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Effect of Carbon Black Content on Curing Behavior of Polysulfide Elastomer

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ABSTRACT

Polysulfide is well known elastomer for use in aerospace applications due to providing flexible coating and chemically resistant sealants. In this work, the effects of carbon black content on curing behavior of polysulfide elastomer were investigated and rheological properties for samples with different filler content (15, 20 and 25 phr) were evaluated by rheometric mechanical spectrometer (RMS). According to RMS analysis, sample with 20 phr carbon black had minimum gel point temperature and loss factor and highest elasticity. Also, the time sweep test for the optimal sample resulted from temperature and frequency sweep at 90 °C was done and gel time obtained less than a few minutes. From the dynamic differential scanning calorimetry (DSC) diagram for polysulfide sample with 20 phr carbon black observed one exothermic peak in heat flow for uncured sample that corresponded to the formation of cross-linking network and curing of polysulfide elastomer. Prog. Color Colorants Coat. 11 (2018), 103-112© Institute for Color Science and Technology.

1. Introduction

Liquid polysulfide polymers with thiol-terminated functional groups are widely used as sealant in the aerospace industry because of properties such as chemical resistance and high flexibility [1, 2]. Curing of polysulfide elastomers are based on the oxidation of thiol end-groups with oxidative coupling agent. Manganese and lead dioxide are widely used as a curing agent for polysulfide by producing disulfide linkages (Eq. 1) [3-6].

$$2R\text{-}SH + O \rightarrow P\text{-}S\text{-}S\text{-}R + H_2O \qquad (1)$$

Sealants are divided into one-part and two-part categories, depending on the handling of polymer and its curing agent. The two-part sealants contain one polymer and one curing agent. These two parts are not reactive alone, and should be mixed together to cause crosslinking [7, 8]. Aircraft sealants usually are two-part sealants that need to be mixed accurately and be applied within a certain time span [9, 10].

The polysulfide sealant should contain some additives such as curing modifier, fillers, plasticizer, and adhesion additives to obtain the optimum properties. Many publications have been conducted on the effect of curing agent, filler, plasticizer and accelerator in mechanical, thermal and rheological properties of polysulfide sealants [11-15]. The effect of

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*Corresponding author: o.moini@eng.ui.ac.ir thermo-oxidative ageing on aviation polysulfide sealants at 85 °C was investigated by Wang et al. [16]. They found that, during ageing the chemical structure of the sealant was not changed while hardness and storage modulus increased and tensile strength decreased.

Fillers are widely used as modifiers in sealant formulation to improve mechanical and chemical properties and to reduce cost. Calcium carbonate is the most commonly used filler for polysulfide sealants [17]. Carbon black (CB) fillers have been studied by many researchers because of their significant effects on mechanical properties of polysulfide sealants [17, 18]. The nanosize fillers have also been studied. Lu et al. for example have used silicon dioxide to improve compression performance of polysulfide [19]. Two types of fullerene materials have been investigated by Zaitseva et al. to enhance the physicochemical, mechanical and adhesive parameters of polysulfide sealant [20].

Understanding the formation of cross-linking networks will be very helpful in evaluating the properties of polymers [21]. Many different analytical methods such as differential scanning calorimetery (DSC) and rheological mechanical spectrometer (RMS) have been used to characterize the curing process of polysulfides. For cross-linking monitoring with rheological technique, a sinusoidal shear at low strains is applied to the sample while curing. The response of the samples are the shear storage modulus (G') and the shear loss modulus (G"), which indicate the elastic character and the viscous response of the material, respectively. Material can show liquid-like behavior when G" value is greater than G' and conversely behave as solid when G' is higher than G". The loss factor or tan (δ) is the ratio of loss modulus to storage modulus. Thus, the loss factor exhibits the relation between elastic and viscous portion in materials. Three major kinds of test modes to investigate these rheological properties of polymers are temperature, frequency and time sweep tests [22-24]. DSC also can provide valuable data such as glass transition temperatures, onset temperature of cure, completion of cure, residual heats of cure [5, 25]. The kinetics of the curing of poly (alkyltetrasulfide) studied rheologically by Kalaee et al. [26]. In-situ dielectric analysis (DEA) was also performed to monitor the curing process of polysulfide sealant by Zhou et al. [27].

