Application of Vietnamese Nano Graphene as SBR Rubber Reinforcement for Abrasion Resistance Conveyors

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Abstract

Graphene has been extensively considered as an ideal additive to improve the mechanical properties of many composite materials, including rubbers, because of its novel strength, high surface area, and remarkable thermal and electron conductivity. Styrene Butadiene Rubber (SBR) is considered a good material for abrasion resistance conveyors in industries. However, the mechanical properties of SBR still need to be improved. This study shows the enhancement of Vietnamese nano graphene (GNPs) on mechanical properties of SBR rubber such as tensile strength, tear strength, abrasion resistance, and adhesion strength. The distribution of the Dioctyl Phthalate (DOP)-modified GNPs in the SBR matrix was investigated using scanning electron spectroscopy. Results show a significant increase in SBR/GNPs nanocomposite mechanical properties with the presence of GNPs (tensile strength, and tear strength increased by 29.67% and 31.89% respectively in comparison with SBR rubber without GNPs, and abrasion weight loss was decreased by 30.84% in comparison with SBR and adhesion strength with polyester fabric was 3 times higher than that of SBR). The evaluation of GNPs content in SBR/GNPs nanocomposite material was carried out. Results show that 0.5 phr of GNPs content in SBR/GNPs nanocomposite material was the optimal GNPs content with good mechanical properties, high abrasion resistance, and good adhesion with polyester fabric.

Keywords: Vietnamese nano graphene, SBR, abrasion resistance conveyors

1. Introduction

Rubber is considered as one of the most commercially used polymers in every aspect of living and industrial activities. Rubber precursors could be categorized into natural and synthetic rubber types (polybutadiene rubber, styrene-butadiene rubber, isobutylene isoprene rubber…) [1]. Among these, styrene-butadiene rubber (SBR), a transparent thermoplastic, is commonly utilized in industrial packaging and many consumer products [2, 3]. SBR was first synthesized in 1929 to replace the reduction of natural rubber.
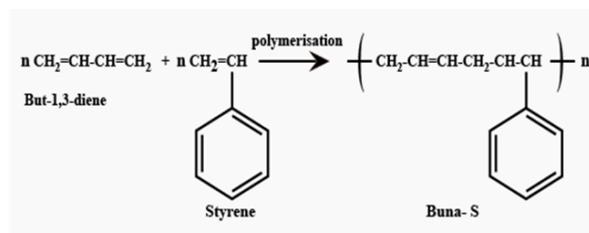
SBR rubber has the better higher abrasion resistance than that of natural rubber. On the other hand, SBR rubber also is a cheap price rubber with high water, acid, and base resistance, and durability. However, some remained disadvantages of SBR rubber can be pointed out such as low UV resistance, weather, and thermal aging [1].

One of the most used fields for SBR rubber is the conveyor industry, which requires high wear resistance, tensile strength, and durability [4]. Since the nature of the pristine SBR rubber is stiff and brittle, it is necessary to compound with fibers and fillers to improve the mechanical properties for tire application [5]. Many fillers such as carbon black, silica, clay, natural fiber, and biomass fillers have been commonly used to reinforce rubber [6, 7]. However, such filters need to be added in a high proportion to the SBR rubber to enhance the mechanical properties, mainly the carbon black filler, resulting in high density and expensive production of the rubber composite [8]. It is also well-perceived that the production of carbon black filler emits a considerable amount of CO_2 and pollutant wastes, which causes severe problems for the ecosystem and human health [9]. Recently, alternative nano-scale fillers have been extensively studied and considered as an ideal replacement for conventional fillers in the rubber industry [10, 11].

Graphene has been discovered since 2004 and it has been paid attention from both industry and academia. Graphene is single layer of carbon atoms arranged in a honeycomb structure [1, 2, 13].

