Research Article

Quantitative Analysis of Damping Enhancement and Piezoelectric Effect Mechanism of CNTs/PMN/EP Composites

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Received 2 March 2018; Revised 2 June 2018; Accepted 11 June 2018; Published 30 July 2018

Academic Editor: Marino Lavorgna

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New types of piezoelectric damping materials, including carbon nanotubes (CNTs)/lead magnesium niobate (PMN)/epoxy (EP) resin, are developed. The tan δ area (TA) analysis method is selected to evaluate the damping properties which obviously clarifies the effect of maximum loss factor (tan δ) and effective temperature range on damping properties. Furthermore, the dominant factor of damping enhancement is quantitatively analyzed via the value of TA. Compared with PMN, the interfacial friction of CNTs acts as the dominant factor for the content less than 0.6 wt.%. The maximum damping percentage of CNTs reaches 29.14%. CNTs form loop circuits gradually with the content of CNTs increasing, and electrical energy generated via piezoelectric effect of PMN becomes the dominant factor as the content of CNTs exceeds 0.8 wt.%, and the damping percentage reaches 47.43% at the content of CNTs of 1.0 wt.%.

1. Introduction

In the past few decades, the viscoelastic material with an inherent high loss factor is widely applied in automobiles, aircraft, and military equipment to suppress vibration and impact noises [1]. For example, soft viscoelastic layers in viscoelastic sandwich structures are provided as the damping component in order to improve dynamic response [2]. A new type of damping enhancement with piezoelectric and conductive materials as fillers has been developed by Hagood and von Flotow [3, 4]. Electrical energy, generated by piezoelectric effect of piezoelectric ceramics, can be efficiently dissipated by external electronic circuits [5]. Conductive fillers are introduced into piezoelectric-ceramic/polymer composites as passive electrical network, such as carbon nanotubes (CNTs), carbon black (CB), graphite, and aluminum particles [6–13]. CNTs are widely used due to the high electric current carrying capacity (10^11–10^12 A/cm²) [14]. It is revealed that the CNTs provide superior conductivity at very low concentrations which can transfer electrical energy into thermal energy efficiently [14]. Tian et al. reported a type of CNTs/lead zirconate titanate (PZT)/EP composites. They found that the generated electrical energy was well dissipated, and the loss factors of composites were improved by the incorporation of PZT and CNT at critical electrical percolation [7, 8]. Carponcin et al. studied the influence of piezoelectric on damping properties of CNTs/PZT/polyamide composites, and it was found that the polarization of piezoelectric ceramic particles improved the loss factor of 20% reaching to 0.052 [9]. PMN as another piezoelectric material with perovskite structure also possess high piezoelectric coefficient and dielectric permittivity. PMN piezoelectric materials were used in 0–3 piezoelectric composites for damping enhancement gradually [10–12]. Li and Du focused on damping properties of nitrile-butadiene rubber/phenolic resin/PMN/CB composite. Mechanical energy was converted efficiently via piezoelectric...
effect at PMN volume content of 50%, and the maximum loss factor reached 0.813 [10].

Shamir et al. found that adding CB to the composites reduced the peak damping intensity but enhanced damping at higher temperature, and the effective damping temperature range was widened [15]. Chang et al. investigated the damping property of polyurethane composites with different ultraviolet absorbents, and they found that the tan δ increased at the temperature range of higher than the glass transition temperature though the tan δmax was gradually reduced [16]. Thus, in this study, tan δ area (TA) and loss modulus area (LA) values are selected as damping performance parameters of materials which obviously clarify the effect of maximum loss factor and effective temperature range on damping properties [17–20]. Furthermore, TA analysis method can be used for quantitative analysis of damping enhancement.

In this study, conductive phase (CNTs) and piezoelectric phase (PMN) are introduced into epoxy matrix to fabricate piezoelectric damping composites. Electrical energy generated via piezoelectric effect of PMN is efficiently dissipated through conductive network. Thus, damping performance of CNTs/PMN/EP composites is effectively improved. The damping enhancement effect of each component is specifically clarified, and the damping percentage is quantitatively analyzed based on the TA analysis method.

