Effect of Bismaleimde on Heat Resistance of Nitrile Rubber Composites

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Abstract—Nitrile rubber composites were prepared by the addition of asbestos and bismaleimide (BMI). The effect of asbestos and bismaleimide on thermal stability was studied.

Both Thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA) reflect much better thermal stability for the prepared composites. TGA results showed an increase in onset temperature from 360 °C of pure NBR composite to 360.8 °C and 401.3 °C for NBR/Asbestos(100) and NBR/BMI(100) composites respectively. Tg of nitrile rubber increased from -5°C to 2.2°C and 12.2°C of NBR/Asbestos(100) and NBR/BMI(100) composites respectively.

The work compares between asbestos and asbestos free nitrile rubber composites. Asbestos introduced as a high temperature filler but have a lot of environmental and health effects. Bismaleimide which is biocompatible proved to be a good replacement for asbestos for high temperature rubber composites.

Keywords— Nitrile rubber, thermal resistance, bismaleimide.

I. INTRODUCTION

Attempts have been made to prepare rubber composites suitable for high temperature applications and to understand how high temperature fillers influence the thermal stability of the elastomeric materials.

Thermal stability means the ability of a material to maintain the required properties such as strength, toughness, or elasticity at a given temperature. A detailed understanding of how polymers break down on heating is important in the design of elastomeric materials with improved properties for particular application.[1]

Compound formulation development and reformulation provide a means to rapidly meet new regulatory requirements, respond to competitive concerns, improve existing products, and facilitate new product development[2].

Large amounts of rubber materials are used in modern industry. Rubber has unique properties like the ability to resist large deformations without break(it stretches easily several times and even more than fifteen times in some cases), and recovery to almost 100% instantly etc[3]. This

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makes it important and necessary for many products, like tires, hoses, gaskets, washers, vibration dampers, conveyor belts, etc.

Nitrile rubber, also called nitrile-butadiene rubber, an oilresistant synthetic rubber produced from a copolymer of acrylonitrile and butadiene. The uses of nitrile rubber include non-latex gloves for the healthcare industry, automotive transmission belts, hoses, O- rings, gaskets, oil seals, V belts, synthetic leather, printer's roller, and as cable jacketing; NBR latex can also be used in the preparation of adhesives and as a pigment binder.

More than 50% of the O-rings sold are Nitrile O-rings, commonly used in hydraulic/pneumatic motors, cylinders, pumps and valves.

NBR is also employed in textiles, where its application to woven and nonwoven fabrics improves the finish and waterproofing properties[4].

II. MATERIALS AND METHODS

A. Materials Used

Nitrile rubber (NBR), zinc oxide, stearic acid, tetramethylthiuramdisulfide (TMTD), mercaptobenzothiazoldisulfide (MBTS), caster oil, sulfor, 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ). Carbon black (N 326), used in this study was supplied by Babylon tire company.

Bismaleimide (BMI) used in this study was supplied by Taizhou Huangyan Donghai Chemical CO .

B. Preparation Method

The formulation of the rubber composites are given in Table 2.I. Mixing was carried out in a two-roll mill. The ingredients were added according to ASTM D3182-89.

Vulcanization was done in 150 °C and the time required was 15 minutes which gives the best properties.

Recipe	Pure composite	NBR/asbestos	NBR/BMI	NBR/PI
Ingredients	Phr	Phr	Phr	Phr
NBR	100	100	100	100
asbestos	100	(25, 50, 100)	100	100
Bismaleimide			(25, 50, 100)	
polyimide				(25, 50, 100)
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
TMQ	2	2	2	2
MBTS	1.5	1.5	1.5	1.5
TMTD	0.5	0.5	0.5	0.5
Sulfur	1.5	1.5	1.5	1.5
Carbon Black 320	40	40	40	40
Castor oil	10	10	10	10

TABLE 2.1

III. CHARACTERIZATION AND TESTING

A. Thermogravimetric Analysis

The measurements were made under a heating rate of 20 $^{\circ}$ C/min at a temperature range 25 $^{\circ}$ C to 600 $^{\circ}$ C. The experiments were done in atmosphere. About 15–16 mg of the sample was used for the analysis.

B. Dynamic Mechanical Thermal Analysis (DMTA)

The storage modulus (E) and dynamic loss factor $(\tan \delta)$ were measured as a function of temperature with a dynamic mechanical thermal analyzer under the tension mode at a frequency of 1 Hz. The strain amplitude in the temperature range of -50 to 280 °C was 0.1%. The heating rate was 5 °C/min.

IV. RESULTS AND DISCUSSION

A. Thermogravimetric analysis (TGA)

Figure 4.1 shows the thermogravimetric (TGA) curves for NBR and its composites containing 25, 50 and 100 phr of asbestos and bismaleimide respectively. NBR and its composites present only one thermal degradation step in the temperature range 100-600 °C. The incorporation of Asbestos and Bismaleimide causes a shift towards higher temperatures.

