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Broadband Dynamic Responses of Flexible Carbon Black /Poly (vinylidene Fluoride) Nanocomposites: A Sensitivity Study

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Abstract

Nanocomposites fabricated based on the compound of carbon nanofillers and polymer matrix exhibit extraordinary piezoresistive performance, and the capacity of nanocomposite sensors in measuring structural dynamic strains has been widely demonstrated. However, the sensitivities of existing nanocomposite strain sensors are limited, particularly in aspects of sensing precision and response frequency. This study focuses on sensitivity investigations of flexible nanocomposite sensors fabricated using the compound of carbon black (CB) fillers and polyvinylidene Fluoride (PVDF) matrix, which have shown promising potential in perceiving extremely weak strain signals within a considerably broad range of response frequencies. Sensing precision as a highly important indication of sensitivity was characterized in a quantitative manner. And broadband spectrum analysis was conducted, as an effective way to examine sensor performance in perceiving minimal disturbances in dynamic strains. The response disturbances were generated, in two experiments, by introducing local material and geometric variations into the inspected structures, in terms of mass attachment and structural damage. The effectiveness of the nanocomposites in structural damage detection was demonstrated. Moreover, the experimental results indicate promising potentials of nanocomposite-based strain sensors for applications such as advanced bioelectronics, ultrasonic inspection, *in-situ* structural health monitoring, etc.

***Keywords*:** Nanocomposites; Dynamic strains; Sensing resolution; Spectrum analysis; Damage detection

1. Introduction

Nanoparticle filled polymeric nanocomposites have been proven to be unique in a variety of aspects such as mechanical and electrical properties. In particular, nanocomposites were deemed as competitive candidates for new generation flexible strain sensors due to their extraordinary piezoresistive performance [1-3]. To date, extensive studies have been focused on investigating the piezoresistivity of various types of nanocomposite strain sensors, and a wide range of engineering tasks in fields such as biomechanics [4-6] and structural health monitoring [7,8] are expected to be fulfilled practically in future.

For nanocomposite strain sensors, the enhancement of gauge factor (GF), an important sensitivity indicator defined as the ratio of sensor resistance variation to strain magnitude, has been the focus of efforts during past decades. GF can be effectively increased using different ways, such as optimizing the combination of component materials (i.e., fillers and matrix), or adjusting the weight ratios of nanofillers. Until now, considerably high GFs have been obtained in several studies [9,10], considered as remarkable progress in sensor development. However, the reported high GFs were mostly achieved under relatively large strain magnitudes (e.g., >1%), whereas investigations on strain sensing precision, associated with the minimum strain magnitude that can be identified by nanocomposite sensors, have rarely been mentioned. Sensing precision is no doubt a crucial indication of sensitivity calling for intensive investigations, since it is directly linked with the capacity of sensors in measuring weak strain signals. In medical science, it is normal that the signs of health abnormality are weak signals that hidden in strong ones, such as murmurs hidden in breath or heart beat signals. Another example is that for structural damage diagnosis, locally small damage, in either a body part (e.g., an arm bone) or an engineering structure (e.g., an aircraft wing), can only induce extremely weak disturbance into the global strain response of the structure. And with minimal strain magnitudes, the disturbances measured on skins or structural surfaces are often one or two orders of magnitudes lower than the strong/global signals, which can only be identified relying on an extraordinarily high sensing precision [11-13].

The mechanisms of sensors' piezoresistive behaviors subject to large and small strains are different. That is, large strains can easily trigger breakdowns of the filler-to-filler conductive networks, and in turn cause significant resistance variations of the sensors (i.e., significant piezoresistivity); whereas small strains, particularly those with minimal magnitudes (e.g., <10 microstrains), could not induce sufficient number of network breakdowns, and the sensors' piezoresistivity mainly rely on the variations of inter-particle resistances due to tunneling effect [2]. Generally, network breakdowns lead to much higher GFs than tunneling effect does.