Graphene has a very high modulus [3] and surface area [4]. Furthermore, graphene has good mechanical, thermal conductivity and electrical conductivity properties [5, 12, 14, 15]. For those reasons, graphene was used as reinforcement for rubber and plastic in many applications [2].
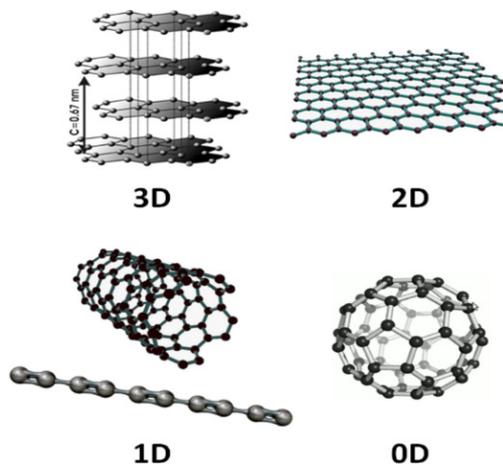

Fig. 1. Graphene structure [1]

With a high surface area of nano graphene, when applied nano graphene in styrene butadiene rubber, the interfacial effects between SBR and graphene have improved the permeation of nitrogen gas through SBR [6]. The friction and wear restance of SBR/NR blend in the dry sliding condition were increased with the combination of nano graphene and nano cellulose as reinforcements [7]. The thermal and wear resistance also improve when using graphene and SiO2 on SBR eco-green tires [8-9].

In recent years, common rubber materials do not reach the industrial application requirements. Therefore, advanced rubbers such as nanocomposite based on rubber are considered. [2].

Rubber nanocomposites with nano filler such as silica, carbon nanotube, and nano clay,… have been investigated since the end of the XX century. However, those materials are exhibited as hight applicable materials because of their high mechanical properties, good modulus, low heat hysteresis, and good solvent absorption resistance [3].

In this research, Vietnamese nano graphene was dispersed into SBR rubber for nanocomposite. The enhancement of Vietnamese nano graphene on mechanical properties such as tensile strength, tear strength, hardness, abrasion resistance capacity, and adhesion capacity with polyester fabric was investigated to optimize GNPs content in SBR/GNPs nanocomposite material.

2. Experiment

2.1. Materials

Oleic acid modified Graphene nanoplatelets were obtained from VNgraphene Joint Stock company,

Vietnam. Sodium dodecyl sulphate (SDS), naphthalene oil, zinc oxide (ZnO), stearic acid, N-tertbutyl-2-benzothiazolsunfenamite, carbon black N330, and sulfur were purchased from Xilong Chemical Co. Ltd. Styrene-butadiene rubber 1502 was provided by Kumho (Korea). All the chemical was used as received without any further modification.

2.2. Fabrication of SBR/GNPs Masterbatch

The masterbatch of SBR/GNPs with 2 %wt. of GNPs was fabricated by using hot melted mixing equipment. Oleic acid modified nano graphene was first mixed with naphthalene processing oil to obtain a naphthalene/GNPs mixture. Naphthalene/GNPs mixture and SBR rubber were then mixed in hot melt mixing equipment at 110 ºC to obtain a masterbatch SBR/GNPs. Masterbatch of SBR/GNPs was rolled with two rolling mills and finally sheet-roll to obtain the final product.

2.3. Fabrication of Nanocomposite Material Based on SBR Rubber and Nano Graphene (SBR/GNPs)

The SBR\GNPs nanocomposite was fabricated using two rolling mills equipment (the rolling speed ratio between two rolls is 1:1.1) with the compositions as presented in Table 1. Firstly, the SBR rubber was mixed with the SBR/GNPs 2 %wt. masterbatch, ZnO, stearic acid, N-tertbutyl-2-benzothiazolsunfenamite accelerator, and sulfur to obtain mixture 1. The SBR rubber was mixed with the SBR/Carbon black 50 phr masterbatch, ZnO, stearic acid, N-tertbutyl-2-benzothiazolsunfenamite accelerator, and sulfur to obtain mixture 2. Mixture 1 and mixture 2 were then mixed to obtain SBR/GNPs nanocomposite material. Finally, SBR/GNPs nanocomposite was sheet-rolled, followed by a pressed vulcanization process to form the final products. The control sample was also fabricated using the same approach without the addition of the SBR/GNPs masterbatch for comparative purposes. Nanocomposite SBR/GNPs recipe as in Table 1.