The initial decomposition temperature at weight loss of 5wt% of pure NBR is 360°C. The incorporation of asbestos into the NBR increased the initiation of degradation due to the high temperature asbestos filler. The final char residue of NBR and its composites is shown in table 4.1. For NBR/asbestos the thermal stability enhanced because of the high thermal resistance of the inert asbestos and the interaction between the filler particles and the rubber matrix where the asbestos has a needle shape particles. It is generally believed that the inclusion of inorganic components into organic materials can improve their thermal stability [5].

In the other hand, the incorporation of BMI in to NBR increased the initiation of degradation temperature and the final char residue as shown in table 4.1. In NBR/BMI composites the thermal stability increased as BMI content increases due to the presence of high thermally stable BMI particles in NBR matrix.

The combination of high onset temperature and high final char residue of the degradation process is a good reference of the thermal stability of the composite material.

TABLE~4.1 The initial decomposition temperature of NBR and its composites at 5% mass loss and the final char residue at 600 C°

	Initial decomposition temperature C°	Final char residue wt%
Recipe		
Pure	360	32
NBR/asbestos 25 50 100	360.8 352 350	38.5 43.5 49
NBR/BMI 25 50 100	361.6 377 401.3	34 36 38

B. Dynamic mechanical thermal analysis

Figure 4.2 shows the dynamic mechanical thermal analysis (DMA) of NBR and its composites. It can be seen that Tg of pure NBR is -5 °C table 4.2. The Tg of NBR increased from - 5 for pure NBR to -0.6, 1 and 2.2 for NBR/asbestos(25), NBR/asbestos(50) and NBR/asbestos(100) respectively. The higher Tg values are related to the high thermal resistance of asbestos.

The Tg of NBR/BMI further increased to higher temperatures as BMI content increased table 4.2. This indicates that the mobility of NBR chains in NBR/BMI composites was restricted. Also the high temperature resistance of BMI and PI cause an increase in Tg of NBR composites.

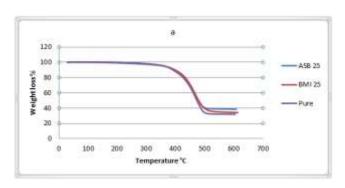
It should be noted that a good increase in the Tg of NBR/BMI(100) is observed by the curing of NBR/BMI(100) in 180°C instead of 150°C figure 4.3. In addition to this, an interesting point should be noted is the addition of (20 Phr) novolac (phenol formaldehyde resin) to NBR/BMI(100) where the Tg shifted to higher temperature figure 4.3. This implies that novolac may have an effect in improving the interaction of BMI and NBR that leads to increase thermal stability. Also the storage modulus(\bar{E}) for NBR/(BMI 100+20novolac) and NBR/BMI(100) cured at 180°C is higher than that of NBR/BMI(100) due to the higher crosslink density.

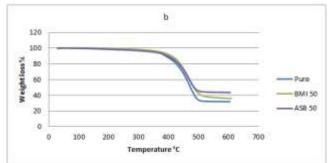
TABLE 4.2 GLASS TRANSITION TEMPERATURE AND LOSS TANGENT OF NBR AND ITS COMPOSITES OBTAINED FROM DMA ANALYSIS.					
Recipe	Glass transition temp.	Loss tangent tanð			
Pure		1.11			
NBR/asbestos 25 50	-0.6 1	1.09 1.04			
100 NBR/BMI 25	2.2 13.6	0.82 0.90			
50	10.6	0.75			

12.2

0.52

100





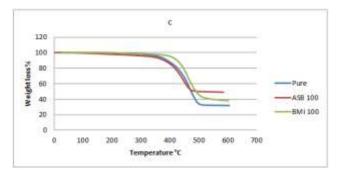
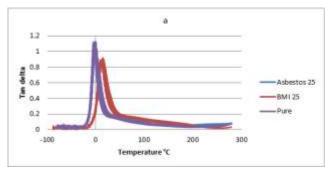
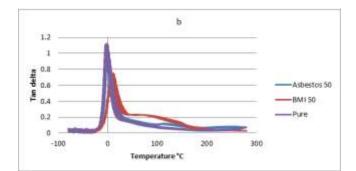


Fig. 4.1 TGA curves of NBR composites with different loadings a) 25 Phr b) 50 Phr c) 100 Phr





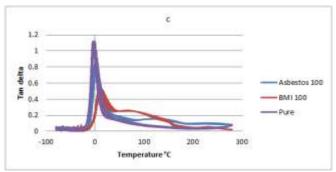


Fig. 4.2 DMA curves of NBR composites with different loadings a) 25 Phr b)50 Phr c) 100 Phr

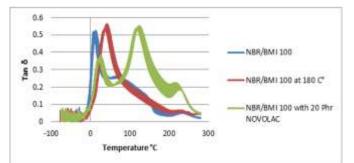


Fig. 4.3: DMA curves of NB/BMI 100 with different treatment.

V.CONCLUSIONS

NBR composites where prepared by the addition of Asbestos and bismaleimide (BMI) as a high temperature filler. Thermal stability of NBR and its composites were studied and compared to each other. It was found that the initial decomposition temperature at 5% weight loss for pure NBR composite is lower than that of NBR/asbestos and the latter is lower than NBR/BMI composites. High Tg values of NBR/BMI as compared to the lower values of NBR/asbestos is a clear evidence of the better thermal stability coupled with environmentally friendly materials used.

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