For small strain measurement, where tunneling effect dominates the piezoresistive performance of the sensors, the inter-particle resistances are directly linked with inter-particle distances. And the effective inter-particle distances capable of triggering tunneling effect are highly sensitive to the pattern of movement and deformation of the nanofillers. In other words, the movement/deformation pattern of the nanoparticles could be the major factor influencing the sensing precision of nanocomposite-based strain sensors. For carbon nanotubes (CNTs) as the most popular options adopted in existing nanocomposite sensors, their one-dimensional, high aspect ratio geometries lead to significant anisotropy of the composites [14]. And under strains, the CNTs exhibit not only translations but substantial rotations as well. Since experimental results of sensing precision estimation are rare, a numerical evidence can be found in [2]. Close to the conductivity percolation threshold of the sensor fabricated using CNTs, the piezoresistivity curve shows a zigzag shape. This implies that if the curve is observed within a largely reduced strain range, the sensor resistance is probably not able to signify the strain correctly. Thus the sensing precision of the sensor is considered as limited, and the unstable piezoresistive performance is mainly due to the substantial rotations of the CNTs. Apart from movement patterns, it is assumed that the complex deformations of CNTs due to their high aspect ratios, such as bending and buckling [15-19], could also induce negative influence on the sensing precision, although evidences are still needed from experimental or numerical investigations.

For dynamic strain measurement, another important aspect of sensor performance is the response frequency. The reported frequencies measured by existing nanocomposites are mostly around or much lower than 100 Hz [7, 20-25]. However, for applications such as structural health monitoring or ultrasonic inspection that rely on measuring vibration or ultrasonic wave signals, it is normal for the signals' central frequencies to reach several kilo- to even mega-Hertz [13, 26-28]. The sensor performance in measuring dynamic responses is partly associated with the viscoelastic behavior of the composite, and another crucial factor is the sensing precision, since in engineering practice, increasing frequencies are almost always associated with decreasing strain magnitudes.

The present study aims at addressing the existing limitations in sensitivity investigations for nanocomposite strain sensors. By using strain sensors based on carbon black (CB) nanoparticles and PVDF matrix, which have been used to capture high-frequency dynamic strains in a recent study [29], sensing precision and response frequency were chosen as two important sensitivity indicators to be explored comprehensively. The sensor fabrication process was optimized, and strain signals subject to structural vibrations were measured in two experiments for the analysis in both time- and frequency-domain. In time domain, the sensing precision was characterized by taking into account signal hysteresis. In frequency domain, spectrum analysis, crucial in fields such as mechanical engineering or medical science, was performed for the first time using nanocomposite-based sensors. Specifically, the distributions of frequency response functions (FRFs) of the vibrating structures were measured using the CB/PVDF sensors, and the FRFs were then demonstrated able of identifying minimal strain disturbances associated with mass attachment and structural damage. The experimental results demonstrate the effectiveness of the CB/PVDF sensors in detecting structural damage. Furthermore, the reported sensing precision and response frequency open new possibilities of achieving other advanced applications by using nanocomposite-based strain sensors.

2. Sensor fabrication

The material fabrication process is similar with that introduced in [29]. CB nanoparticles (N220, supplied by CABOT) were dispersed in PVDF (Kynar k721, supplied by ARKEMA) using an internal mixer. The hybrid was then hot-pressed and immobilized to obtain CB/PVDF films with uniform thicknesses. The conductive percolation threshold of the material was measured to be a CB weight ratio of 6.5wt%. It has been widely demonstrated that the highest GFs can be obtained at the percolation threshold of nanocomposite strain sensors [X,X]. However, pursuing high GFs was beyond the scope of this study. Thus the CB weight ratio was increased to be 8% to enhance the stability of piezoresistivity, and certain amount of decrease of GF due to increased CB weight ratio is considered as acceptable. The SEM image of the particle dispersion is presented in figure 1(a). It is seen that the CB aggregates possess ellipsoidal or nearly spherical geometries, considered to be much more compact than the geometries of CNTs. It can be imagined that subject to strains, the compact CB aggregates will exhibit very simple movement pattern mainly in terms of translations, whereas particle rotations, bending or bulking are rarely involved. The simple movement/deformation patterns of the CB aggregates are believed to guarantee rapid and precise response of the sensor resistance to dynamic strains with minimal magnitudes.

