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Influence of Silica (SiO₂) Loading on the Thermal and Swelling Properties of Hydrogenated-Nitrile-Butadiene-Rubber/Silica (HNBR/Silica) Composites

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Abstract: Hydrogenated-Nitrile-Butadiene-Rubber (HNBR) is known for its good physical strength. It is a widely used rubber in electrical insulation and other high performance applications. Performance of HNBR is affected in high temperature and an aggressive fluid environment. Adding silica to HNBR may overcome this problem. In order to investigate the effect of fluids and temperature on HNBR/silica composites we prepared multiple composites of HNBR with 8.3, 16.7, 33.4, 50 and 66.7 phr of silica (SiO₂) by two roll compounding method. Swelling index and thermo gravimetric analyses were performed. Calculations of swelling indexes were performed at different time periods with ethanol, toluene and water. For thermo gravimetric analysis (TGA), thermo grams of samples were obtained and % char yields at 550 °C were analyzed for all samples. Improvements with the addition of silica were recorded up to a great extent in both analyses. Swelling index decreased with the addition of silica as compared to neat HNBR and reached an optimum position with 50 phr silica loading in ethanol, 8.3 phr in water and 66.7 phr in toluene. Moreover, the HNBR composite with 66.7 phr of silica was found to be the highest thermally stable sample and lost less than 60% of weight at 550 °C in comparison to neat HNBR in which 80% of weight loss occurred at 550 °C.

Keywords: HNBR; Composites; Silica; Loading; Filler; Mechanical properties

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1 Introduction

Hydrogenated-Nitrile-Butadiene-Rubber (HNBR) is a prominent and widely used elastomer [1]. It is obtained by hydrogenation of Nitrile Butadiene Rubber (NBR) [2, 3]. HNBR is known for sustainability of its physical strength and other properties in exposure to heat, oil and other chemicals [4]. This tough nature of HNBR is provided by its saturated structure and existence of many polar groups. Due to this exceptional nature, it finds usage in many industries e.g. automotive, aerospace and electrical and thermal insulations etc. [5, 6]. Although HNBR is advantageous over NBR in fuel and oil resistance and has also better oxidation and heat resistance than Ethylene-Propylene-Diene-Monomer (EPDM), it decays in high temperature environments and also swells when exposed to solvents [7,8]. Thus, the resistance of HNBR needs to be enhanced for applications in high temperature and aggressive solvent environments.

Enhancement in the properties of materials has been an area of research for a long time. Addition of fillers, to the neat materials is an efficient method to enhance their properties [9-12]. Different types of fillers are used to enhance properties of polymers. In order to get optimum results from fillers, some parameters are of great concern during the preparation of composites e.g. mixing time, mixing temperature and modifier content etc. [12, 13]. Fillers are broadly categorized in two classes, extended fillers and reinforcing fillers [14,15]. Extended fillers are generally used for the extension of formulation e.g. ATH, ZnO and ground quartz. Whereas, reinforcing fillers are used for improvement of properties e.g. physical, mechanical and thermal properties. Examples of reinforcing fillers are silica and carbon black etc. Thus, the addition of

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fillers may result in increased thermal and swelling resistance of overall HNBR composite. Several types of fillers were used previously to improve properties of HNBR [16] e.g. CNT [17, 18] ATH [19] and CB [20] etc. However, very limited work has been carried out on the investigation of thermal and swelling properties of HNBR composites [21–23] and almost no literature is available on these properties for HNBR/silica composites.

Silica is a reinforcing filler which has good resistivity and thermal stability thus it can bring superior enhancements in the properties of the HNBR. Interaction of silanol group of silica and hydrogen bond in polar HNBR is the reason of improvement in the properties in HNBR/SiO₂ composites [24]. However, further studies are required to find the effect of loading of silica to achieve the utmost thermal properties and swelling behavior of HNBR [25].

Like other fillers, concentration of silica is also an important parameter for the stability of polymer [26–28]. Although HNBR has been studied for silica fillers, thermal and swelling properties of HNBR/SiO₂ composites for different concentration of silica has not been reported yet. This is necessary to achieve high performance HNBR/SiO₂ composites.

Keeping in view the importance of thermal stability and swelling behavior for HNBR/SiO₂, we fabricated neat HNBR and its five HNBR/SiO₂ composites with 8.3, 16.7, 33.4, 50 and 66.7 phr of micro silica by two roll compounding as per recommendation of standard ASTM D-3182-07. Later on, all samples were tested for swelling behavior in ethanol, toluene and water. For investigation of thermal properties thermo gravimetric analysis (TGA) was used.

