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Poly(butylene trisulfide)/CNT nanocomposites: synthesis and effect of CNT content on thermal properties

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ABSTRACT

Polysulfide polymers are classified as high-performance materials due to their high solvent resistance and good thermal stability. In the present study, poly(butylene trisulfide) (PBTRS) was synthesized using 1,4-dichlorobutane (DCB) and sodium trisulfide (Na_2S_3). Then, nanocomposites are synthesized using carbon nanotube (CNT). The PBTRS characteristics were investigated by X-ray diffraction (XRD), proton nuclear magnetic resonance (^{1}H NMR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). Also, nanocomposites were investigated by SEM, XRD, DSC, and TGA. The results showed that the melting temperature (T_m) and glass transition temperature (T_g) by increasing CNT in the matrix, occurs at higher temperatures. Moreover, with the increase of CNT in the matrix, the formation of crystals increases.

Introduction

One of the most important elements is sulfur, which usually has an eight-membered ring structure and is mainly produced as a byproduct of crude oil refining [1]. Due to the high production of sulfur, it accumulated is done in the open spaces of the refineries, which increases these environmental concerns, and even several million tons of unused sulfur are discarded annually [2]. However, sulfur is used in various applications such as sulfuric acid, fertilizer, matches, detergents, fungicides, gunpowder, pharmaceuticals, polysulfide rubbers, and vulcanized rubber [3]. As mentioned, the preparation of polysulfide rubbers is one of the uses of sulfur. Due to its thermodynamic flexibility, strong adhesion, self-healing, as well as high resistance to many solvents and chemicals, polysulfide rubbers are used in various applications such as sealants, adhesives, coatings, insulation, hoses, solar cells, and batteries [4-33]. One of the easiest methods for the synthesis of polysulfide rubbers is *in situ* polymerization, which leads to excellent dispersion and distribution of the filler [34].

Herein, a polysulfide polymer has been synthesized of DCB and Na_2S_3. Then, nanocomposites are synthesized using CNT. The effect of CNT on morphology, structure, and thermal behavior was investigated by SEM, XRD, TGA, and DSC, respectively. Also, ^{1}H NMR was used to characterize the structure of synthesized polysulfide polymer and also, calculate the molecular weight.

Results and Discussion

The characteristics of PBTRS were identified by ^{1}H NMR and XRD (see Figure 1). The relative signals for polymer appeared at 1.91 and 3.72 ppm [3,8]. Also, signals at 1.8 and 3.63 ppm are related to DCB (monomer) and the relative signal for DMSO (solvent) at 2.47 ppm [32]. Moreover, the signal at 2.58 ppm was related to R-S-S-SH end groups [8]. Furthermore, the molecular weight could be calculated according to the peak area ratio of monomer (DCB) to the polymer (PBTRS) [3]. These signal's area ratio for the polymer (1:34) correspons to the molecular weight of around 5168 g/mole. The XRD pattern shows that the polymer included an amorphous broad peak centered at 20.7°, which originates from the amorphous nature of polysulfide rubber chains [3,8]. This amorphous peak is observed in many polysulfide polymers (linear and aromatic), in general, crystallization in polysulfide polymers depends on factors such as sulfur content in the structure and the number of carbon atoms in the polymer chain [3,7]. Crystallinity decreases with the increase of each of the mentioned factors [3].

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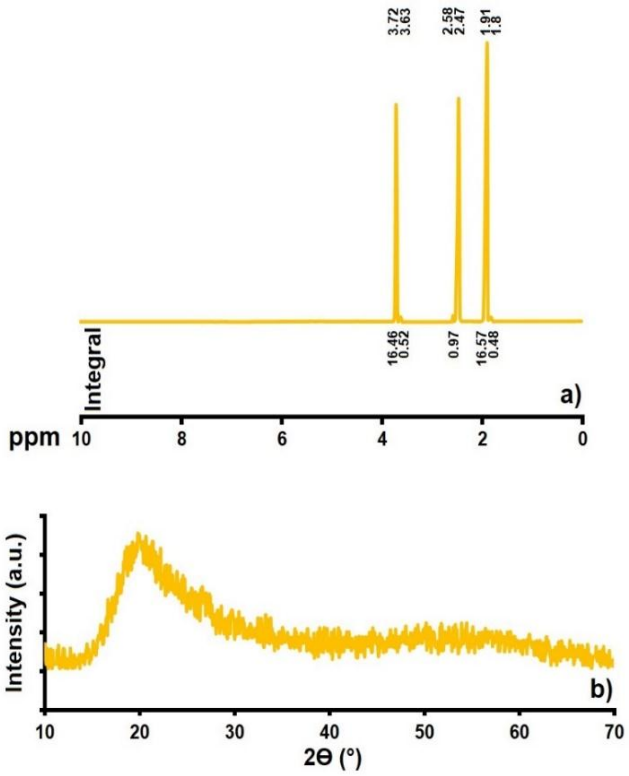

Figure 1. [1]H NMR and XRD patterns of PBTRS.