The resistances of the nanocomposite sensors were controlled to be standard 120 or 350Ω by tailoring the sensor dimensions and the distances between opposite electrodes (made of electrical wires and conductive silver pastes), as shown in figure 1(b). The sensors were then integrated in a signal conditioning device (Kyowa®CDV-900A) and bridge boxes

(Kyowa® DB-120A or 350A). In the following experiments, sensor resistances were transferred into voltages by the bridge boxes and recorded using an oscilloscope (Agilent® DSO9064A).

3. Experiment I: Dynamic strain measurement on a composite beam

The experiment was designed to quantify the sensing precision of the CB/PVDF sensors and to examine the sensor performance in spectrum analysis. Minimal disturbances in dynamic strains were induced by mass attachment, and the disturbances were then identified from the variations of FRF distributions.

3.1 Set-up

Vibration responses were measured on a cantilever beam made of glass fiber reinforced polymer (GFRP), measuring 210 mm in length, 40 mm in width and 2 mm in thickness, as shown in figure 2. The beam was excited by an electromagnetic shaker (B&K®4809), with a force transducer (B&K® 8200) installed at the excitation point to monitor the variation of excitation force. A CB/PVDF sensor was attached on the beam surface. For comparison, the vibration responses were measured simultaneously using a Doppler laser scanning vibrometer (PSV®-400B), the laser beam from which was focused on the surface of the CB/PVDF sensor. In addition, three metal-foil strain gauges (Huangyan® BX120-5AA) were attached in parallel at the backside of the CB/PVDF sensor for strain measurement. By referring to the coordinate system as presented in figure 2, relevant locations in the experimental setup are listed in table 1. The added masses were tiny aluminum blocks, each weighting 1 g, with dimension as shown in figure 2. Two mass locations were selected along the central line of the beam, as shown in table 1.

3.2 Results and discussion

Dynamic strains were first measured on the GFRP beam by the CB/PVDF sensor and the strain gauges without any mass attachment. Two vibration frequencies were selected of being 20 Hz and 20 kHz, where 20 kHz is the upper limit provided by the shaker. The measured strain signals in time domain are presented in figure 3(a) and (b) in terms of voltage variations. To achieve optimal measurement accuracy, strain signals were measured by all the three strain gauges and then were averaged. The strain measured by sensors can be calculated from the voltage signals according to

$$\varepsilon_s = \frac{V}{N \cdot g_s}, \tag{1}$$

where V, N and g_s are the voltage, the amplification factor of the signal amplifier and the GF of the sensor, respectively. Since the GFs of the strain gauges were fixed to be 2.07, the total strain range corresponding to 20 Hz, as shown in figure 3(a), can be calculated using equation (1) to be $[-79, 79]\mu\varepsilon$. In the figure, the GF of the CB/PVDF nanocomposite was estimated to be 4.2, around twice as high as that of the strain gauges. Considering 51 sampling points within a single vibration period, the sensing precision of the CB/PVDF was estimated to be around 6.3 $\mu\varepsilon$, which corresponds to the average strain range identified between adjacent sampling points. In figure 3(a), a large degree of signal hysteresis associated with the CB/PVDF sensor can be seen by referring to the signal measured by the strain gauges. The hysteresis was mainly due to the viscoelasticity of the PVDF matrix which become obvious under the current vibration frequency.

Under 20 kHz as presented in figure 3(b), the total strain range was calculated based on the signal measured by the strain gauges according to equation (1) to be $[-10.5, 10.5]\mu\varepsilon$. Thus the sensing precision of the CB/PVDF was estimated to be $1.7\mu\varepsilon$ by considering 25 sampling points per vibration period. Remarkably, such sensing precision is capable of perceiving minimal strain variations induced by sources such as structural damage or ultrasonic waves []. The GF of the nanocomposite was observed to be more than three times as high as that of the strain gauges. Different GFs in figure 3(a) and (b) was considered to result from the nonlinear dependence of sensor resistance of the CB/PVDF on the distances between adjacent nanoparticles triggering tunneling effects [30-32], which are extremely sensitive to strain magnitudes. Nevertheless, performance degradation of the strain gauges subject to high-frequency vibration, as high as 20 kHz, is another possible cause of the varied GFs in figure 3(a) and (b), requiring further investigations.

