Auxetic Nanocomposite Based on Styrene Butadiene Rubber (SBR) Foam with Varying Nano-carbon Loading

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Abstract Styrene-butadiene rubber (SBR) is a synthetically produced general-purpose rubber which is fabricated by copolymerization of styrene and butadiene. It is widely used in automobile tires owing to its good abrasion-resistance, enhanced crack resistance, and improved aging properties. Strength of SBR is improved by reinforcing it using fillers such as carbon black. Presence of gaseous phase in foamed structure of SBR increases volume along with improvement in various matrix characteristics. SBR matrix was transformed into foamy product during curing in the presence of chemical blowing agents. This paper presents preparation and characterization of SBR foam with varying nano-carbon loading causing development of a variety of foamy structures; processes like compounding and vulcanization altered the mechanical properties to a great extent. Mechanical characterization revealed that incorporation of 20% carbon in the SBR caused 140% rise in tensile strength and 90% increase in hardness with a corresponding decrease in elongation to about 35%, compared with neat SBR. The 'cure rate index' increased to 200% with 20% carbon concentration, whereas 'loss modulus' and 'tan δ ' increased to 135% and 80%, respectively, as determined at maximum viscosity. Overall a significant improvement in mechanical properties and damping characteristics was observed.

Keywords Styrene Butadiene Rubber (SBR), Nanocomposite, Viscoelasticity, Loss Modulus, Storage Modulus, Scorch Time

building blocks. Having the bulk of application in tire industry, styrene butadiene rubber possesses superior crack and weather resistance. In order to get good mechanical properties the rubber is reinforced with fillers like carbon. High filler content increase the weight of the final product as well as reduces processability due to which nano fillers are used in the rubber to accomplish the reinforcement for the applications [2, 3]. Foaming significantly increases a range of properties of the base material. This enhancement in properties creates applications for foams which cannot be simply filled by fully dense solids. Choice of properties like density, compressive strength, young modulus and thermal conductivity grows for foams as compared to dense solids [3]. Incorporation of nano fillers other than carbon has also been studied, e.g. use of varying particle sizes of kaolinites was recently studied Zhang et al [4].

The unique physical, mechanical, and thermal properties held by polymeric foam, are controlled by (1) its cellular structure and (2) the gas composition. It is a natural composite wherein the gaseous component and the polymer are constituents. The thermodynamic properties like specific heat, the equilibrium constant, and the heat conductivity depend upon the individual elements [5].

The foaming characteristics are determined by structural parameters generally related to cell properties like density, expansion ratio, size distribution, open-cell concentration and integrity. These parameters are regulated by foaming technology which often relies on the type of the polymer.

1. Introduction

SBR is a synthetic rubber, derived from petroleum oil, primarily developed as an alternative for natural rubber; it consists of a compound obtained by mixing ~75 percent butadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$) and 25 percent styrene ($\text{CH}_2=\text{CHC}_6\text{H}_5$) [1]. The raw gum rubber has many subcategories such as solution or emulsion polymerized, subject to the method of synthesis of polymer and fraction of styrene and butadiene which are the two core chemical

2. Experimental

Materials. SBR was used as a base polymer with nominal composition of 25% Styrene and 75% Butadiene, having a specific gravity of 0.86. Nano-carbon black was added in varying concentration of 0%, 5%, 10%, 15% and 20% to various samples. The type of carbon black used was N-330 having an average particle size of 70 nm. Blowing agent (ACPW China) along with other additives i.e. zinc oxide, DPG (Diphenyl guanidine), MBTS (2-mercaptobenzothiazole) and sulfur, were added in

specific amounts as given in Table-1. Apart from analytical grade of zinc oxide all other constituents were of commercial grade. Wax and stearic acid were also employed during compounding process.

Compounding. The rubbers used were modified by the process of 'Compounding'. Polymer (SBR), filler (N330 carbon black), stabilizer (antioxidants and waxes), vulcanization aids (sulfur, accelerators and waxes) were added and mixed during compounding. Samples of neat SBR were also processed in the same way as other formulations, for reference. A two-rolls mill having a friction ratio of 1.006 was employed for the compounding process. The mixing happened at the squeeze area between the mill-rolls. At the roll nip, a lateral shearing was produced by the compression as well as the rolling action of the rolls, causing mixing to occur along circumference of the rolls. Damping properties, high elasticity, and abrasion resistance were among few properties expected to be enhanced by compounding [3].