In this work, we have mainly focused on finding the effect of silica loading to achieve enhanced swelling and thermal properties of HNBR/SiO₂ composites.

2 Materials

2.1 Ingredients

HNBR was procured from Lanxess Chemicals (Germany) and micro-silica (5 μm) was obtained from Wuhan Newreach Chemicals (China). Other constituents such as zinc oxide (ZnO), stearic acid (SA), mercapto-benzothiazole (MBT), sulfur (S), Tetramethyl Thiuram Tetrasulfide (TMTD) and dioctyl phthalate (DOP), Pyrolytic Boron Nitride (PBN) were industrial grade products.

2.2 Preparation of Composites

Neat HNBR and its composites were fabricated with different loadings of silica. Two roll compounding method according to ASTM D-3182-07 was used for the preparation of samples [29]. At the start HNBR was masticated and then sulphur, ZnO, stearic acid were added one after other in a sequence as given in Figure 1. The vulcanizates were made in a bolt press machine by curing them at 165 °C temperature and 10 MPa pressure for 40 minutes. All constituents were mixed in parts per hundreds ratio (phr) as given in Table 1.

Figure 1: Sequence of constituents' addition in preparation HNBR Composites

3 Measurements, Instruments and Conditions

3.1 Swelling Properties

All six samples in approximately 1 cm × 1 cm of area and 2 mm thickness were used for the measurement of swelling properties [30–34]. Three solvents (water, ethanol and toluene) were used in the experiment. The dry samples' weight (W_d) was initially recorded by an electronic digital sample having accuracy of 0.001 mg. The samples were then dipped in solvent. After a specific amount of time the weight of the swelled samples (W_s) was recorded. The measurements were also taken for multiple durations to find the effect of dipping time on the swelling of HNBR.

Table 1: HNBR Composites formulation recipes

S.No.	Constituent	A/U	HNBR-0 Blank (neat) HNBR	HNBR-1 HNBR with 8.3 phr silica	HNBR-2 HNBR with 16.7 phr silica	HNBR-3 HNBR with 33.4 phr silica	HNBR-4 HNBR with 50 phr silica	HNBR-5 HNBR with 66.7 phr silica
1	HNBR		100	100	100	100	100	100
2	S		1.5	1.5	1.5	1.5	1.5	1.5
3	ZnO	phr	5	5	5	5	5	5
4	SA		1	1	1	1	1	1
5	Silica		0	8.3	16.7	33.3	50	66.7
6	PBN		1	0	0	0	0	0
7	MBTS		1	1	1	1	1	1
8	TMTD		0.5	0.5	0.5	0.5	0.5	0.5
9	DOP		2.5	2.5	2.5	2.5	2.5	2.5

The percentage swelling ratios for neat HNBR and its silica based composites for each solvent were then determined by the following formula [30–34].

$$\% \text{ S.R.} = 100 \times [(W_s - W_d) / W_d]$$

(a)

(b)

Figure 2: Swelling behavior of HNBR in ethanol (a) swelling ratio vs. swelling time (b) swelling ratio vs. silica concentration

(a)

(b)

Figure 3: Swelling behavior of HNBR in toluene (a) swelling ratio vs. swelling time (b) Swelling ratio vs. silica concentration

(a)

(b)

Figure 4: Swelling behavior of HNBR in water (a) swelling ratio vs. swelling time (b) Swelling ratio vs. silica concentration

4 Thermal Properties

For measurement of thermal properties Thermo Gravimetric Analysis (TGA) was performed using TGA Q50 (TA instruments, USA) following ASTM E1131 and ISO 11358 standards [35, 36]. To investigate weight loss by increasing temperature, the temperature was varied from room temperature up to 550 °C and thermo grams were obtained for the samples. For comparative analysis, temperatures for 10 % weight loss and 50 % weight loss of all samples were recorded. Moreover, the % char yield was also analyzed for samples at 550 °C.

5 Results and Discussions

5.1 Analysis of Swelling Behavior

Measurements for swelling index recorded for each solvent (ethanol, toluene and water) were different. The reason for the different swelling behavior is the exertion of different magnitudes of force from each solvent which depends upon the static fluid pressure of the solvent. Swelling properties of HNBR for ethanol, water and toluene are discussed below.