Comparatively, the signals in figure 3(b) are much noisier than those in figure 3(a), because of the significantly lower strain magnitudes in figure 3(b) than in (a). However, it is also seen that signal hysteresis associated with the nanocomposite basically disappears in figure 3(b), since the drastic increase in dynamic strain rates made the PVDF matrix to behave mostly under its glassy state, where polymer viscoelasticity was minimized [33]. Such a finding is an evidence indicating the advantages of nanocomposite sensors in measuring high-frequency dynamic strains.

With demonstrated sensing precision and response frequency up to 20 kHz, the nanocomposite sensor was then used for spectrum analysis by constructing FRFs, which were defined as the ratio of frequency responses to excitation force variation in frequency domain [34, 35]. The FRF measurement is considered as an efficient way to fully explore sensor's performance, as a single FRF curve could include dynamic strain signals under a large variety of frequencies and magnitudes. By using the shaker, excitation frequencies were swept continuously from 0 to 2200 Hz, and the frequency responses were measured by the nanocomposite sensor and the laser vibrometer, in terms of strains and velocities, respectively. As presented in figure 4(a) and (b), the first six orders of vibration modes of the beam are included in the FRF curve. Large consistency in the natural frequencies, identified by the CB/PVDF and the laser vibrometer, respectively, and be observed. Thus the CB/PVDF is deemed as accurate in measuring frequency responses. The signal measured by the CB/PVDF contains larger noise influence within 500 to 2200 Hz (see figure 4(b)) than within 0 to 500 Hz (see figure 4(a)), because of the reduction of strain magnitudes subject to increased frequencies. In figure 4(b), there is an extra peak between the 5^{th} and 6^{th} modes, which corresponds to a vibration mode in the lateral direction of the beam.

Subsequently, tiny aluminum masses were attached on the beam surface, as illustrated in figure 2. Two cases of mass attachment were adopted: Case I, including a single mass attached at x = 60 mm (mass location 1 in Table 1), and Case II, including two masses attached at x = 60 and 110 mm (mass location 1 and 2 in Table 1), respectively. The shifts in FRFs subject to the two cases are presented in figure 5(a) and (b), where the baseline FRFs, corresponding to the beam state without mass attachment, are also presented for comparison. It can be realized that the natural frequencies have been changed due to mass attachment. Specifically, the fundamental (first-order) natural frequency in figure 5(a) is not sensitive to either of the two cases, whereas for the second- and third-order modes, variations in natural frequencies are obvious, as clearly identified by the CB/PVDF sensor. In particular, the third-order natural frequencies associated with Case I and II are indistinguishable, because mass location 2 was at a node in the third-order strain mode shape, the deformation of the beam surface at which was considerably small [36]. Compared with figure 5(a), the higher-order modes presented in figure 5(b) are more sensitive to mass attachment, not only showing changes in phases but also in amplitudes. Specifically, the shifts of the fourth- and sixth-order natural frequencies can be observed easily. For the fifth mode, however, frequency shift can hardly be noticed because both of the masses were attached close to the nodes in the fifth-order strain mode shape.

4. Experiment II: Dynamic strain measurement on a metal beam

In this section, FRFs were measured on a cracked aluminum (AL 6061) cantilever beam using a CB/PVDF sensor. Compared to the previous experiment, the beam material has been changed, because it is much easier to create a crack and increase its depth *in-situ* in aluminum than in conventional composite material. Based on the CB/PVDF sensor, minimal disturbances in dynamic strains corresponding to different crack depths were identified in frequency domain.

4.1 Set-up

As shown in figure 6, the beam measuring 440 mm in length, 40 mm in width and 8 mm in thickness, was excited by the shaker. A CB/PVDF sensor was attached on the beam surface to measure dynamic strains and vibration velocities were measured by the laser vibrometer. A through-width crack measuring 1 mm in width was cut in the beam using a saw. Referring to the coordinate system in figure 6, relevant locations in the experimental setup are listed in table 2. The severity of damage was signified by the ratio of the crack depth to the beam thickness, defined as β, which were adjusted to be 0.1, 0.3 and 0.5 in the following tests. Upon on the completion of measurement under a given β, the crack depth was increased *in-situ* by the saw. During the saw-cut process, the middle span of the beam was clamped tightly to prevent unwanted change of boundary conditions.