Vulcanization. Vulcanization generally used for elastomeric materials in order to develop a cross linked molecular network. This process enhances elasticity and reduces plasticity; this occurs as result of increase in retractile forces. This in turn decreases the amount of remaining permanent deformation when the deforming forces are removed [6].

Crosslinking of polymer chains produced a network juncture by a chemical process. A crosslink may be a polyvalent metal ion, a carbon-carbon bond, a single sulfur atom, an ionic cluster, a polyvalent organic radical, etc. [7]. Simultaneous heating and mixing of rubber with vulcanizing agents was carried out in a mold at a pressure of 3 MPa using an electrically heated hydraulic press (Shinto-Japan, 50 Tons Capacity). Time allowed for the vulcanization was 20 minutes at 150°C.

3. Characterization

Mechanical properties. Tensile strength and % elongation were determined as per ASTM D 412 C using Tensor Check profile Gibitre Instruments S.R.l. (Italy). Tests were carried out at a strain rate of 200 mm/min.

Rheological investigations. The viscoelastic property of rubber makes it significant to characterize the rate of flow under various conditions of stress, temperature and time of application of stress. The lowest torque, highest torque and Tangent Delta were determined using Rheocheck Profile-MD, Gibitre Instruments S.R.l (Italy). The temperature of the upper and lower plate was kept at $190^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$. Oscillation angle was 0.5° and the test time was 3 minutes. In order to quantify the rate of vulcanization, the cure rate index (CRI) was calculated which was dependent on scorch time (t_{s1}) and optimum vulcanization time (t_{90}); it was determined by the following formula [8]:

$$\text{CRI} = 100/(t_{90} - t_{s1})$$

Scanning Electron Microscopy. The SBR/Carbon nanocomposite foamy structure was examined under Scanning Electron microscope (SEM). Gold-sputtered samples of the nanocomposite were observed at various magnifications using JEOL JSM-6490A instrument with an accelerating voltage of 15 kV

Table 1. Ingredients for various formulations of SBR-carbon nanocomposite foams (all ingredients except carbon were kept constant in all formulations)

Ingredients, pphr (parts per hundred)	Samples				
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Rubber	100	100	100	100	100
Carbon black N -330	0	5	10	15	20
Blowing Agent (ACPW)	5	5	5	5	5
MBTS	5	5	5	5	5
Stearic Acid	1	1	1	1	1
Wax	1	1	1	1	1
Zinc oxide	1	1	1	1	1
DPG	1	1	1	1	1
Sulfur	1.5	1.5	1.5	1.5	1.5

4. Results and Discussion

It was empirical that mechanical properties and viscoelastic nature of nanocomposites varied with loading of reinforcing filler material [9, 10]. The SEM micrograph exhibited the type and extent of the foamy structure formed. The cell structure was mostly closed-cell, however, few open cells were also visible.

Although cell size is considered to be an important parameter, however, most mechanical and thermal properties are dependent on cell shape rather than the size [11]. As evident in Fig. 1 (a-e), the cell size and cell size distribution varied with carbon loading.

(a) Sample 1 (0% C)

(b) Sample 2 (5% C)

(e) Sample 5 (20% C)

(c) Sample 3 (10% C)

(d) Sample 4 (15% C)

Figure 1. Scanning electron micrographs of the SBR foams

Tensile testing performed at a strain rate 200 mm/min, demonstrated variation in stress strain behavior for varying percentage of carbon. The mechanical behaviors of the nanocomposites are given in Fig. 2, Fig. 3 and Fig. 4. The nano-filler content increased the strength of samples. Sample-1 containing 0 pphr nano-carbon exhibited the lowest strength and sample 5 having the highest amount of nano-carbon (20 pphr) exhibited the highest tensile strength. This phenomenon was attributed to cross linking of carbon atoms at the active sites of branched chains of SBR [13]. In addition, nano carbon movement to the physical micro voids in the polymer increased strength and hardness of the ultimate product [14]. The same phenomenon also supported the decrease of elongation at break (Fig.3).