The sodium polysulfide and blend of natural rubbers treated carbon black were also investigated by Wampler et al. [28] and maximum value of rheological properties at 30 and 60 °C and mechanical properties for treated and non-treated samples were reported. Rezaeian et al. [18] optimized the effective parameters in liquid polysulfide curing system by D-optimal design method. They presented the maximum tensile strength and optimum cure time for the optimized sample.

The purpose of this work is to study the effect of different contents of carbon black as filler on the curing process of polysulfide elastomer by evaluating the viscoelastic properties and degree of cure by RMS and DSC scanning.

2. Experimental

2.1. Material

Commercially available liquid polysulfide (Thioplast® G 21: SH% = 2.5-3.1 and M_w = 2100-2700 g/mol) produced by AkzoNobel in Germany , phenolic resin (resol) and carbon black (with mesh size of 60) were supplied by iran polymer and petrochemical institute and iran carbon company, respectively. Lead dioxide (PbO_2), 1,3-diphenylguanidine (DPG), stearic acid, dibutyl phthalate and calcium carbonate were purchased from merck company and used as received.

2.2 Preparation of samples

The typical compositions of polysulfide elastomer containing different additives are listed in Table 1. As observed, the three samples (PS1, PS2 and PS3) differ just in the CB content. The two parts are made separately, and then mixed together immediately before use. The first part consists of the base polymer, phenolic resin as adhesion additive and calcium carbonate and carbon black as filler. The other part (curing paste) was made of lead oxide and dibutyl phthalate as curing agent and plasticizer, respectively. The rule of diphenylguanidine and stearic acid were curing modifier.

2.3. Characterization methods

Rheological properties including complex viscosity and gel point of the samples with different filler content were determined using MCR-301 rheometer (Austria).

Table 1: Typical composition of polysulfide sealants.

Materials (phr*)	PS1	PS2	PS3
Polysulfide	100	100	100
PbO_2	14	14	14
DPG	2	2	2
Stearic acid	2	2	2
Dibutyl phthalate	10	10	10
Phenolic resin	30	30	30
Calcium carbonate	15	15	15
Carbon black	15	20	25

* part per hundred rubber

The liquid samples were loaded between two 25 mm aluminum plates with 1 mm gap. In order to control the temperature of samples the test was carried out in an environmental test chamber (ETC). Rheological properties were evaluated at three modes: temperature, time and frequency sweeps. First the samples were kept at 23 °C for 5 minutes in order to reach the thermal equilibrium. For temperature sweep, the temperature was ramped up to 150 °C and 10 Pa shear stress at 10 (Hz) was applied with 1% strain to ensure a linear viscoelastic response. Then, the frequency sweep was done at 90 °C, 1% strain and at different frequencies among 1 to 250 (Hz), and according to the obtained results from the temperature and frequency sweeps, the characterization has been done at time sweep. For time sweep mode, the experiment conducted at 1% strain, 10 (Hz) and 90 °C.

The DSC analysis was carried out using a NETZSCH STA449F3 analyzer (Germany). The uncured sample sealed in aluminum pan was heated under a nitrogen atmosphere. The flow rate of nitrogen was maintained at 30 mL/min during the entire heating process and the weight of the sample was approximately 20 mg.

This test was performed on PS2 sample and investigated the onset temperature and degree of cure. The dynamic temperature scan was performed from room temperature to 150 °C, at the rate of 10 °C /min to observe the curing behavior of uncured polysulfide elastomer.

3. Results and Discussion

3.1. Rheological Properties

The gelation is transition from liquid to solid state that may occur with formation of crosslinks in polymers. The gel point is a temperature at which the viscosity approaches infinity is generally determined by the rheological method. In the graphs of G' and G" versus temperature, the intercept of storage modulus (G') and loss modulus (G"), is considered as the gel point (Figure 1) [29, 30]. At the beginning of the curing process, G" is greater than G' because of the liquid like behavior of sample, then with progression of cross-linking reaction and network formation, G' reaches to maximum value [31]. As shown in Figure 1 (a, b, c)., the gel points are about 46, 28 and 40 °C for samples with carbon black contents of 15, 20 and 25 phr, respectively. The sample with 20 phr of carbon black has the lowest gel point temperature. This could be due to the formation of a stronger network that leads to less mobility of polymer chains.

