# The Effect of Exfoliated Graphite on the Thermal Properties of Dynamically Vulcanized PS/SBR Composites

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**Abstract -**This study in the first stage aims at producing exfoliated graphite sheets (EXG) from commercially available natural graphite flakes (NGF). The modification technique was through strong acid treatment followed by thermal shock at 900 $^o$C. The prepared sheets of EXG were characterized with respect to thermal stability via thermo-gravimetric analysis (TGA). Their morphology and particle size were evaluated using scanning electron microscope (SEM). As a second aim of this work the potential of the EXG on the thermal properties of dynamically vulcanized polystyrene/styrene butadiene rubber (PS/SBR) composites was investigated as well. The glass transition temperature ($T_g$) and the oxidation temperature were investigated using differential scanning calorimeter (DSC). The impact strength of the composites was inspected as a function of filler type, i.e. modified or unmodified.

**Keywords:** Grapheme, Thermoplastic elastomers, Composites, Exfoliated, Graphite.

## 1. Introduction

Alloying of two polymers is a possible way to design their individual properties in a single material. Over the years this technique has undergone an extensive growth in production. The material would possess characteristics of thermoplastics and technical properties of elastomers. Vulcanization is the process in which the polymer is converted to an elastic state or a hard rubber state. The process is brought about by traditional or dynamic vulcanization technique. Dynamic vulcanization is a process of in-situ cross-linking the elastomer component during the melt mixing stage (Coran,1988 ). It can improve various properties such as mechanical properties, resistance to heat and chemical resistance, that means the attack by chemical liquids (Mousa et al , 1997, 2000). The addition of fillers in such alloys produced a new class of material known as thermoplastic elastomer composites. Fillers are implemented to enhance the service age as well as to reduce material cost. This target depends on the source of filler, type of filler, method of preparation and treatment. For example: exfoliated graphite (EXG) which is a light carbon material with couple of unique properties such as resistance to aggressive media, improved specific surface area and flexibility (Mousa et al 2006, Mehrabzadeh M. and Delfan N., 2000). Such characteristics have attracted the attention of various researchers to EXG in various polymer systems (Chen et al, 2004,). The objective of the present work is to prepare EXG from commercial grade of natural graphite flake (NGF) as first stage. In the second stage we compare the influence of EXG on the thermal and impact strength of NGF filled PS/SBR composites.

## 2. Experimental
### 2.1. Materials and Formulation

Natural graphite flake (NGF) was supplied by Royal Scientific Society of Jordan. Polystyrene was supplied by Sabic – Saudi Arabia. Styrene Butadiene Rubber (SBR) was produced by Bayer AG, Germany. Zinc Oxide and sulfur were of commercial grade donated by local rubber processing factory (Jordan). The recipe used to produce the composites is shown in table 1.

Table 1. Recipe used to produce polystyrene mix with rubber based on 100 php polymer.

| PS(%) | SBR(%) | ZnO(%) | Sulfur (%) | NGF(php) | EXG(%) |
|-------|--------|--------|------------|----------|--------|
| 80 | 20 | 4 | 1 | 0 | 0 |
| 80 | 20 | 4 | 1 | 3 | 2 |

Php : part per hundred part polymer

## 2.2. Preparation of EXG

10 grams of natural graphite were swollen in concentrated Sulfuric and nitric acids consequently in the presence of water bath to decrease the heat produced by the reaction. The reaction solution was left to homogenize for 24 hours using magnetic stirrer. The solution was filtered and the treated graphite was dialyzed against water until neutral pH of the filtrate was achieved. The neutralized samples were dried in an air oven at 80 $^o$C overnight. Finally the intercalated graphite was expanded in a furnace at 1000 $^o$C for 2 minutes. The expanded graphite sheets were later separated into individual sheets by sonication in an acetone bath.

