Strain dependent hysteresis in XNBR-CNT nanocomposites

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Abstract. Advanced nanocomposites are in the focus now owing to their prominently enhanced properties that can be designed even at low filler loading. The current literature has not much explored the application of nanocomposites for vibration damping applications – especially the impact of transient strain effects. This study focusses on the effect of incorporation of multiwall carbon nanotubes (MWNT) in carboxylated nitrile rubber (XNBR) and the effect of applied strain and volume fraction of MWNT on the damping properties, as studied in a universal testing machine in tensile and compression modes. In the compression mode, the percent damping decreases initially up to 0.5 vf of MWNT and then increases and remains constant. The percent damping varies from 16-35%. In the tensile mode, the damping increases continuously with increasing nanofiller content, with percent damping varying from 22-38%. The results indicate that the same nanocomposite behaves differently depending on the type and amount of strain, especially where the damping is important as in the case of vibration isolation and vibration damping applications.

1. Introduction

Structural vibrations are undesired phenomenon causing component fatigue due to periodic oscillations and human discomfort created by unwanted noise. Hence, they are of great concern to big structures like aircrafts or ships as well as to minute electronic assemblies. The suppression of vibration and the resultant noise is also an important acoustic stealth measure in marine vessels. The vibrations due to the installed machinery and propellers may get transmitted through hull vibration into the sea water, which can easily be detected by specific underwater sensors. Management of unwanted vibrations is commonly carried out through design changes to reduce the vibration at source, altering the mass and/or stiffness to shift the resonance and by utilizing viscoelastic damping materials [1–3].

Though vibration mounts reduce the intensity of machinery vibration, the residual vibration gets transmitted along the path and can be still large enough for generating radiated noise in many cases. Numerous types of damping and isolation treatments are extensively used to improve the signal-to-noiseratio of underwater sensors. In theory, they decouple and isolate the structure-borne noise from a ship’s hull and provide proper impedance backing for theacoustic sensors [4,5]. The standard practise is to introduce damping at source, in the pathway or near the target thereby improving the structural integrity and longevity. Damping is the process by which the amplitude of vibration steadily decreases due to the dissipation of the kinetic and strain energy of the vibrating system through heat and friction loss mechanisms [6, 7].

The viscoelastic nature of rubber and rubber-like materials plays a major role in damping of structural vibrations. The extent of damping depends on the type of rubber, vulcanization, type of filler and the amount of filler incorporated. In most of the practical scenarios, many applications call for the rubber component to be subjected to cyclic loads [7-9]. Rubbers filled with reinforced fillers demonstrate many exciting nonlinear effects like the Mullins effect, the Payne effect, and hysteresis energy loss, especially when subjected to cyclic deformations [9]. Rubber compounds having good hysteresis...
energy loss are preferred in marine platforms to absorb structural vibrations which improve the sensor performance. Conventionally, rubbers filled with micrometer sized fillers (> 30%) such as carbon black and nonblack fillers are used as vibration damping composites [8]. The discovery of nano materials has turned the attention towards the development of advanced rubber nanocomposites [10, 11]. A variety of nanomaterials such as carbon nanotubes (CNT), nanofibers, and inorganic nanomaterials are used as fillers in rubber compounds [12]. CNTs are used primarily in rubber nanocomposites due to their very high mechanical properties coupled with functional properties for many applications[10-12]. Out of the single wall nanotube (SWNT) and multi wall nanotube (MWNT), MWNT is widely used for the development of materials having high damping at very low level of filler loading as they can be produced at low cost and possess high performance properties[13-17].

The current literature has not much explored the application of nanocomposites for vibration damping applications – especially the impact of time-dependent strain effects. Hence, in the present work, efforts are made to understand the role of applied strain on the hysteresis damping of carboxylated nitrile rubber (XNBR) reinforced with multiwall carbon nanotubes (MWNT).

2. Experimental
The XNBR used was Chemigum NX-146, obtained from M/s Eliochem, India. It has a Mooney viscosity of ML 1+4[100°C] 45±5, 33% acrylonitrile content, and 1.0% carboxylic content. The MWNT, having a purity of 95% and average diameter of 20-30 nm, was supplied by M/s Chemapol, Mumbai. A two-roll mill was used to compound the rubber with various volume fractions of MWNT (vf) (0, 0.5, 1.5, 3.5 and 5 %), along with required parts per hundred of rubber (phr) of zinc oxide, stearic acid, n-cyclohexyl-2-benzothiazole-sulfenamide (CBS) and sulfur. The cure time of the rubber was found out from a rheometric study in Monsanto Rheometer 2000, and stocks were cured to 90% (t90) under pressure at 150°C.