2. Experimental Procedure

2.1. Materials. The lead magnesium niobate (PMN) ceramic powder was supplied by Baoding Hengsheng Acoustics Electron Apparatus Company with the mean particle size of 1–10 μm. The dimensions of CNTs (supplied by XFNANO) were 10–20nm in diameter, and the purity of CNTs was >95%. Epoxy resin was diglycidyl ether of bisphenol-A type with an epoxide equivalent weight of >95%. Epoxy resin used in experiment was trans-
fused with curing agent used in experiment was trans-
formaldehyde. Epoxy resin was transf-
ferred into three-dimensional network structure by catalytic polymerization and addition polymerization reaction between molecular chains when polyethylene polyamine was introduced into epoxy, which resulted in the curing of composites.

2.2. Preparation of CNTs/PMN/EP Composites. CNTs were functionalized by 3:1 H2SO4 (98%)/HNO3 (70%) acid treatment to obtain carboxyl and hydroxyl groups. Matrices of epoxy resin (EP) with different contents of acid-treated CNTs were made. Then, PMN ceramic was preprocessed by silane coupling agents KH-560 to improve interfacial contact performance and then added to CNT/EP solution. The solution was stirred at 60°C for 12 h with magnetic stirrer and then placed in vacuum drying oven for gas evaporation. Finally, solution with curing agent was cast into a mold and cured for 5 h at room temperature, with a subsequent step at 105°C for 2 h.

The fracture surface analysis was performed by field emission scanning electron microscope (FE-SEM, Hitachi S-4800). The investigation of viscoelastic behavior was performed by dynamic mechanical thermal analysis (DMA, PYRIS-7e). Resistivity was tested by impedance analyzer (HP4294A).

2.3. TA Analysis Method. The TA analysis method is selected to evaluate the damping properties, which obviously clarifies the effect of maximum loss factor and effective temperature range on damping properties. Fradkin et al. proposed the definition of damping functions [21]:

\[
\begin{align*}
LA &= \int_{T_G}^{T_R} E'' dT = \frac{R}{(E'_G)_{avg}} \frac{\pi n^2}{2} \frac{g''}{g}, \\
TA &= \int_{T_G}^{T_R} \tan \delta dT = \frac{\ln E'_G - \ln E'_R}{(E'_G)_{avg}} \frac{R}{2} \frac{\pi n^2}{2} \frac{g''}{g},
\end{align*}
\]

where \(E''\) is the loss modulus, tan \(δ\) is the loss factor, \(T_R\) is the glass transition temperature, \(E'_G\) and \(E'_R\) are the storage modulus in glassy and rubbery states, \(T_G\) and \(T_R\) are the initial and final temperature of glass transition, \((E'_G)_{avg}\) is the activation energy of the relaxation process, and \(R\) is the gas constant.

Materials show obvious damping performances for the loss factor reaching 0.3 around damping peak, which means composites reach effective loss factor. Thus, in this research, we choose effective damping temperature range (tan \(δ\) ≥ 0.3) as integral region. \(T_G\) and \(T_R\) in formulas (1) and (2) are replaced with the initial and final temperature of which tan \(δ\) reaches 0.3. Then, TA values are obtained through integral calculation of loss factor curves over the temperature range. Toshio Ogawa proposed that loss factor had more practical significance than loss modulus in noise control and damping analysis [17]. Amorphous polymer, semicrystalline polymer, and single damping peak copolymer were used as research objects, and the functional relation between TA values and group numbers was shown as follows:

\[
TA = a_0 + \sum_{i=1}^{n} a_i X_i,
\]

where \(X_i\) is the number of group \(i\), \(a_i\) is the regression coefficient which means the contribution of TA values by each group, and \(a_0\) is a constant.

The group contribution analysis method is used to calculate theoretical TA values and develop a relation between the contribution of each functional group and damping properties. Thus, TA values can be used for quantitative analysis of damping enhancement. The damping percentage of each component is quantitatively analyzed based on following formulas:

\[
\begin{align*}
TA_i &= TA_i - TA_{i,0}, \\
D_i &= \frac{TA_i}{TA} \times 100%.
\end{align*}
\]
where $D_i$ is the damping percentage of component $i$, $T_{A_i}$ and $T_{A_c,i}$ are the TA value of component $i$ and composite, and $T_{A_c,0}$ is the TA value of composite at 0 wt.% content of component $i$.

