy and defense, 90-125, (2016), with permission from Elsevier.](image)
3.2 Characterization of sulfur copolymers

3.2.1 FTIR of sulfur copolymers. The Fourier-transform infrared (FTIR) spectra of sulfur copolymers (SDIB-40, SDIB-50, and SDIB-60) showed evidence of consumption of sulfur with DIB during the copolymerization reactions as shown in figure 3. The characteristic absorption peaks due to C=C–H stretching vibrations was visible at 2880-3000 cm\(^{-1}\) while C=C stretching vibrations was present at 1580-1650 cm\(^{-1}\). The presence of absorption peaks at 680-900 cm\(^{-1}\) was associated with cis di-substituted alkene C–H bend. These absorption bands all showed reduction in intensity with the increasing amount of sulfur which confirmed the reaction of the double bonds of the crosslinkers DIB with sulfur in the copolymerization reactions. These result were in agreement with the results presented in the works of Chung et al. [1]

![Figure 3. FTIR spectra of sulfur copolymers.](image)

In addition to the confirmation of copolymerization reactions, the spectroscopy of SDIB revealed the copolymers structural evolution from branched to hyper branched structure influenced by the change in composition of S\(_8\) and DIB. For higher content of DIB, the degree of branching progressively increases in the copolymers while higher content of sulfur resulted to the formation of branched with longer polysulfide loops in the copolymer backbone. The higher sulfur ratio indicates that the copolymers contained more S-S repeating units. This result was confirmed with the appearance of characterization absorption peak at 500-540 cm\(^{-1}\) (weak) assigned to the S-S bonds in the copolymers. This was also indicated in the characterization absorption peak at 620-650 cm\(^{-1}\) which was attributed to the C-S bond formed when copolymerization occurs.

3.2.2 Thermal Stability and Property of sulfur copolymers. The formation of new material from the inverse vulcanization of S\(_8\) with DIB was also confirmed using Thermogravimetric analysis (TGA) as shown in figure 4a. Elemental sulfur starts its degradation at 180 °C and complete weight loss was observed at 315 °C [1]. Comparing the TGA thermograms of SDIB (SDIB-40, SDIB-50 and SDIB-60) in comparison to the degradation of unreacted sulfur, there was an increase in onset temperature of degradation at around 200 °C. This indicated that polymeric sulfur material was formed from the copolymerization reaction that had taken place. In addition, the TGA thermograms showed more thermally stable materials with the significant amount of mass remaining even after heating to 800 °C. As observed in the thermograms, the percentage mass remaining of SDIB increases as a function of the proportion of DIB used in the reaction.

Differential scanning calorimetry (DSC) profile as shown in figure 4b further confirmed that sulfur was fully consumed in the copolymerization reaction with the absence of two characteristic melting transitions (\(T_m\)) from the orthorhombic and monoclinic phases at 109 °C and 119 °C, respectively. The absence of melting point with DIB content of ≥ 30 % indicated that these sulfur copolymers were found to be amorphous glasses. These observations were apparent in all varying mass ratios of sulfur to DIB. Moreover, the glass transition temperature (\(T_g\)) for the polymers were found to slightly increase (18-24 °C) as a function of the DIB feed ratios as shown in figure 4b-c. The \(T_g\) increased from 18.2 °C with 40 wt% DIB to 20.4 °C with 60 wt% DIB. This tendency of the \(T_g\) to increase with the amount of crosslinker DIB used in the reaction was caused by the increased in branching of the structure and compositional
heterogeneity of polymeric material [3]. The presence of branching sites confirmed that the incorporated sulfur is stable against decomposition back to S8.

Figure 4. Thermal stability and property of SDIB showing (a) TGA thermograms, (b) DSC profile and c) Tg as function of DIB amount.

3.3 Preparation of Polymer Blend

The confirmation of the structure-property relationships of SDIB copolymers is important in its processability. SDIB having a composition of 50 wt% S is fully soluble in organic solvents which makes it solution processable into polymer blending preparation. Simple technique of mixing polymers in common solvent or mixture of solvents was employed in the polymer blending process. The first approach involved the preparation of PBz solution in the mixture of DMSO/THF while the PMMA in the mixture of THF/DMF. Then, the SDIB copolymers were added to the PBz and PMMA solutions, and mixed thoroughly. However, the results of this method did not produce homogenized blends but instead the mixtures formed into gel.

In the second approach, the preparation process was changed by combining two separate solutions of SDIB and component polymers. This blending method resulted to more compatible blends with synergy formed between the two polymers [11]. SDIB and PBz dissolved in each other to produce blends with homogeneous, transparent and single-phase structure as shown in figure 5. According to Mazinani et al. [14], the mixing of polymers result to a miscible blend due to the interactions that exist between the component polymers. The miscibility in polymer blend of SDIB and PBz indicated the presence of stronger interactions between the two polymers. This could be attributed to the nature of the random copolymers SDIB and PBz, which both have aromatic rings. They tends to have special attraction and associate with each other during mixing allowing the polymers to mix and formed miscible blends [12].
In the case of SDIB and PMMA polymer blend, the degree of miscibility was not good compared to SDIB and PBz. The polymer blend produced was not clear homogenized solution but cloudy as shown in figure 6. This could be due to the weaker interactions between SDIB and PMMA as compared to the other blend.

The polymer blends were used in electrospinning process to show its compatibility to nanofiber formation as shown in figure 7. Both blends produced nanofibers but amount of SDIB and process parameters of electrospinning process need further optimization to produce more uniformed fiber structure and morphology.

4. Conclusion
This study on utilization of S₈ as feedstock has demonstrated the significant contribution of inverse vulcanization process in probing the influence of the S₈/DIB comonomer ratio in the structure-property relationships of the copolymers. It was confirmed in this study that copolymerization reaction of S₈ and DIB was able to prepare a new material with changing microstructures of copolymers from simple variation on compositions of comonomer that have beneficial effects on its properties. These results are in agreement with the results of previous study. The processability of SDIB (50 wt% S) was shown in polymer blending process with two types of component polymers, PMMA and PBz. By applying suitable blending method, it showed that simple technique of mixing polymers can combine SDIB with other component polymers to produce synergy. Strong interactions that exist between the polymers result in homogeneous miscible blends of SDIB/PBz. While SDIB/PMMA blend displayed observable difference in structures and behaviour which was partially miscible with noticeable phase separation and non-transparent solution. Thus, the processability issues of SDIB was addressed by polymer...
blending and electrospinning as new options in exploiting its potential in delivering high performance materials. But optimization of SDIB content in polymer blends needs further study to take advantage of the distinct properties from the high sulfur content formed in synergy with other polymer.

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