The Dynamic Properties of Hindered Amine GW-944/Nitrile-butadiene Rubber Hybrid Damping Materials

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Abstract. This work was try to study the damping properties of the hindered amine GW-944/nitrile-butadiene rubber (NBR) composites. FTIR shows that hydrogen bond –CN…NH- formed between the GW-944 small molecular and the NBR matrix. The DMA results that the tan δ peak values and the damping temperature at high temperature both become larger with the GW-944 contents increasing, indicating a better damping performance of GW-944/NBR composite.

1. Introduction
With the development of science and technology and the improvement of productivity, vibration and noise pollution have gradually become the focus issues of human society in the 21st century. The use of rubber damping materials for vibration and noise reduction is an effective way to alleviate these problems. [1, 2] Because of its unique viscoelasticity, rubber damping materials are widely used in automobiles, construction, aerospace and other areas of national defense and people's livelihood. [3] As an important strategic resource, the final performance of materials is also more and more demanding, so how to prepare high-performance rubber damping materials has become a research hotspot.

In recent years, many researchers have attempted to modify the rubber materials to achieve its high damping performance with a wide temperature range. [4, 5] Organic hybrid damping materials are relatively new in the research of rubber damping materials. Chinese scholar Wu added organic small molecules such as hindered phenol and accelerator DZ to polar substrates such as chlorinated polyethylene (CPE) and polyacrylic ester (ACR), using the reversible hydrogen bonds formed between organic small molecules and polymer substrates to get organic hybrid damping materials with high loss factors. [6, 7] In this study, nitrile-butadiene rubber (NBR) was selected as a substrate material for organic hybridization because of its good damping properties. Hindered Amine GW-944 containing polar amines and imide groups were selected as polar small molecules. It is hoped that strong hydrogen bonding between GW944 and NBR can be formed to improve the damping properties of the material.

2. Experimental Methodology

2.1. Materials
NBR (N220S) with an acrylonitrile mass fraction of 41% was provided by Japan Synthetic Rubber Co.,
Ltd. (Tokyo, Japan). Hindered amine GW-944 were purchased from Beijing Additives Institute (Beijing, China). The samples was made by adding 5.0 phr of zinc oxide, 2.0 phr of stearic acid, 0.5 phr of dibenzothiazole disulfide, 0.5 phr of diphenyl guanidine, 0.2 phr of tetramethylthiuram disulfide, and 2.0 phr of sulfur with different GW-944/NBR mass ratios. The chemical structures of NBR and GW-944 are shown in Fig.1.

![Chemical structures of NBR and GW-944](image)

**Figure 1.** Chemical structures of (1) NBR and (2) hindered amine GW-944

### 2.2. Sample Preparation
Firstly, the Hindered amine GW-944/NBR rubber composites at different blending mass ratios were then kneaded at room temperature for 5 min. Secondly, the composites were kneaded on the two-roll mill at 150°C for 5 min to fully fuse the hindered amine molecules. Thirdly, the composites were mixed with compounding and crosslinking additives mentioned above. The composites were then kneaded on the two-roll mill at room temperature for 10 min. Finally, the composites were hot-pressed and crosslinked at 160°C under the pressure of 15 MPa for different periods of time, and then naturally cooled down to room temperature to prepare the hindered amine GW-944/NBR samples.

### 2.3. Characterization
The FTIR measurements were conducted on a Nicolet 8700 FTIR spectrometer made by Thermo Fisher Scientific Inc. (USA) at the wavenumber range of 400 cm⁻¹ to 4000 cm⁻¹. DSC measurements were performed on a TGA/DSC calorimeter made by Mettler-Toledo Co (Switzerland). Samples were heated from room temperature to 100°C and keep the temperature for 3 min to eliminate heat history, and then heated from -60°C to 150°C again. The whole process were at a heating rate of 10 °C/min under a nitrogen atmosphere. The DMTA measurements were conducted in a tension mode by using a VA 3000 dynamic mechanical analyzer made by Rheometric Scientific Inc. (USA). The temperature dependence of the loss factor (tanδ) for various samples was measured between -50°C and 250°C at a constant frequency of 10 Hz and a heating rate of 5°C/min.
3. Results and Discussion