Figure 2. Effect of carbon concentration on tensile strength at break.

Figure 3. Effect of carbon concentration on Elongation (%).

Figure 4. Effect of carbon concentration on hardness.

Nano-carbon movement to physical micro voids in the polymer also influenced the increase in hardness with the increase of carbon black content; the results are given Fig.4. Fig.5 shows variation of torque values for the SBR based nanocomposites as a function of amount of carbon. The measured torque depended on the system viscosity and elasticity, consequently it was increased as a result of enhanced crosslinking [12]. The minimum torque was a measure of the viscosity while maximum torque was related to crosslink density. Initially, the torque values of all the samples were comparable when the samples were in the form of semi-solid (jelly-like). This jelly-like nature allowed the material to move easily in the mould and permanent cross linking took place as the reaction proceeded with time. The torque values in Fig.5 clearly show that with the increase in carbon content the torque values of the SBR based nanocomposite increases [13]. The properties of SBR based nano composite foams were supported with the fact that the

direct result of the incorporation of fillers in molten polymers caused significant change in shear viscosity behavior and viscoelastic properties [14].

Figure 5. Effect of % carbon on viscosity variation in SBR

Fig. 6 shows scorch and cure time behavior with increase in carbon content. The measure of the premature vulcanization i.e. the scorch time significantly decreased with addition of carbon black compared with the optimum cure time (t_{90}). This behavior could be attributed to the rise in viscosity with the addition of nano-carbon. The optimum cure time (t_{90}) offered only small variations with the addition of nano carbon fillers. Since the weight of curing agents was proportional to the core rubber it was quite likely that for high volume of rubber the diffusion rate of curing agents within the matrix decreased and consequently the curing time reduced [15].

Figure 6. Variation in scorch and cure time with % carbon in SBR

Fig.7 exhibits cure rate index with an increase in carbon content. Cure rate index was significantly increased with an increase in filler materials. As cure rate index has a relationship with optimum cure time and scorch time, the

difference in the rate of decrease in both the characteristic times as a function of carbon content resulted in the ultimate increase of cure rate index. It was demonstrated that cure rate index was more dependent on vulcanization temperature than to the filler content [16].

Figure 7. Effect on cure rate index with variation of % carbon in SBR

The result of increasing carbon content on the loss modulus is shown in Fig.8. It is evident that S'' at both ML and MH increases with increase in carbon content. As the loss modulus is related to damping characteristic, it is logical to conclude that the increase in nano carbon volume in SBR based foam will boost its damping attributes [17]. Tangent Delta i.e. the ratio of the loss modulus to the storage modulus is plotted against increasing carbon content in Fig. 9. The values of loss modulus increase with time which consequently increases the tangent modulus.

Figure 8. Variation in loss modulus with % C in SBR

Figure 9. Variation in tan delta with % C in SBR

5. Conclusions

1. The amount of formation of foam in SBR/carbon nanocomposite is determined by the quantity of nano carbon filler in the polymer. This phenomenon has a direct influence on mechanical properties of the foamy material.
2. A maximum torque is the measure of polymer melt's density of crosslinking which supports the fact that the crosslink density increases with increase in carbon content the nanocomposite. This relation is tantamount to the fact that incorporation of filler content changes the shear viscosity behavior and viscoelastic properties
3. The ascent in $\tan \delta$, loss modulus and cure rate index values is also accredited to the increase in carbon content in the in the nanocomposite. Loss modulus and $\tan \delta$ is related to damping characteristic therefore the rise in damping properties with rise in percentage volume of carbon content is rational.
4. Scorch and cure time values declined with the addition of carbon content in the polymer composite.
5. The lowest torque values, which are a measure of stock viscosity, were not affected by the amounts of fillers.
6. Tensile strength, hardness, tensile strength at break increase by increasing carbon content whereas elongation at break decreases by increasing carbon content.

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