### 3. Results and Discussion

As shown in Figure 1, CNTs dispersed well in the chemically functionalized CNTs/EP composites at 0.2 wt.% CNT content, which improves interfacial frictional energy dissipation of CNTs. As we can see from the magnified SEM image, the interparticle distance between carbon nanotubes is very close. When CNT content is up to 1.0 wt.%, no obvious agglomeration is observed in the matrix, and the dispersion state in the whole region still keeps well. With the content of CNTs increasing, some matrix-rich (not containing CNTs) regions appear, and some CNTs entangle with each other as shown in Figure 1(c). As we can see from the magnified SEM image, the agglomeration of CNTs weakens the interfacial contact between CNT fillers and epoxy matrix.

Dynamic mechanical analysis (DMA) of CNTs/EP composites are shown in Figure 2(a). In general, damping materials reach maximum loss factor ($\tan \delta_{\text{max}}$) at glass transition temperature ($T_g$). $T_g$ of CNTs/EP composites is in correspondence with pure epoxy materials. $\tan \delta_{\text{max}}$ at $T_g$ increases sharply and reaches optimal value at the CNT content of 0.2 wt.%, due to the interfacial friction when CNTs uniformly dispersed in epoxy matrix. High content of CNTs widens effective temperature range, while $\tan \delta_{\text{max}}$ decreases due to agglomeration of fillers and high viscosity of composites. Thus, TA values are selected as damping performance parameter which obviously clarifies the effect of maximum loss factor and wide temperature range on damping properties. Based on loss factor curves of CNTs/EP composites, TA values of composites with different contents of CNTs are obtained as shown in Figure 2(b). The frictional energy dissipation between conductive phase and epoxy matrix rises as the content of CNTs increases. The TA value of CNTs/EP composites increases correspondingly and reaches the maximum value at 0.6 wt.% content of CNTs, for the reason that CNTs widen effective temperature range at 0.6 wt.% content of CNTs compared to 0.2 wt.% CNTs/EP composite. As the CNT content increases gradually, CNTs/EP composites show higher viscosity. The effective temperature range keeps constant when the content of CNTs exceeds 0.8 wt.%. The entanglement of CNTs in epoxy matrix results in the decrease of TA value. However, the effective temperature range is widened significantly when the content of conductive phase exceeds percolation threshold. The TA value of CNTs/EP composites increases at CNT content of 2.0 wt.% consequently. Damping percentage of CNTs and epoxy matrix can be calculated by formulas (4) and (5). The damping percentage of CNTs and composite. As the CNT content increases gradually, CNTs/EP composites show higher viscosity. The effective temperature range keeps constant when the content of CNTs exceeds 0.8 wt.%. The entanglement of CNTs in epoxy matrix results in the decrease of TA value. However, the effective temperature range is widened significantly when the content of conductive phase exceeds percolation threshold. The TA value of CNTs/EP composites increases at CNT content of 2.0 wt.% consequently. Damping percentage of CNTs and epoxy matrix can be calculated by formulas (4) and (5). The damping percentage of CNTs and composite.

As shown in Figure 4(a), $T_g$ of PMN/EP composite is lower than pure epoxy material, and the effective temperature range is efficiently widened. Based on loss factor curves of PMN/EP composites, TA values of composites with different contents of PMN are obtained as shown in Figure 4(b). Piezoelectric effect of PMN ceramic is generated by external force. Bound charge exists on the crystal surface which cannot be transferred into other forms of energy. As a result, the enhancement of damping properties is mainly achieved by the interfacial friction of PMN ceramics. TA values of PMN/EP composites increase with the increase in the content of PMN and reach 14.4 at 40 wt.% content of PMN. On the one hand, the interfacial friction between fillers and polymer chains over...
the transition range is enhanced with the increase in the content of PMN. On the other hand, fillers reduce the free volume of elastic polymers which results in the decrease of viscoelastic damping. It means that the increase in frictional energy dissipation can be massively offset by the decrease in viscoelastic damping of matrix; thus, TA values of PMN/EP composites decrease correspondingly. Damping percentage of PMN and EP can be calculated by (4) and (5). The damping percentage of PMN shows the similar trend with TA values and reaches 33.95% at PMN content of 40 wt.%.