Compression studies were carried out at room temperature according to ASTM standard D 575-91 in a Zwick 1476 (Germany) universal testing machine. The crosshead speed was kept constant at 10 mm/min. The test specimens were of 20 mm diameter and 10 mm thickness. The sample was kept in between the platens and compressed to 25% and then the load was removed, also at 10mm/min speed. The loading and unloading cycles were repeated ten times. The tensile experiments were carried out on test specimens of 60 mm length, 4 mm width and 2 mm thick in the same UTM (as per ASTM D 614) at a crosshead speed of 50 mm/min at room temperature. The applied strain was 25% and then the load was removed at 50 mm/min speed. The loading and unloading cycles were repeated ten times.

3. Results and Discussion
Cyclic experiments in UTM, in compression as well as tensile mode, provide more information about the energy density dissipated by the rubber sample which can be equated to actual operational environment. The typical stress-strain plots of XNBR and nanocomposites in compressive and tensile loading cycles are displayed in Figure 1.

It can be seen from the Fig. 1 that for the same amount of applied strain, the magnitude of stress developed and energy dissipated are significantly higher in the case of compressive load. The shape of hysteretic loop also changes with the MWNT content, indicating nonlinearity. XNBR without nanofillersexhibits a relatively stiff response on loading. On subsequent loading, the stress-strain curve follows a softer path. This typical stress softening is the Mullins effect. The response stabilizes by the forth cycle, and hence the area of the fifth cycle is taken as the constant area. Mullins effect implies that the stress and the area of the hysteresis loop decrease significantly between the first two cycles. It is observed that with increasing MWNT content, the loop area of all the cycles increases proportionately along with the difference in loop area between the first and second cycles. This shows that Mullins effect also increases when the MWNT content is increased in the nanocomposite. This points to the fact that, in addition to the increasing reinforcement by MWNT, there is a formation of agglomerates at the microscopic level that breaks down with the strain. The increased energy loss per cycle may be attributed to the high degree of internal friction that results from poor interactions of
MWNT with elastomeric chains, unlike the carbon black that has both physical and chemical interactions through structural irregularities and defects.

Figure 1: Hysteresis plots of stress vs strain of XNBR & XNBR nanocomposites with 5%vf MWNT (a) under compressive cyclic load and (b) under tensile cyclic load.

If \( U_1 \) is total strain energy, \( U_1 - U_2 \) is the area inside the loop, the hysteresis loop area can be used to express the easily perceivable percentage damping as [8]

\[
\% \text{ damping} = \frac{U_1 - U_2}{U_2} \times 100
\]

The percent damping calculated for tensile and compressive strains is tabulated in Table 1.

| MWNT Content | % Damping at 25% strain |
|--------------|-------------------------|
| phr\(^a\)    | \( \text{vf}\)\(^b\) (%)| Tensile cycles | Compressive cycles |
| 0            | 0                       | 22.8          | 16.2             |
| 1            | 0.5                     | 24.4          | 15.5             |
| 3            | 1.5                     | 26.3          | 17.2             |
| 5            | 2.5                     | 29.7          | 20.8             |
| 7            | 3.5                     | 31.9          | 30.5             |
| 10           | 5                       | 38.8          | 35.2             |

\(^a\)phr = parts per hundred rubber, \(^b\)\( \text{vf} \) = volume fraction

When the percent damping is calculated from the constant area loops, it may be seen that the incorporation of CNT into XNBR matrix increases the percentage damping from 16% in unfilled to 35% in the case of compressive loads and 22% to 38% in the case of tensile loads. The percentage damping seems to be higher in the case of tensile loading, though the absolute magnitude of damping is higher in the case of compressive load due to the higher degree of energy dissipation as observed in the hysteresis plots. The increasing amounts of CNT in the nanocomposite leads to higher friction at the rubber-CNT interface leading to increasing percentage damping.

In many of the applications of rubber-metal or rubber-composite structures, the rubber is present as interface layers in constrained/extensional damping treatments, or mounts and bushes. In these, it experiences different extent of strain and loading cycles. It is expected that the observed results would facilitate in the design of specific nanocomposites depending on the type of application, as it is observed that the nature and extent of damping behaviour depend on the nanofiller content as well as the type of strain.

Conclusion
The study shows that the addition of MWNT enhances the damping efficiency of the XNBR rubber and that the hysteresis loss depends on the MWNT content and type of loading. The percent damping decreases in the compression mode up to 0.5 vf of MWNT and then increases up to 3.5 vf and subsequently remains constant. The percent damping varies from 16 to 35%. In the tensile mode, the damping increases continuously with increasing nanofiller content and the percent damping varies from 22 to 38%. It is clearly inferred that the same nanocomposite behaves differently depending on the type of strain and the filler content, especially when damping applications are considered.

Acknowledgement
The authors wish to thank Director, NPOL for granting permission to present this work.

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