3.1. Analyze the Hydrogen Bonds of GW-944/NBR Composites by FTIR

![FTIR spectra of (a) GW-944 and (b) GW-944/NBR at various GW-944 contents]

Figure 2. FTIR spectra of (a) GW-944 and (b) GW-944/NBR at various GW-944 contents

Figure 2 show the FTIR spectra of GW-944 and GW-944/NBR composites. The spectrum for GW-944 indicates the significant absorption in 3443 cm$^{-1}$ was assigned to the imino group -NH-. In figure 2(b), a broad peak appears in the range 3100-3600 cm$^{-1}$ at high contents of GW-944 (mass ratios >11). Increasing the GW-944 content shifts this broad peak to lower wavenumbers. This red shift is attributed to the hydrogen bonding between the -NH- group of GW-944 and the –CN group of NBR. The absorption at 2237 cm$^{-1}$ was assigned to the –CN group, which weakened with increasing GW-944 content also indicating hydrogen bonds interactions have become stronger.

3.2. Glass Transition of GW-944/NBR Composites

Figure 3 shows the thermal properties of GW-944/NBR composites. GW-944 is a non-crystalline small molecule with a glass transition temperature (Tg) of 87.7°C. All the GW-944/NBR composites have one glass transition temperature, indicating GW-944 small molecular evenly dispersed in the NBR
matrix. As the contents of GW-944 increase, the Tg of GW-944/NBR composites increase. This increase is due to the hydrogen bond between the NBR and the GW-944.

![Figure 3. DSC results of GW-944/NBR composites](image)

**Figure 3.** DSC results of GW-944/NBR composites

### 3.3. Dynamic Mechanical Properties

Figure 4 shows the temperature dependence of tanδ for GW-944/NBR composites with various mass ratios. The tanδ was defined as the ratio of the dispersed energy in one deformation cycle to the energy accumulated during the same cycle, reflecting the internal and external friction and expresses. The higher the tanδ, the wider the damping range, and the better the damping performance of the material.

![Figure 4. Temperature dependence of loss factors for GW-944/NBR composites](image)

**Figure 4.** Temperature dependence of loss factors for GW-944/NBR composites

Table 1 lists the values of the tanδ of GW-944/NBR. As the GW-944 content increases, the first tanδ peak values of GW-944/NBR gradually decreases from 1.90 to 0.46, the pure NBR matrix has the highest value and greatest tanδ area (TA). However, the damping range shifts to higher temperature with increasing GW-944 contents. As the GW-944 content exceeds 22 phr, the damping temperature at
high temperature becomes larger, and the tanδ peak values at high temperature become higher, indicating the strong interaction between NBR and GW-944, consistent with the DSC and FTIR results above. The damping properties of GW-944/NBR, especially in the high temperature region, have been improved by adding the GW-944 small molecular.

Table 1. Values of the tanδ peaks in GW-944/NBR composites

| GW-944/NBR | tanδ peak height | Temperature range >0.3 (°C) | The total TA value |
|------------|------------------|-----------------------------|-------------------|
|            | tanδ peak height | Temperature range >0.3 (°C) |                    |
| 0/100      | 1.90             | 34.55                       | 34.55             |
| 11/100     | 1.69             | 32.90                       | 32.90             |
| 22/100     | 1.43             | 32.75                       | 32.75             |
| 44/100     | 0.93             | 28.65                       | 43.6              |
| 67/100     | 0.75             | 26.90                       | 58.6              |
| 89/100     | 0.46             | 23.15                       | 55.85             |

4. Conclusions
We have performed FTIR, DSC and DMA methods to investigate the dynamic performance of GW-944/NBR composites with various mass ratios. There are hydrogen bonds formed between the -NH- group of GW-944 and the –CN group of NBR. As the GW-944 content increases, the damping properties of GW-944/NBR have been improved especially in the high temperature region. The GW-944 small molecular can be used to adjust the dynamic properties of NBR matrix to get better damping material.

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