PMN fillers are uniformly dispersed in the matrix and improve damping properties through frictional energy dissipation efficiently while maintaining the inherent viscoelastic damping of epoxy. However, damping properties cannot be improved obviously with the content of PMN exceeding 60 wt.%. The increase in frictional energy dissipation is massively offset by the decrease in viscoelastic damping of epoxy matrix, so the damping percentage of PMN is merely 4.28% at 60 wt.% PMN content.

Loss factor curves of CNTs/60 wt.% PMN/EP composites are shown in Figure 5(a). The increase in frictional energy dissipation can be massively offset by the decrease in free volume of matrix at 60 wt.% content of PMN, and the impact of piezoelectric effect on damping properties can be significantly indicated. As shown in Figure 5(a), \( \tan \delta_{\text{max}} \) increases sharply at 1.0 wt.% content of CNTs. Combined with TA values of CNTs/EP composites, the damping percentage of each component is shown in Figure 5(b). TA values of CNTs/60 wt.% PMN/EP composites increase gradually with the increasing content of CNTs and reach 21.26 at 1.0 wt.% CNT content. The effect of piezoelectric phase (PMN) and conductive phase (CNTs) on damping properties can be explained from two aspects. On the one hand, the interfacial friction between fillers and epoxy matrix promotes energy dissipation efficiently. On the other hand, piezoelectric effect of PMN results in the enrichment of positive and negative charge on crystal surface. Then, electrical energy converted from mechanical energy is dissipated through continuous conductive network (CNTs). When the content of CNTs is less than 0.6 wt.%, CNT fillers exist as independent units rather than conductive network. Thus, bound charge on the crystal surface cannot be transferred into other forms of energy. The interfacial effect of CNTs is the dominant factor of damping enhancement
the damping percentage of CNTs reaches 29.14% at CNT content of 0.6 wt.%. The conductive network generates gradually for the content exceeding 0.8 wt.%. Electrical energy generated via piezoelectric effect of PMN is dissipated in the form of thermal energy; thus, piezoelectric phase (PMN) becomes the dominant factor of damping enhancement. Damping percentage of PMN increases obviously and reaches 47.43% at 1.0 wt.% CNT content. When the content of CNTs reaches percolation threshold (1.0 wt.%), the conversion efficiency of electrical energy is the highest. When the CNT content increases to 2.0 wt.%, the high viscosity of composites results in the agglomeration behavior of fillers which reduces functional energy dissipation. Furthermore, high content of CNTs forms short circuit network which decreases energy conversion efficiency. As a result, TA values of CNTs/60 wt.% PMN/EP composites and the damping percentage of PMN decrease. The damping percentage of PMN shows the similar trend with TA values. It is indicated that damping properties of composites are significantly improved by piezoelectric effect of PMN. Thus, the effective method for damping enhancement of piezoelectric damping materials is to realize efficient energy conversion by improving piezoelectric effect.

**Figure 4:** Damping properties of PMN/EP composites as a function of PMN content: (a) loss factor curves; (b) TA values and damping percentage.