Table 1. The composition of SBR/GNPs nanocomposite

No.	Components	Content, part per hundred (phr)
1	SBR rubber	100
2	Naphtalene-modified GNPs	0.1 - 0.7
3	N330 Carbon black	40
3	Stearic acid	2
4	ZnO	5
5	TBBS accelerator	1.5
6	S	2

2.4. Characterization of SBR/GNPs Nanocomposite Material:

The tensile strength and tear strength were measured according to ASTM D412 and ASTM D624 standards by INSTRON 100kN (USA) mechanical testing machine respectively with the specimens thickness of 1.00 mm. Shore A hardness was measured according to TCVN 1595 - 88 by TECLOCKTGS instrument (Japan). The abrasion resistance of SBR/GNPs nanocomposite was evaluated according to DIN - 53516 by GTFO12D instrument (Japan). The dispersion of GNPs in the SBR matrix was observed via morphology of material by Scanning Electron Microscopy (SEM) Hitachi TM4000Plus (Japan). The adhesion strength of SBR/GNPs nanocomposite material with polyester fabric was carried out by INSTRON 100kN (USA) mechanical testing machine according to TCVN 1596:2016. Before testing, the specimens were placed into a climate-controlled box with a temperature of 25 °C and humidity of 60% for 24 hours. Thermal aging of SBR/GNPs nanocomposite with various GNPs contents was evaluated according to TCVN 2229:2007 standard.

3. Results and Discussion.

3.1. Effect of GNPs Contents on Tensile Strength of SBR/GNPs Nanocomposite

The effect of GNPs content on the tensile strength of SBR/GNPs nanocomposite was investigated with the content of 0.3, 0.5, and 0.7 phr of GNPs. Other compositions of the nanocomposite recipe are shown in Table 1. Results of tensile strength and elongation at break are shown in Fig. 2, Fig. 3 below.
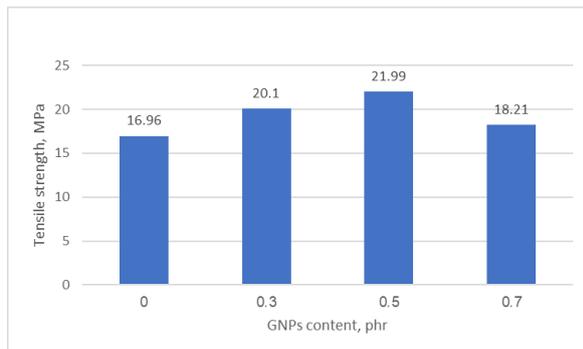

Fig. 2. Tensile strength of SBR/GNPs nanocomposite

The results in Fig. 2 and Fig. 3 show that the tensile strength of SBR/GNPs was significantly increased with the addition of GNPs in comparison with SBR without GNPs (tensile strength of 0.3, 0.5, and 0.7 phr of GNPs increased by 18.51%, 29.67%, 7.37% than that of SBR without GNPs). The tensile properties were increased with the increasing of GNPs content. The increasing in tensile properties of SBR/GNPs nanocomposite with the presence of GNPs can be supposed because of the high stiffness, good modulus, and substantial surface area of GNPs. The

well dispersion of GNPs in SBR matrix via masterbatch SBR/GNPs led to improve the reinforcement capacity of GNPs for SBR rubber. In addition, at the GNPs content of 0.7 phr the SBR/GNPs tensile properties were slightly decreased, which can be due to the aggregation of GNPs with high volume fraction (GNPs has a low density of 0.015 g/cm^3) in the material.
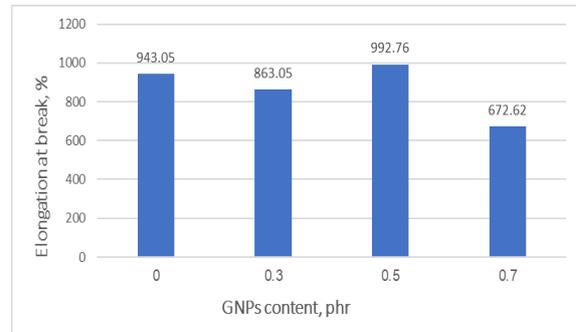

Fig. 3. Elongation at break of SBR/GNPs nanocomposite

3.2. Effect of GNPs Contents on Tear Strength of SBR/GNPs Nanocomposite.

The effect of GNPs content on tear strength of SBR/GNPs nanocomposite was investigated with the content of 0.3, 0.5, and 0.7 phr of GNPs. Other compositions of the nanocomposite recipe are shown in Table 1. Results of tear strength are shown in Fig. 4 below.
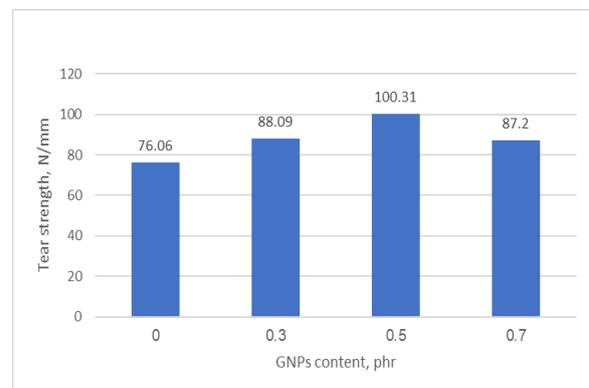