Viscoelastic properties at temperature sweep mode for three formulations are represented in Figure 2 (a, b, c). In this figure, increase in G', G" and η^* was first happened for all samples so that a local maximum is observed at about 90 °C. After a slight reduction, a further increment was occurred once again for these parameters around 110 °C. The reduction in viscoelastic properties after 90 °C may be due to mobility enhancement of the polymer chains with increasing temperature. It is implied that crosslinking reaction is then promoted at higher temperatures.

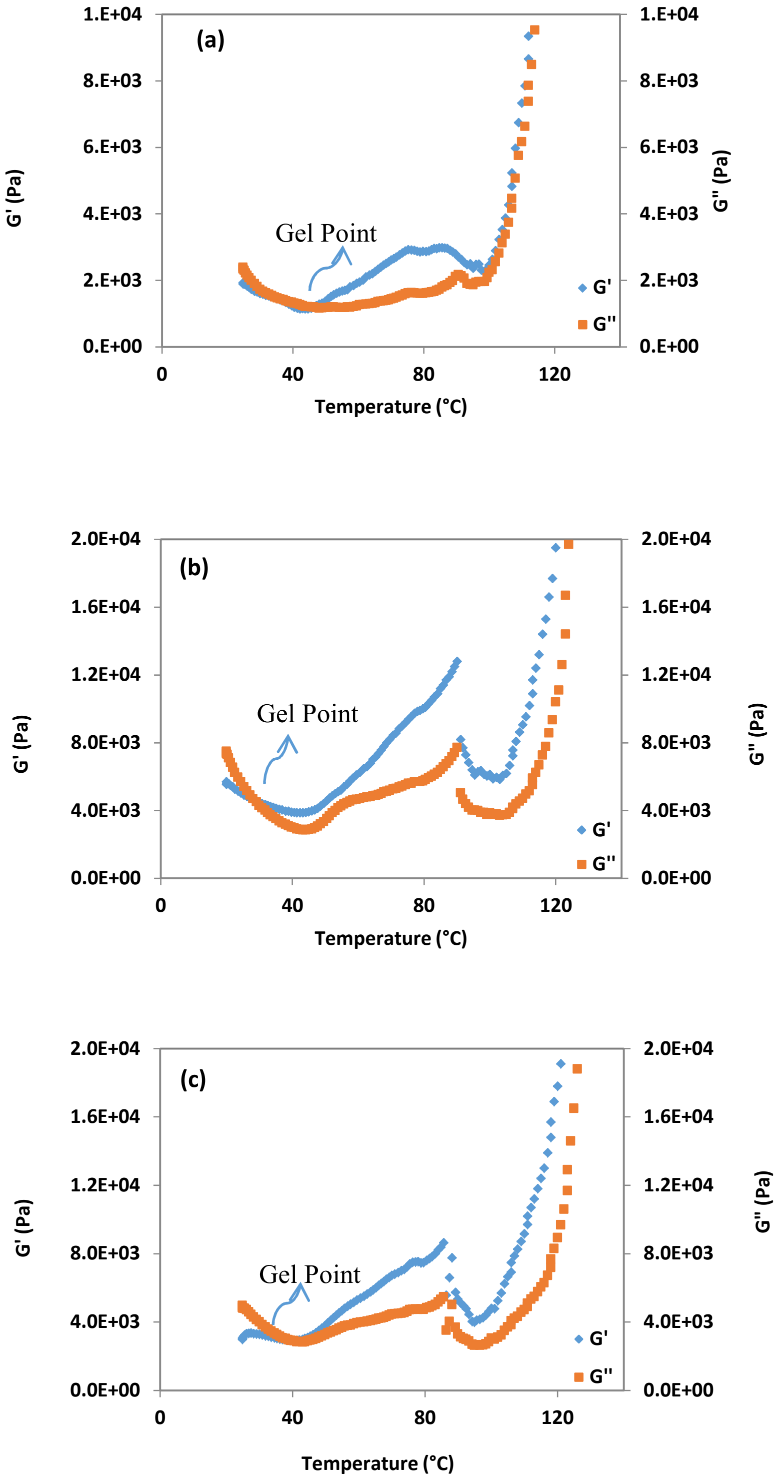

Figure 1: Storage and loss moduli variation during the curing process at temperature sweep mode: a) PS1, b) PS2 and c) PS3.