The XRD patterns of PBTRS/1% CNT and PBTRS/2% CNT nanocomposites were used to study the influences of CNT on PBTRS, as shown in Figure 2. The XRD patterns of the samples show an amorphous peak in 20.7°, which is related to the matrix (PBTRS). The peaks observed in 25, 43, and 44° are related to CNT and with the addition of CNT content [34], the intensity of the peaks increases sharply. In fact, CNT blocked the free movement of polymer chains and increase the formation of crystals, which also this behavior has been reported in other polymers' matrix [35-37].

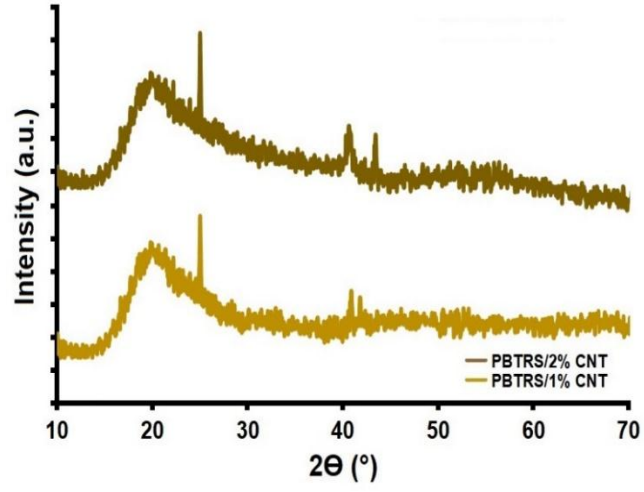

Figure 2. XRD patterns of nanocomposites.

The morphology of PBTRS and PBTRS/2% CNT were investigated using SEM images (see Figure 3). The surface of PBTRS, like many synthesized polysulfide polymers, is cauliflower-shaped [8,34]. The SEM image of the nanocomposite shows the presence of CNTs in the matrix. It can be said that polymer macromolecules can grow easily in the presence of CNTs and the CNTs are well placed in the matrix [34].

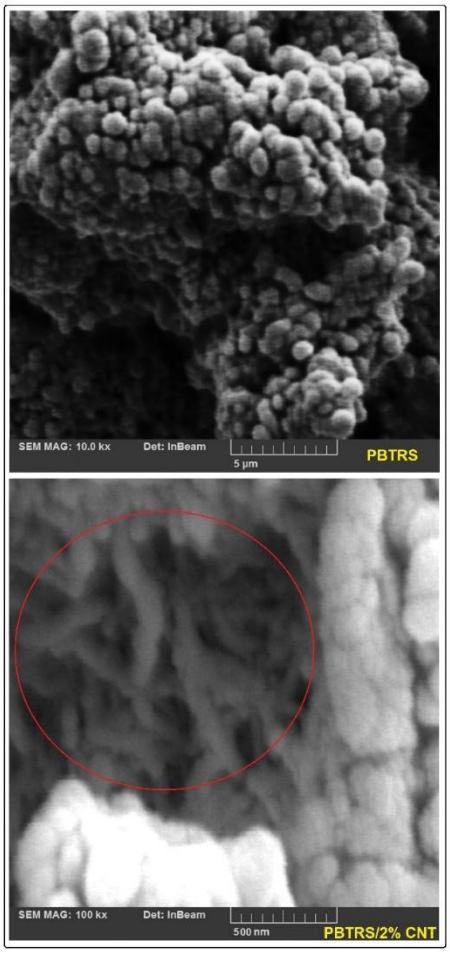

Figure 3. SEM images of PBTRS and PBTRS/2% CNT.

Thermal properties were evaluated by TGA and DSC (see Figure 4). The thermal decomposition temperature of the PBTRS, PBTRS/1% CNT, and PBTRS/2% CNT, were about 239, 251, and 264 °C, respectively. The results show that the addition of CNT to the structure increased the thermal resistance and increased the degradation temperature up to 25 °C. The results obtained from DSC showed that the T_g of PBTRS, PBTRS/1% CNT, and PBTRS/2% CNT were -39, -37.7, and -36.8 °C, respectively. As can be seen, T_g has increased in nanocomposites with increasing CNT content, which is due to the reduction of the mobility of the chains. Also, the T_m of PBTRS, PBTRS/1% CNT, and PBTRS/2% CNT were 38, 49, and 57 °C, respectively. The T_m of nanocomposites shifted to higher temperatures compared

to PBTRS. This behavior is due to the presence of CNTs that have high thermal stability [34].