Fig. 4. Tear strength of SBR/GNPs nanocomposite

As can be seen in Fig. 4, the presence of GNPs with high modulus, high surface area, and well dispersion in SBR significantly improves the tear strength as well as in the case of tensile properties (31.89% higher than that of SBR without GNPs). The GNPs nanoplatelets can fill and cover the defectiveness, and resist the defectiveness propagation in the material during the force application, thus can improve the mechanical properties of SBR rubber. On the other hand, the aggregation of nano particle also leads to the slightly decreasing of tear strength.

3.3. Effect of GNPs Contents on Shore A Hardness of SBR/GNPs Nanocomposite

Results of the effect of GNPs contents on Shore A hardness of SBR/GNPs nanocomposite is shown in Fig. 5. The presence of GNPs with high stiffness did not enhance the Shore A hardness of SBR/GNPs nanocomposite material, which can be seen in Fig.5, Shore A hardness was slightly increased along with the increasing of GNPs contents from 0.3 to 0.7 phr (60 to 62.4 Shore A respectively). On the other hand, the increase of naphtalene processing oil accompanied by the increase of GNPs content led to the softness of nanocomposite material. Therefore, the slight increase in Shore A hardness with GNPs content is attributed to two phenomena such as increased hardness by GNPs filler and plasticized by naphthalene oil.
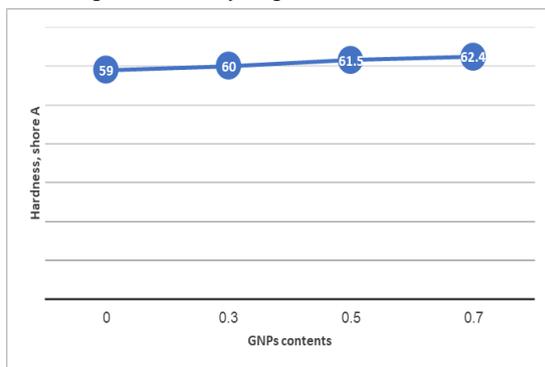

Fig. 5. Shore A hardness of SBR/GNPs nanocomposite

3.4. Effect of GNPs Contents on SBR/GNPs Nanocomposite Abrasion Resistance

One of the most studied applications of graphene used as filler in rubber composite is to improve the abrasion resistance of the composite because of the high stiffness, good modulus, and high surface area of nano graphene particles. The effect of GNPs contents on abrasion resistance of SBR/GNPs nanocomposite was determined by the weight loss after one cycle on the rotating cylindrical drum device with a drum diameter of 450 mm x 450 mm, and a pressing force of 2.5 N. Fig. 6 shows the weight loss of SBR/GNPs nanocomposite with various content of GNPs such as 0.3, 0.5, and 0.7 phr.
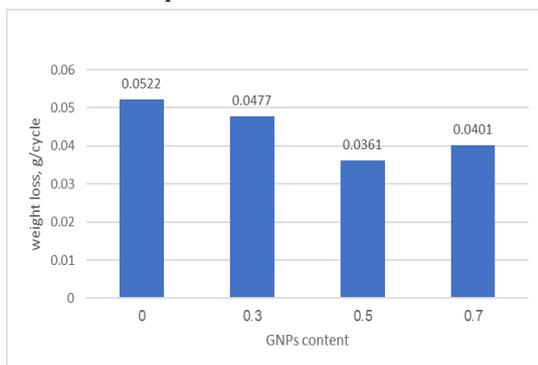

Fig. 6. Abrasion weight loss of SBR/GNPs nanocomposite material

It can be seen in Fig. 6 the weight loss of SBR material without GNPs is determined to be approximately 0.0522 g/cycle. With the presence of GNPs in the SBR matrix the weight loss is significantly decreased. The SBR/GNPs nanocomposite weight reduces from approximately 0.0477 (8.7%) to 0.0361 (30.84%) along with increasing GNPs content of 0.3 to 0.5 phr. The best abrasion resistance of SBR/GNPs nanocomposite is observed at 0.5 phr of GNPs. The agregativeness of a high volume fraction of GNPs with high GNPs content can affect the networking formation of the rubber chain. Thus, at 0.7 phr of GNPs the abrasion loss of SBR/GNPs is slightly increased, which means the reduction of abrasion resistance of nanocomposite material.