Another reason for the above behavior could be the dual effect of temperature on the viscosity of sample in curing process. The increasing of temperature causes the viscosity reduction. On the other hand, temperature increment leads to higher reaction rates and enhancement of viscosity, subsequently [30]. Figure 2 indicates that the maximum values of G', G" and η^* was observed for polysulfide elastomer with 20 phr carbon black.

The loss factor was drawn for all samples as shown in Figure 2 (d). As previously mentioned, the loss factor indicates compares elastic and viscous characters in materials. In this figure, lower loss factor is observed for samples with higher content of filler (20 and 25 phr), that is, PS2 and PS3 samples are more elastic than PS1 [18]. As seen, a greater reduction is occurred in loss factor for PS2. Therefore, the sealant with 20 phr carbon black was considered as the optimum sample.

Comparisons of viscoelastic properties at frequency sweep mode for three samples are shown in Figure 3 (a, b, c). According to the figure, for all samples the G' is greater than the G" over the entire frequency range. For the sample with higher content of filler, G' is much greater than G" that showed the elasticity of the samples is enhanced by the presence of filler and both G' and G" are almost independent of frequency [32]. Thus, nonterminal behavior was observed for samples that indicate the presence of networks of filler between polymer chains which restrains the motion of them [33].

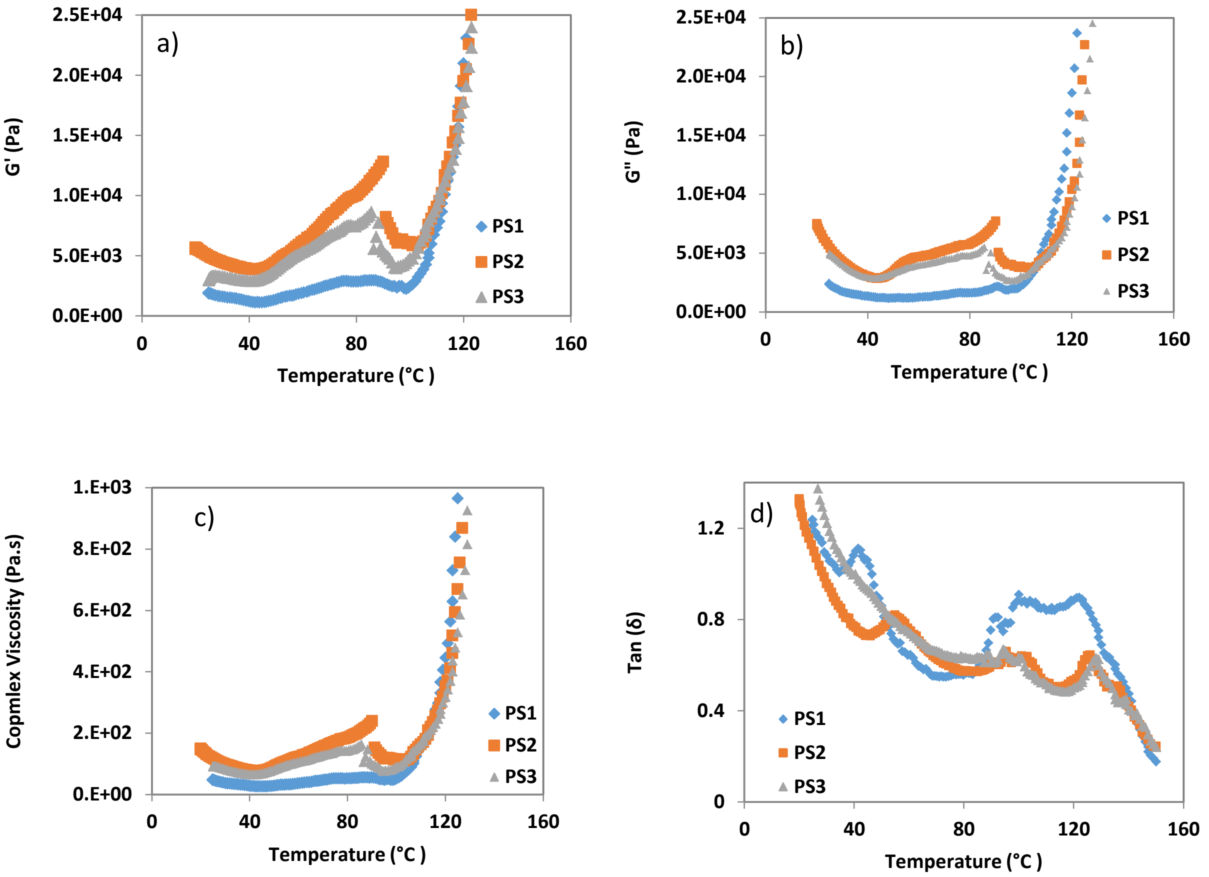

Figure 2: a) Storage modulus, b) loss modulus, c) Complex viscosity and d) loss factor variation during the curing process at temperature sweep mode for PS1,PS2 and PS3.