## 2.2.    Composites Fabrication

Samples were melt mixed using a Brabender plasticorder internal mixer, model PL- 331 at 180 $^o$C and 60 revolutions per minute. At first the PS was initially loaded into the mixing chamber and preheated for 4 minute before the rotors were started. SBR was loaded and mixed for three minutes until homogenous mix was obtained as indicated by the stable torque. Other ingredients such as zinc oxide were added at the 7th minute, followed by sulfur which was mixed for another two minutes. As for the filled system, the filler was added at the 4th minute.

## 2.3.    Compression Molding

2 mm rectangular sheets were molded using Carver compression molding machine. The samples were preheated for two minutes without any pressure then the samples were compressed between the two plates at 10 MPa pressure and 160 $^o$C for 10 minutes.

## 2.5. Differential Scanning Calorimeters (DSC)

Thermal properties of the specimens were tested using Perkin-Elmer DSC-6. Few millgrams of each sample were scanned in the temperature range from 25 to 300°C at heating rate of 10 K/min using 7.6mg Indium as a reference sample. The temperature scanning of the samples was carried out under $N_2$ atmosphere up to 150 °C. Beyond this temperature the samples were scanned under $O_2$ atmosphere. From the complete DSC thermo-grams the glass transition temperature ($T_g$) and oxidation temperature of the samples were obtained.

## 2.6. Impact Testing

Notched Izod impact test was carried out according to ASTM D-256, using CEAST impact testing machine with hummer energy equals to 7.5 J and velocity of 3.0 m/s. The tested samples were of the following dimensions 62 x 13x 2 mm³ having a V-notch depth 2.5 mm. Three samples were tested and the average value was calculated.

## 3.    Results and Discussions
## 3.1.    Characterization of Unmodified and Modified Graphite

Figures 1a and b shows the SEM micrographs of the as received natural graphite flakes (NGF) and the exfoliated graphite sheets (EXG). It is obvious that the layer structure of NGF shown in Figure 1a is irregular with small layer distance as reflected in figure 1a. This is mostly attributable to the high physical forces among the layers of the graphite due to the van der Waals bonding. Figure 1b shows the topography of the expanded graphite sheets after the expansion process. It is notable that the expanded graphite (EXG) emerges as a loose and porous material consisting of various graphite plates. The observed morphology can related to the heat treatment of the intercalated NGF at 1000 $^o$C. At such high temperature, trapped intercalates between graphite layers decompose and force the

graphite layers to separate randomly as shown in Figure 1b. The layers were later exfoliated into individual plates by sonication in an acetone bath as mentioned earlier and as shown in Figure 1b. Furthermore, Figure 1b confirms that the exfoliated graphite (EXG) is not a single graphite platelet; instead it is a bundle of graphite plates.
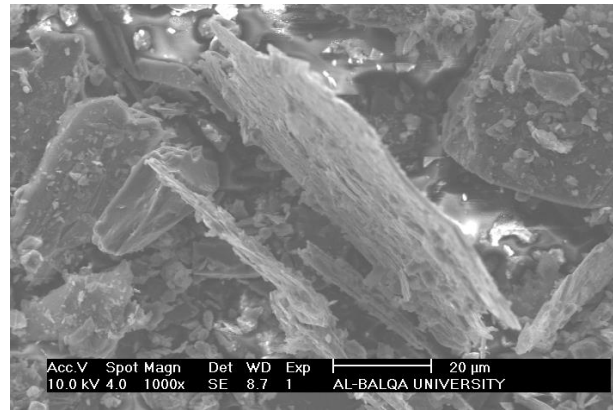


(A)



(B)

Fig. 1. SEM micrographs of (A) Natural Graphite Flakes (NGF), (B) Exfoliated graphite.