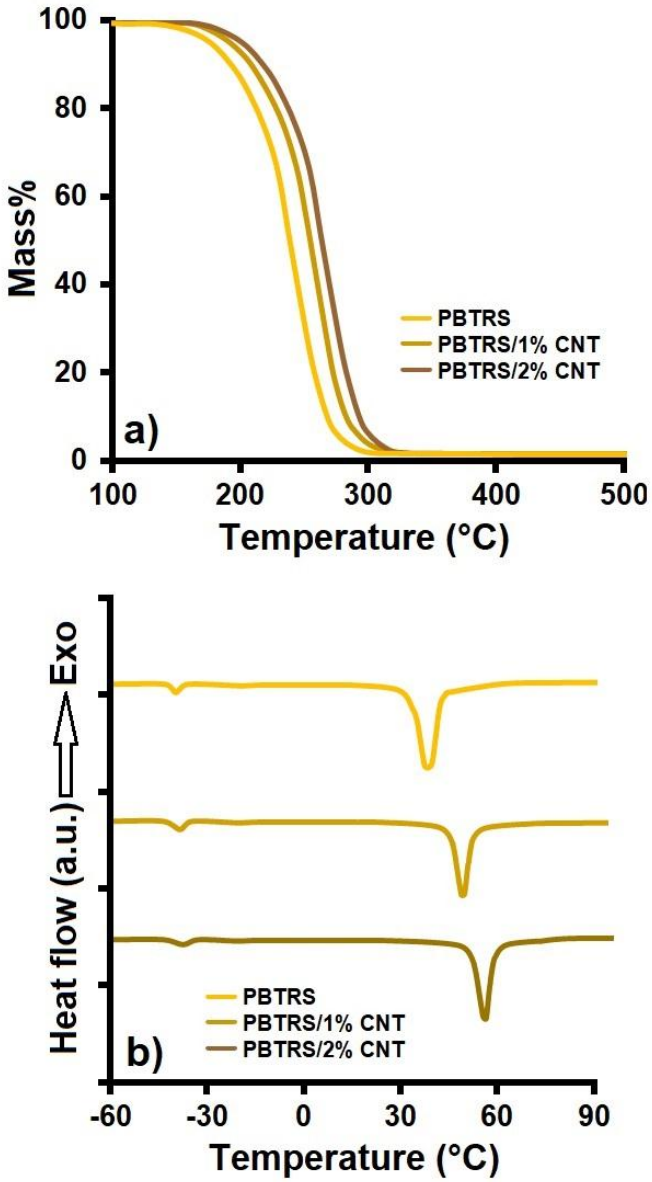

Figure 4. TGA curves (a) and DSC traces (b) of samples.

Experimental

General

1,4-dichlorobutane (DCB), sulfur (S), ethanol, sodium hydroxide (NaOH), and all other solvents and chemicals were purchased from Merck Chemicals Co. (Germany) and used as received. Also, multi-wall carbon nanotubes (CNT) with carboxyl groups (-COOH) were obtained from U.S. research nanomaterials, Inc. ^{1}H NMR measurements were conducted on an Avance 400MHZ (Bruker) with dimethyl sulfoxide (DMSO-*d*6) as solvent. XRD measurements were carried out using a JEOLGSM20A diffractometer using CuKα as the radiation source with a scan rate of 4 °C/min. SEM images were taken with a Tescan VEGA-II apparatus equipped with an energy beam of 20 kV. TGA analysis was performed using a PL-STA-1500 thermal analysis unit equipped with differential thermal analysis. The experiments were carried out in a nitrogen atmosphere at a heating rate of 10 °C/min. The thermophysical properties of samples were recorded *via* DSC using a NETZSCH DSC 200 F3 under N_2 atmosphere at a heating rate of 10 °C/min.

Preparation of samples

Based on the procedure described in the literature, Na_2S_3 was synthesized [4,8,9,11]. For the synthesizing of the polymer, 200 mL of Na_2S_3 solution and 120 mL of ethanol (to increase the yield of polymerization were as added to a round bottom flask equipped with a stirrer, a dropping funnel, a condenser, and a thermometer. Then, stirred with constant stirring at 700 rpm and the flask was heated to 70 °C, and afterward, 50 mL of DCB was gently added through a dropping funnel for 60 min. After synthesis, the polymer was filtered and washed, and then vacuum-dried at 25 °C for 24 h. For the preparation of nanocomposites; the CNT firstly was dispersed in 20 mL of deionized water by ultra-sonication. Next, Na_2S_3 was added to the following solution and the polymerization was carried out as before. The prepared solution contained 1 and 2 mass % CNT, respectively.

Conclusion

To sum up, we prepared polysulfide nanocomposites based on DCB, Na_2S_3, and CNT. The results of SEM showed a unique dispersion of CNT in the matrix. The presence of CNTs in the structure would inhibit the free movement of polymer chains and increases the formation of crystals. Also, with the increase of CNT content in the structure, T_g and T_m increased.

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