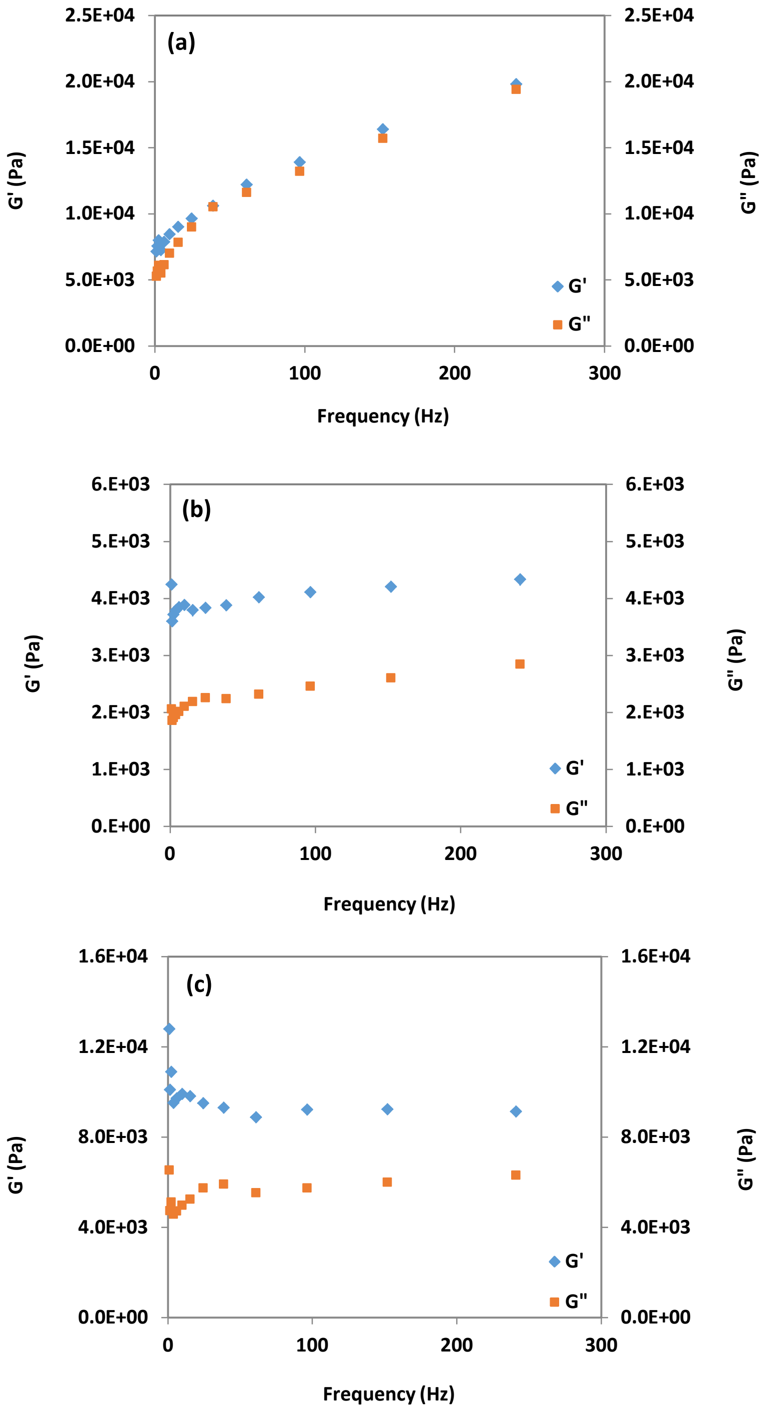

Figure 3: Storage and loss moduli variation during the curing process at frequency sweep mode: a) PS1, b) PS2 and c) PS3.

The variation of loss factor versus frequency is shown in Figure 4 for three samples. The obtained results from this figure are very similar to that obtained from Figure 2 (d) showing a large elastic behavior against dissipation in energy for samples with higher content of carbon black. In this section also the sample with 20 phr carbon black was considered as the optimal state.

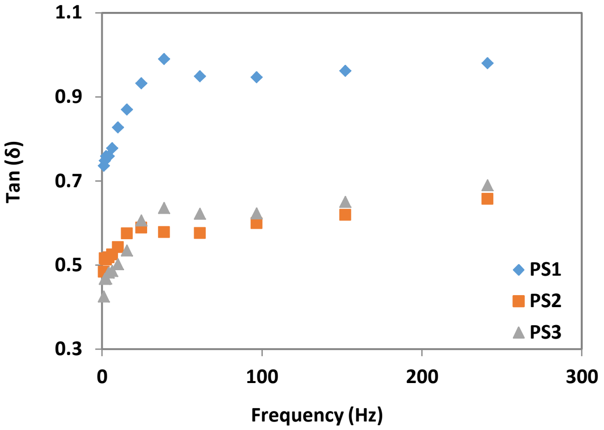

Figure 4: loss factor variation during the curing process at frequency sweep mode for PS1, PS2 and PS3.

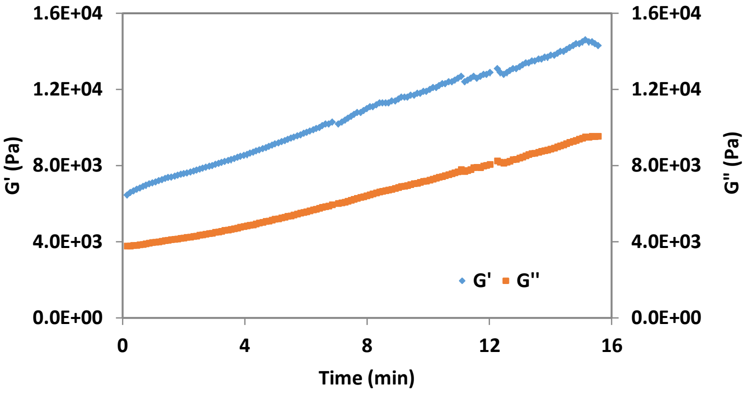

Figure 5: Storage and loss moduli variation during the curing process at time sweep mode for PS2.

Gel time can be obtained from the time interval at which the network formation begins and the viscosity tends to infinity. It was determined by time sweep where the G' and G" curve will intersect [30, 34]. In time sweep, rheological properties of sample as a function of time were recorded. This experiment was performed for the sample with optimum result from temperature and frequency sweep at 1% strain, 10 (Hz) and 90 °C. The result of this test is shown in Figure 5. As seen in the figure, G' is greater than G" from the beginning of the test. Since the preheating and preparing device last some minutes it can be said that the network formation started at the same moments and the gel time at 90 °C were less than a few minutes.

3.2. Differential Scanning Calorimetry (DSC)

DSC diagram of the cure of polysulfide elastomer is shown in Figure 6. According to the scan, with increasing temperature, the sample was cured and an exothermic peaks was observed in heat flow were observed. The onset of curing is the temperature at which the heat flow deviates from a linear response and the exothermic peak temperature reflects the maximum rate of curing of the sealant and formation of cross-links. At the completion of curing or crosslinking, the DSC heat flow returns to a quasi linear response [35]. Therefore, the onset temperature of curing in sample is about 40 °C and formation of cross-linking network was done up to 120 °C.