To further support the fact of volume expansion observed by morphological study, the expansion ratio of the EXG with respect to NGF powder was *calculated* and presented in Figure 2.
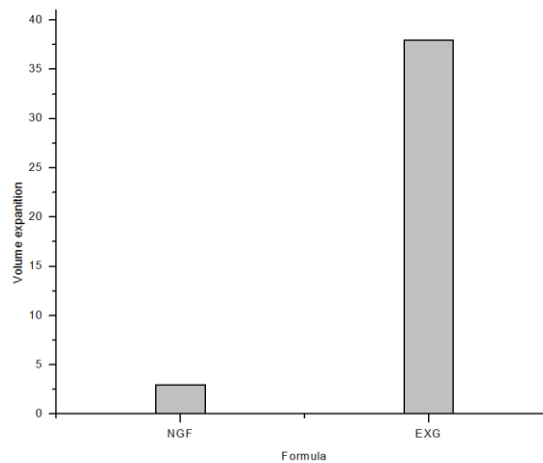


Fig. 2.  Expansion ratio of EXG as compared to NFG.

It can be seen that the volume expansion of the EXG is much higher than that of the NGF. This is most likely attributable to the breakage of bonds between the layers. Furthermore the morphology of the EXG displayed in Figure 1b shows a platy shape as mentioned earlier. Thus it is expected that the graphite sheets have an enhanced surface area. Recall that, the enhanced surface area is related to the particle size reduction, which means the smaller the particle size, the higher is the surface area. In this regard, Figure 3 summarizes the particle size of the NFG powder to the EXG counterpart; it can be seen that the modification of the NFG powder has reduced the particle size as shown in Figure 3. This could be due to the breakage of the bonds between the layers. The average particle size for unmodified graphite is 23 micrometer, whereas for the modified graphite is about 5 micrometer. Therefore these results are expected to affect many properties of polymer systems reinforced with EXG sheets (Chen et al 2004, Zheng et al 2002, Jeong et al 2008).

## 3.2.    Thermal Behavior of Unfilled and Filled PS/SBR Composites

Figure 4 shows the DSC thermograms of the pristine PS/SBR composites reinforced with EXG and NGF. The unfilled PS/SBR blend showed two transition peaks 70 and 85 $^{o}$C, respectively, which are related to the SBR and PS glass transition. Note that the intensity of PS peak was lowered after mixing with SBR, simultaneously the position of that peak was shifted to left by 12 $^{o}$C. Both signs are indicator for partial miscibility of the blend at the preset processing conditions. Upon the incorporation of 3% NGF within the composite, the sample retained two glass transitions similar to the unfilled formula as well. The implication is that the NGF does not enhance the miscibility of the PS/SBR composites.
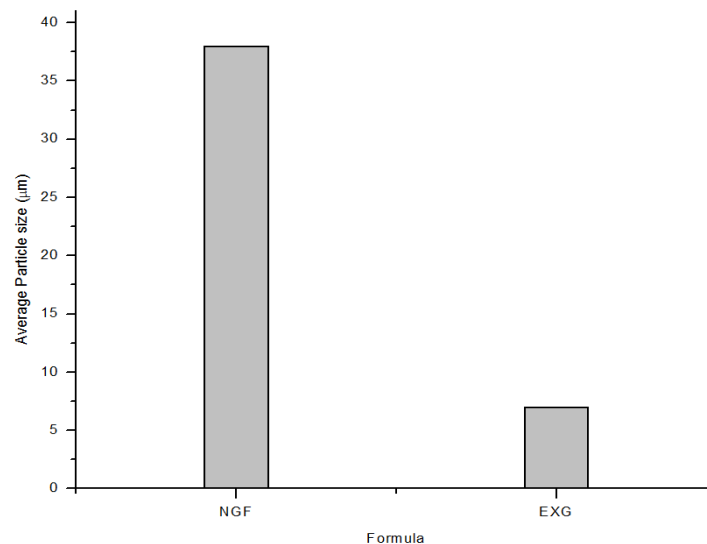


Fig. 3. The average particle size of EXG as compared to the NGF.