3.5. Effect of GNPs Contents on the Adhesion of SBR/GNPs Nanocomposite with Polyester Fabric

The effect of GNPs contents on tear strength of SBR/GNPs nanocomposite was investigated with the content of 0.3, 0.5, and 0.7 phr of GNPs. Other compositions of the nanocomposite recipe are shown in Table 1. Results of adhesion strength are shown in Fig. 7. It can be clearly seen that with the presence of GNPs in SBR matrix, the adhesion strength of SBR/GNPs nanocomposite with polyester fabric is significantly increased. The adhesion strength increase with the increasing of GNPs content. The highest adhesion strength was 13.74 N/mm with 0.7 phr of GNPs, which is approximately 3 times higher than that of SBR rubber without GNPs.
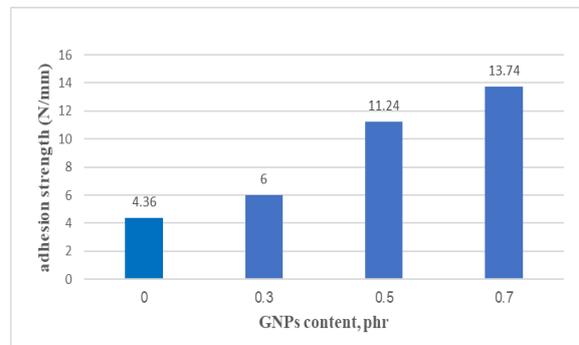

Fig. 7. Adhesion strength of SBR/GNPs nanocomposite with polyester fabric

The explanation of this phenomenon can be assigned to the two factors. Firstly, nano graphene is high thermal conductivity inorganic filler. Therefore, the dispersion of GNPs in the SBR rubber matrix can improve the vulcanization capacity of SBR rubber leading to an increase in adhesion strength. Secondly, the modification of GNPs with oleic acid might has carboxyl functional group (-COOH), which interacts with hydroxyl functional group on polyester fabric by dipole interaction and hydrogen bonding, leading to the increase in adhesion strength.

3.6. Morphology of SBR/GNPs Nanocomposite Material

Fig. 8 shows the morphology of the tensile fracture surface of SBR rubber and SBR/GNPs nanocomposite with 0.5 phr of GNPs.

The tensile fracture surface of SBR/GNPs nanocomposite material with the presence of GNPs was observed rougher than that of SBR rubber (Fig. 8a and 8b). The roughness of SBR/GNPs tensile fracture surfaces with various magnifications as in Fig. 8b, 8c, and 8d shows the crack propagation obstruction leads to increasing obstruction energy. The morphology of SBR/GNPs nanocomposite demonstrates the good

mechanical properties improvement of nano graphene for SBR rubber.