**Figure 5:** Damping properties of CNTs/PMN/EP composites as a function of CNT content: (a) loss factor curves; (b) TA values and damping percentage.

through frictional energy dissipation. The damping percentage of CNTs reaches 29.14% at CNT content of 0.6 wt.%. The conductive network generates gradually for the content exceeding 0.8 wt.%. Electrical energy generated via piezoelectric effect of PMN is dissipated in the form of thermal energy; thus, piezoelectric phase (PMN) becomes the dominant factor of damping enhancement. Damping percentage of PMN increases obviously and reaches 47.43% at 1.0 wt.% CNT content. When the content of CNTs reaches percolation threshold (1.0 wt.%), the conversion efficiency of electrical energy is the highest. When the CNT content increases to 2.0 wt.%, the high viscosity of composites results in the agglomeration behavior of fillers which reduces functional energy dissipation. Furthermore, high content of CNTs forms short circuit network which decreases energy conversion efficiency. As a result, TA values of CNTs/60 wt.% PMN/EP composites and the damping percentage of PMN decrease. The damping percentage of PMN shows the similar trend with TA values. It is indicated that damping properties of composites are significantly improved by piezoelectric effect of PMN. Thus, the effective method for damping enhancement of piezoelectric damping materials is to realize efficient energy conversion by improving piezoelectric effect.

As shown in Figure 6, the $R_c$ value decreases apparently for the content of CNTs exceeding 0.8 wt.%, which implies that CNT particles gradually contact with each other at 0.8 wt.% CNT content. The $R_c$ value is lower than 10$^7$ when the CNT content reaches 2.0 wt.%. The formation status of CNT conductive network at different CNT contents is shown in Figure 7. When the content of CNTs is small (Figure 7(a)), less than 0.6 wt.%, the electrical network cannot form. Thus, the piezoelectric effect of PMN has no significant effect on damping enhancement. With the increase in CNT content, carbon nanotubes start to form small loops around PMN particles (Figure 7(b)). Those loop circuits are taken as conversion units to convert electrical energy into thermal
energy. As shown in Figure 5(b), the damping percentage of PMN increases sharply at CNT content of 0.8 wt.%, which implies that the electrical energy generated by piezoelectric effect of PMN is dissipated efficiently. The maximum energy conversion rate is obtained when the content of CNTs reaches percolation threshold (1.0 wt.%). However, CNT network forms short circuit when the CNT content reaches 2.0 wt.% (Figure 7(c)), and electrical energy generated via piezoelectric effect of PMN cannot be dissipated efficiently. Thus, the enhancement of damping properties by piezoelectric effect is weakened.

4. Conclusions

The present paper has provided a comprehensive study about quantitative analysis of damping properties based on the TA analysis method. The addition of high content of conductive phase would reduce the damping peak intensity but enhance damping at higher temperatures, and the effective damping temperature range is widened. It is difficult to evaluate the comprehensive damping properties of materials by choosing $\tan\delta_{\text{max}}$ as the only performance index. Thus, in this research, the TA value is selected to evaluate damping properties. The TA analysis method obviously clarifies the effect of maximum loss factor ($\tan\delta$) and effective temperature range on damping properties. And synergies of piezoelectric phase and conductive phase are further researched.

(1) The damping percentage of CNTs in CNTs/EP composites reaches 32.22% at CNT content of 0.6 wt.%. The maximum loss factor reaches 0.56, and the effective temperature range is widened.

(2) The damping percentage of PMN ceramics in PMN/EP composites reaches 33.95% at 40 wt.% PMN content. The increase in frictional energy dissipation can be massively offset by the decrease in viscoelastic damping of matrix when the content of PMN exceeds 60 wt.%. So damping properties of PMN/EP composites cannot be improved obviously, and the damping percentage of PMN is merely 4.28%.

(3) The interfacial effect of CNTs acts as the dominant factor of damping enhancement for the content less than 0.6 wt.% in CNTs/PMN/EP composites, and the maximum damping percentage reaches 29.14%. However, PMN becomes the dominant factor of damping enhancement with the content of CNTs increasing, and the damping percentage reaches 47.43% for the content of CNTs reaching percolation threshold. Synergies of piezoelectric phase and conductive phase result in the damping enhancement of CNTs/PMN/EP composites.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.
Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (nos. 51472188 and 51521001), Natural Research Funds of Hubei Province (no. 2016CFB583), Fundamental Research Funds for the Central Universities in China, State Key Laboratory of Advanced Electromagnetic Engineering and Technology (Huazhong University of Science and Technology), National Key Research and Development Program of China (nos. 2017YFB0310400 and 2018YFB0905600), and Joint Fund (Grant No. 6141A0202223).

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