On the other hand it can be seen that the composite with 3% EXG displayed one glass transition. This indicates quite well that the incorporation of the platy EXG has enhanced the miscibility of the composites. The possible explanation is that the smaller particle size of the EXG could act as nucleating agent that enhanced the interaction between the SBR and the PS, concurrently, the higher surface area of the EXG led to better interaction as well. One more comment could be comprehended from the figure is that the glass transition of the EXG filled composite is the lowest in the whole studied set of composites. This is possibly attributable to the platy shape of the EXG that act as lubricant for the composite, hence the flow commences earlier than the other samples. Furthermore, the heat flow of the composite filled EXG has the highest heat flow which is another clue that EXG increased the thermal conductivity of the composite. The thermo-oxidative behavior of the composites is depicted in figure 5. It can be seen that the decomposition of the composite with 3% EXG displayed a single-step degradtion process while the composite with 3 showed two steps degradation pattern. However, it is obvious that the formula with 3% of NGF decomposed earlier than than the

control, practically the onset decomposition for the control sample and the 3% NGF formula commences at 175$^{o}$C while the onset decomposition temperature for the EXG based formula commenced as high as 240$^{o}$C. The conclusion is that NGF was unable to enhance the thermal stability of the composite. This could be related to weak interaction between the NGF and the matrix provided the low heat flow in the presence of NGF where the absorbed heat will be transferred to the matrix resulting in a prematured thermal compound.

### 3.3. Mechanical Properties

Figure 6 compares the influence of NGF and EXG on the impact strength of the various formulations of PS/SBR composites. It is clear that the composite with addition of 3 % NGF displayed lower impact strength as compared to the control sample. On the other hand the EXG containing formula displayed higher impact strength than the sample with the NGF. The observed reflects an improved interaction between the EXG and the PS/SBR matrix. Such scenario is related to the smaller particle size of the EXG, consequently higher surface area. The implication is that the EXG will be able to absorb the impact shock and transfer which protects the matrix from failure. Recall that the destruction of the crystal structure of the graphite resulted in loose and porous plates of EXG, such characteristic grants better dispersion of the EXG within the matrix consequently better impact resistance. Figure 7 shows the influence of NGF with and without modification on the bending strength of PS/SBR composites. It can be seen that the addition of modified graphite increased the bending strength of the composites as compared to the counterpart with unmodified. It is clear the modification has increased the force required for bending due to the platy shape of graphene which increase aspect ratio and increase surface area; therefore the sheet will not be easily broken with small amount of bending force. Figure 8 shows the influence of NGF with and without modification on the wear resistance of PS/SBR composites. It can be seeing that the addition of modified graphite EXG reduced the weight loss; this mean the wear resistance was increased. This is due to increase of surface area for graphene which enhance degree of interaction; as a result this has lead to good wear resistance.
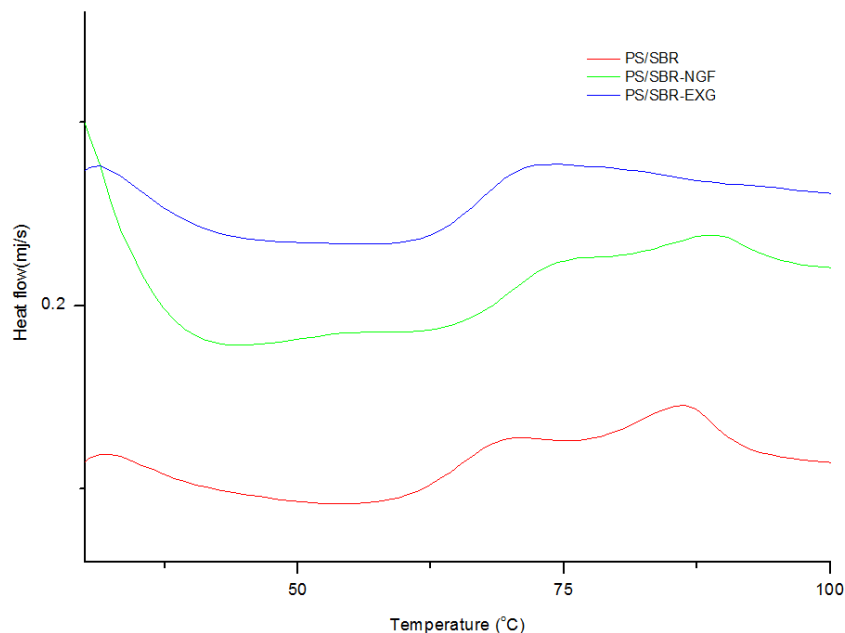