3.7. Effect of GNPs Content on the Thermal Aging of SBR/GNPs Nanocomposite

Thermal aging of SBR/GNPs nanocomposite with various GNPs contents such as 0.3, 0.5, and 0.7 phr was evaluated at 100 °C in 168 hours according to TCVN 2229:2007 standard. The mechanical properties such as tensile strength, tear strength, hardness, and abrasion resistance were measured. Results in the effect of GNPs content on thermal aging of SBR/GNPs nanocomposite material are shown in Fig. 9, 10, 11, and 12.
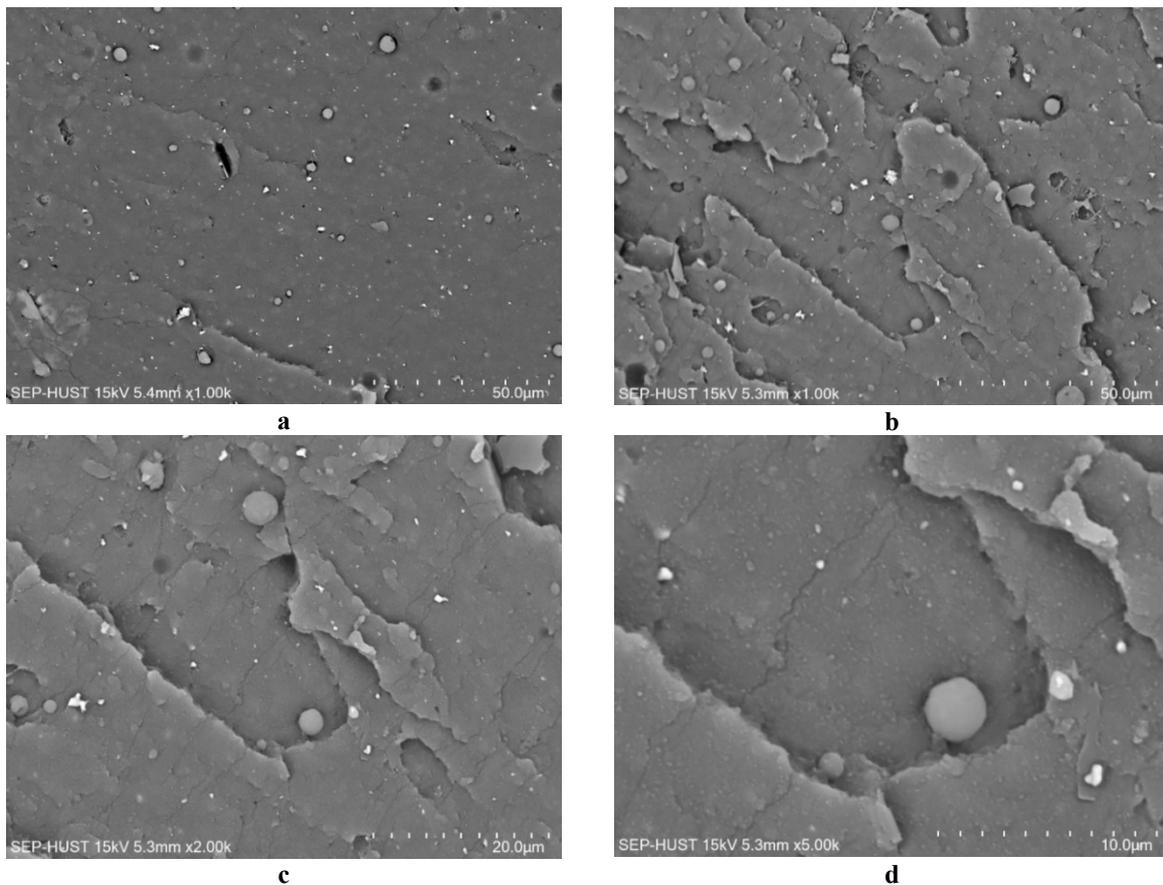

Fig. 8. Tensile fracture surface of SBR rubber with magnification of 1000 (a), SBR/GNPs nanocomposite with magnification of 1000 (b), 2000 (c), and 5000 (d)
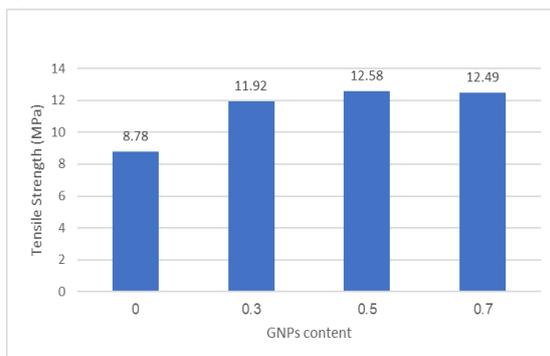

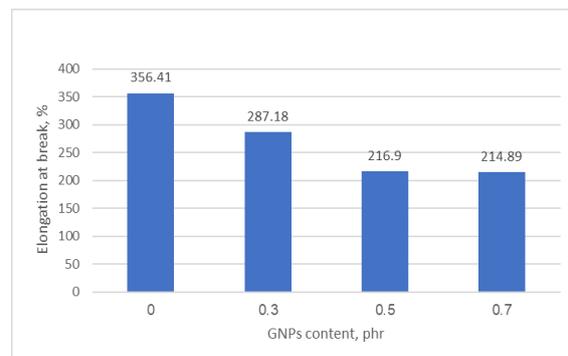Fig. 9. SBR/GNPs tensile strength after 168 h at 100 °C