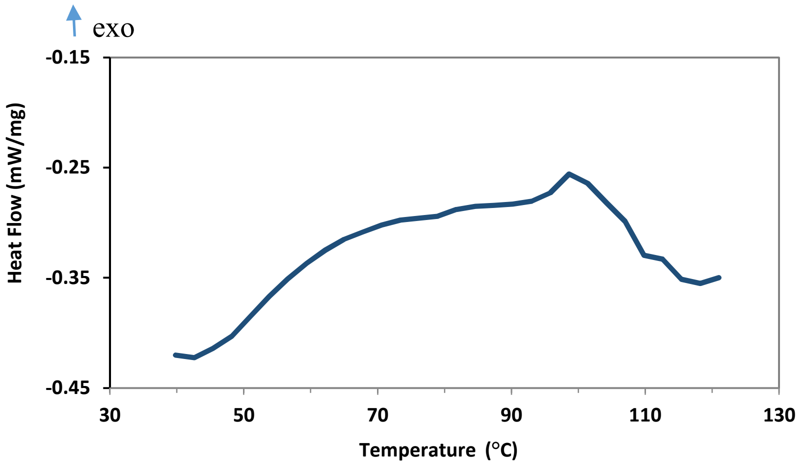

Figure 6: DSC analysis for sample with 20phr carbon black.

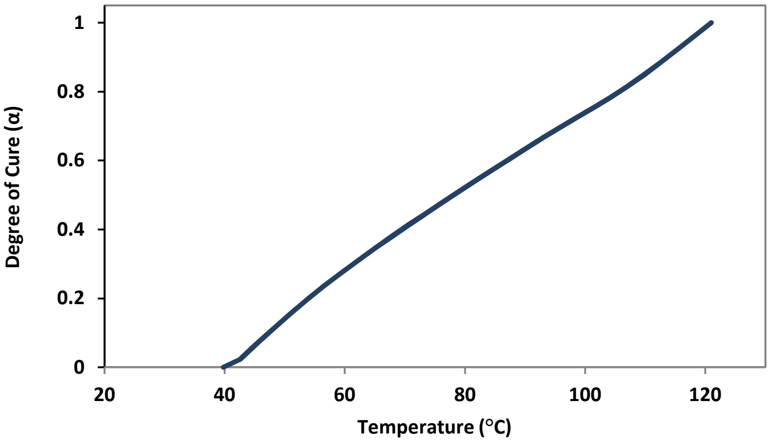

Figure 7: degree of cure versus temperature.

The degree of cure is important parameter for end-use properties and product integrity [36]. In the dynamic scan, the degree of cure was calculated by the following equation equation 2 [37]:

$$\alpha = \frac{\Delta H_T}{\Delta H_{dyn}} \tag{2}$$

Where, α is a degree of cure, ΔH_T show the heat released up to temperature T and ΔH_{dyn} is a total heat for uncured sample. The heat of reaction between polysulfide and curing agent was measured by integration of the exothermic peaks. The area under the DSC curve versus time is used to calculate the amount of heat released from the sample [38, 39]. By considering the first peak of DSC test for cross-linking formation in polysulfide elastomer and calculating the heat of reaction according to Eq. (2), degree of cure for polysulfide sample with 20 phr carbon black versus temperature was obtained and showed in Figure 7.

4. Conclusions

The curing behavior of polysulfide elastomer with different contents of carbon black (15, 20 and 25 phr) was investigated using RMS and DSC analysis. The rheological tests were performed at temperature, frequency and time sweep modes. The obtained results from temperature sweep indicated that the sample with 20 phr carbon black had minimum gel point temperature and maximum value for storage and loss moduli and complex viscosity. According to the frequency sweep, this sample had also the minimum loss factor. Therefore, PS2 with lower loss factor and higher elasticity was considered as the optimum sample. The time sweep test has been done for optimal sample and obtained gel time at 90 °C was about a few minutes. The dynamic scanning DSC has been done for the sample with optimum result from RMS. This analysis showed the exothermic peak in heat flow for uncured sample that the first peak corresponded to curing process of polysulfide elastomer and from this peak the degree of cure for PS2 was calculated from this peak.

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