Fig. 4. DSC thermograms of PS/SBR composites filled with NGF and EXG.

On the other hand the formula with 3% EXG displyed enhanced resistance agains therooxdative conditions. This is again attributed to the enhanced thermal conductivity of the EXG compared to NGF. The enhanced thermal resistance is evidenced from the higher heat flow of recorded by the DSC traces.

## 4.  Conclusion

Based on the previous results, it can be concluded that the modification process of the commercially available NGF has resulted in expandable graphite sheets EXG. This was evidenced by the micrographs of the SEM and the reduction in particle size, the density as well as the expansion volume percentage. Therefore, this was a hint to us that NGF has been successfully converted to EXG sheets The potential of the EXG in polymer based composites was found to enhance the thermal stability of such composite as shown by the DSC.  The mechanical properties were enhanced due to the addition of EXG as compared with NGF.
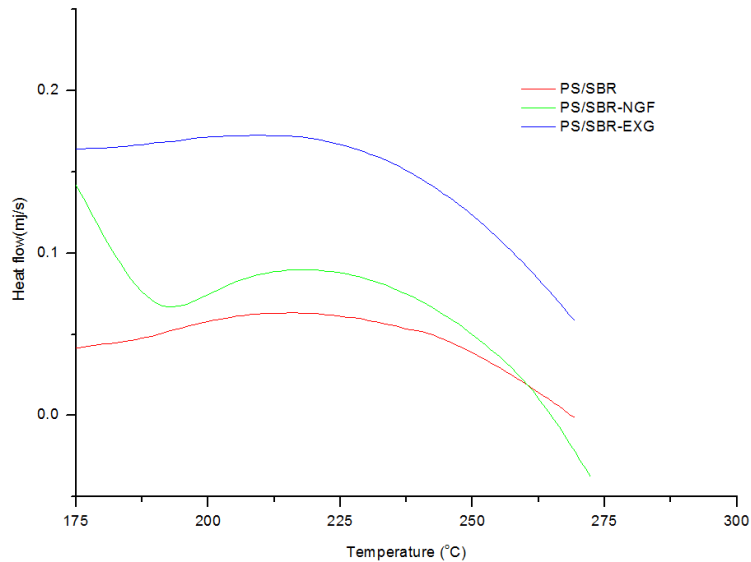
Fig. 5: The effect of NGF and EXG on the oxidation T of PS/SBR compositions.
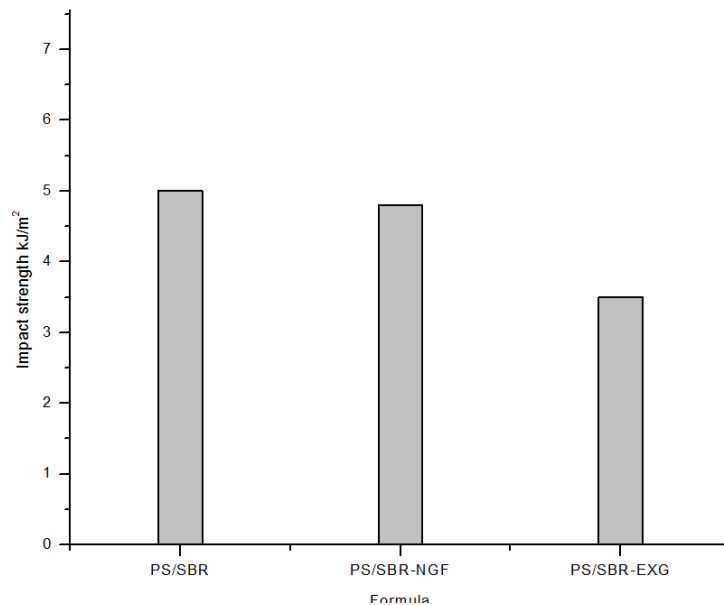
Fig. 6. Comparison of  impact strength of PS/SBR composites as a function of NGF and EXG at various loadings.
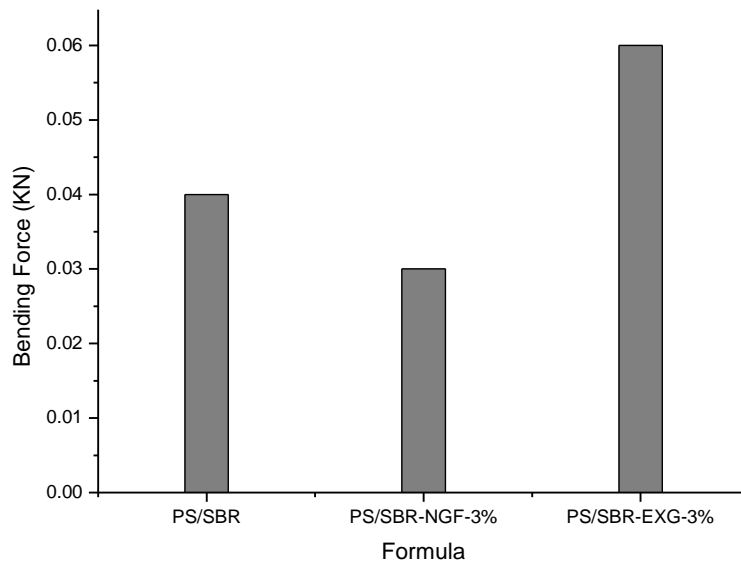
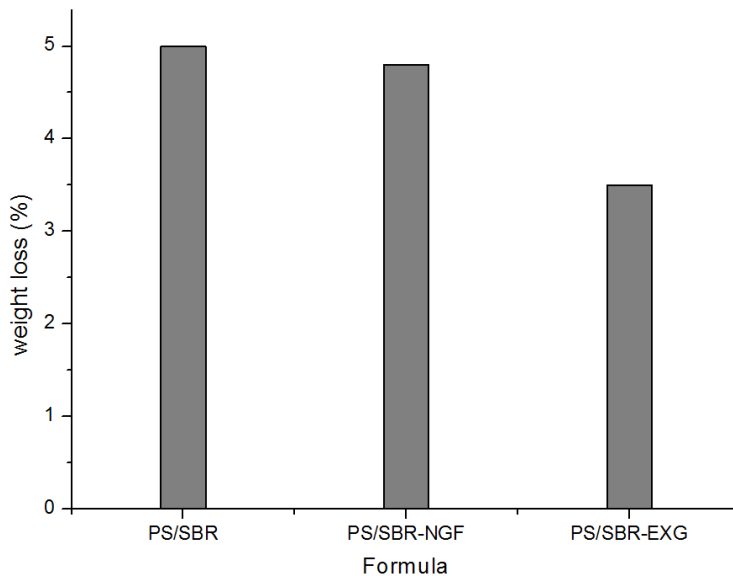Fig. 7: The effect of EXG and NGF on bending force of PS/SBR composites.



Fig. 8. Comparison of weight loss % of PS/SBR composites as a function of NGF and EXG at various loadings

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