Fig. 10. SBR/GNPs elongation at break after 168 h at 100 °C
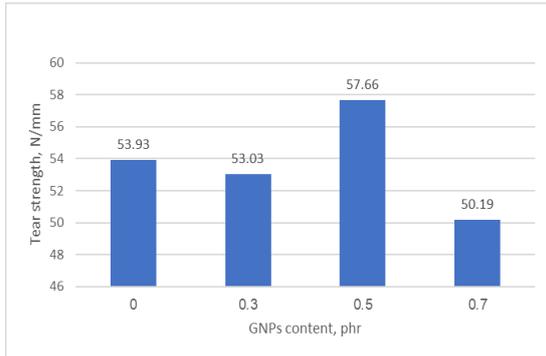
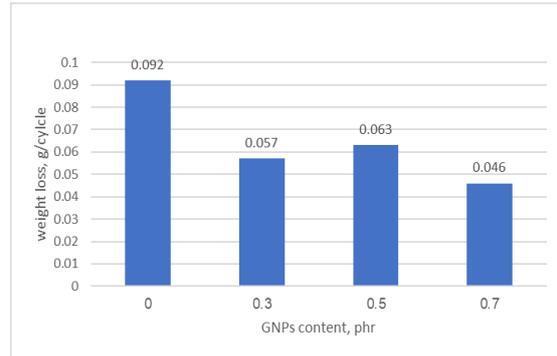Fig. 11. SBR/GNPs tear strength after 168 h at 100 °C

Fig. 12. SBR/GNPs abrasion weight loss after 168 h at 100 °C

As can be seen in Fig. 9 and Fig. 10, the tensile strength of SBR/GNPs nanocomposite is strongly decreased due to the thermal degradation of rubber. In addition, Fig. 11, 12 show the decrease of tear strength and abrasion resistance capacity of SBR/GNPs nanocomposite after 168 h at 100 °C. However, in terms of mechanical properties, the 0.5 phr of GNPs remained higher in comparison with the other GNPs contents. It can be ascribed to the good dispersion of GNPs in SBR matrix by SBR/GNPs masterbatch lead to good heat transfer along the whole sample.

In addition, the thermal aging behavior is clearly seen by the increasing of Shore A hardness of nano SBR/GNPs nanocomposite (Fig. 13).
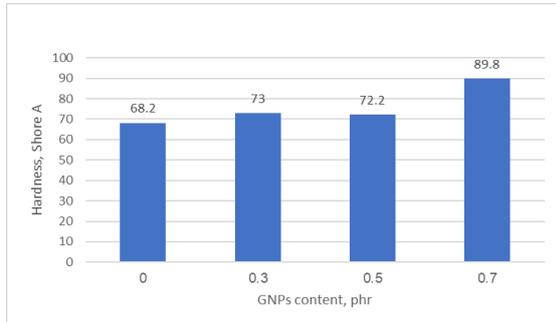

Fig. 13. SBR/GNPs hardness after 168 h at 100 °C

Theoretically, the lower thermal aging index is, the higher thermal aging resistance capacity is. As shown in Table 2 the thermal aging index of SBR/GNPs nanocomposite is decreased with the increasing of GNPs content. It can be explained because of the high thermal conductivity of GNPs led to quick heat transfer from material to the environment. Therefore, GNPs can improve the thermal aging resistance capacity of SBR rubber.

Table 2. Thermal aging index of SBR/GNPs nanocomposite

GNPs content, phr	0	0.3	0.5	0.7
168 h	48.23%	40.69%	38.79%	31.41%

4. Conclusion

The application of Vietnam nano graphene platelets in the SBR rubber matrix was investigated. The mechanical properties of SBR/GNPs nanocomposite were improved with the presence of GNPs in comparison with SBR rubber (tensile strength, and tear strength were increased by 29.67% and 31.89% respectively in comparison with SBR rubber without GNPs, and abrasion weight loss was decreased by 30.84% in comparison with SBR and adhesion strength with polyester fabric was 3 times higher than that of SBR). The optimal of GNPs content in SBR/GNPs nanocomposite was 0.5 phr, which has the highest mechanical properties, good abrasion resistance and good adhesion with polyester fabric.

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