In ethanol, swelling ratio of HNBR varied with the variation in silica loading.

An increase in swelling ratio with the increase of immersing time in ethanol is clear from Figure 2(a). This increase of swelling ratio is up to a certain value and then de-

(a) Thermo gram of HNBR-0

(b) Thermo gram of HNBR-1

(c) Thermo gram of HNBR-2

(d) Thermo gram of HNBR-3

(e) Thermo gram of HNBR-4

(f) Thermo gram of HNBR-5

Figure 5

creases. The decrease in swelling ratio is due to the dissolving of rubber compound in the ethanol [37, 38]. From Figure 2(b) it is clear that the increase in silica loading results in decrease of swelling ratio. The decrease in swelling ratio of HNBR is due to the force involved between silica particles rubber network. In ethanol HNBR-4 which has 50 phr silica shows better swelling behavior as compared to the other samples up to 140 hrs.

Figure 3 shows trend of variation of swelling ratio in toluene vs. immersing time and silica concentration.

In toluene, decrease in swelling ratio was also recorded with the increase of silica loading. Thus, increase of silica resulted in overall compression of the HNBR/silica composite. It also emerged that the swelling ratio of HNBR in toluene was much higher in comparison to ethanol, which reflects higher affinity of HNBR to toluene than ethanol. However, in toluene HNBR-5 with 66.7 phr silica loading showed the best swelling behavior for all time durations, while for ethanol the swelling index reached an optimum point at 50 phr silica loading.

Unexpectedly, the swelling resistance of HNBR was higher in the case of water in comparison to ethanol and toluene.

From Figure 4(a) it is clear that the swelling ratio increases with the increase of immersing time in water. Moreover, it can also be observed that 8.3 phr loading of silica gives a minimum value of the swelling ratio for HNBR/SiO₂ composite. After 8.3 phr loading the swelling ratio continuously increased. This is due to the fact that silica absorbs water, because of the presence of silanol group (Si-OH) in silica which forms a hydrogen bond with water and hence the higher the silica content the higher the swelling of HNBR/SiO₂ composite [39, 40]. However, as shown in Figure 4(b) at 50 phr loading of silica the graph almost becomes a horizontal straight line which means that further loading of silica does not affect the swelling behavior of HNBR. In other words the HNBR reaches its maximum swelling limit.

5.2 Thermo Gravimetric Analysis (TGA)

In order to analyze thermal stability of each formulation its individual thermo gram was obtained which are given in Figure 5(a-e). The loss of weight was faster in the case of HNBR-0 while it was observed that the length of the slope of weight loss curve increased as function of silica loading. At the end of experiment at 550 °C the HNBR-0 lost almost 80% of its weight while HNBR-5 with 66.7 phr silica lost almost less than 60 % which is evident of improved of thermal stability through addition of silica.

From Figure 6 it is clear that sample HNBR-5 is more stable in comparison with other samples and hence gave highest value 383.84 °C for 10 % loss in weight. The same trend was followed when the temperature was increased and HNBR-5 was stable in comparison to other samples by having 50% loss in weight at the highest temperature of 459.23 °C. From Figure 6 it is also clear that by increasing the concentration of silica the thermal stability of rubber increases which is due to the internal strong Si-O bonding in SiO₂ as well as firm interaction of silanol group of silica with polymer network.

Figure 6: Temperature at 10 % and 50% wt. loss with respect silica concentration

Neat sample (HNBR-0) gave the smallest char yield which was approximately 10 % of initial weight of the sample, whereas HNBR-5 gave the highest char yield which is 42.12 % of the initial weight of the sample as shown in Figure 7. From Figure 7 it is also clear the char yield increased with the increase of silica loading.

6 Conclusions

Multiple HNBR/SiO₂ composites were prepared with different loadings of silica and tested for swelling behavior and thermal properties. Silica improved the swelling and thermal properties of HNBR but deteriorated in water. Composite with 8.3 phr silica was found with the best swelling behavior in water and for ethanol and toluene the optimum loadings of silica were 50 phr and 66.7 phr respectively. From TGA it emerged that composite with 66.7 phr of silica was more thermally stable and showed loss of weight less than 60 % at 550 °C, which was less in compari-

Figure 7: Char Yield at 550 °C versus silica concentration

son with other samples. Thermo grams obtained from TGA also showed that by increasing silica loading the weight loss in HNBR/SiO₂ was decreased.

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