4.2 Results and discussion

Within a frequency range from 0 to 1200 Hz, provided by swept excitation, the frequency responses of the aluminum beam were measured by the CB/PVDF sensor and the laser vibrometer. The first five orders of natural frequencies are included in the FRF curves as shown in figure 7. The consistency in the identified natural frequencies demonstrates the high precision of the CB/PVDF sensor in dynamic strain measurement. The sensor was then used to identify FRF shifts corresponding to different damage severities. Figure 8 presents the constructed FRFs under $\beta = 0.3$ and 0.5, by referring to the signal measured under the intact (undamaged) state of the beam. It can be clearly seen that all the natural frequencies show certain degrees of sensitivities to the presence and deterioration of the crack. In particular, the shifts of the fourth- and fifth-order natural frequencies can be clearly observed.

The values of the natural frequencies measured by the nanocomposite sensor, subject to the undamaged state of the beam and the damage cases of $\beta = 0.1$, 0.3 and 0.5, are listed in Table 3, in which relative reductions in natural frequencies are presented as well. In general, decreases in natural frequencies subject to increased crack depth are obvious. The largest relative reductions are associated with the fundamental natural frequency, since the crack locates very close to the clamped end of the beam, at which the beam deformation is large in the first-order strain mode shape. Besides, the second largest relative reductions are associated with the fifth-order mode because the crack location is close to the anti-node in the fifth-order strain mode shape, where beam deformation reach a local maximum. It should be noticed from the table that the second-order natural frequency corresponding to $\beta = 0.5$ is larger than that corresponding to $\beta = 0.3$, which was considered as abnormal in part due to the insensitivity of the second-order mode to the crack, and, on the other hand, due to possible, although slight, changes in boundary conditions caused by the saw-cut process.

5. Conclusions

The dynamic piezoresistive performace of flexible nanocomposite strain sensors made of the compound of CB nanoparticles and PVDF matrix was comprehensively investigated in this study, where sensing precision and response frequency were quantitatively examined as two curial sensitivity indicators that directly determine sensors' performance in practical applications. A sensing precision as accurate as $1.7\mu\varepsilon$ was achieved in time-domain analysis, demonstrating the capacity of the CB/PVDF sensors in perceiving extremely weak dynamic strains associated with sources such as structural damage, high-frequency vibration, ultrasonic waves, etc. In vibration tests, the hysteresis degrees of the nanocomposites are significantly different under 20 Hz and 20kHz, which can be explained by the change of polymer viscoelastic behavior under different frequencies. Exhibiting reduced signal hysteresis along with increased frequency, the advantage of nanocomposite sensors in measuring structural deformations under high strain rates was demonstrated.

The FRF construction is an effective and efficient way to examine sensor performance, because one single test included a large variety of components of dynamic strains under different magnitudes and frequencies, and the natural frequencies of the tested structures can only be identified provided that all strain components were perceived precisely by the sensors. The observed shifts of natural frequencies subject to added masses and damage indicate that the CB/PVDF sensors are significantly sensitive to minimal disturbances of dynamic strains. The reported sensing precision and response frequency of the sensors show promising potentials in advanced applications. For example, the design and formation of flexible nanocomposite-based sensor network, able to capture guided wave signals in engineering structures for the task of *in-situ* structural health monitoring.

The high sensitivity of the CB/PVDF strain sensors, particularly in aspects of sensing resolution and response frequency, is believed to be highly related to the micro geometries of the nanoparticles. Particles with compact geometries (e.g., spheres or ellipsoids) may lead to much simpler deformation patterns of the conductive networks than those associated with less compact particles (e.g., CNTs or graphene). The influence of particle geometries will be analyzed in detail in the future work.

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Figure captions

Figure 1: (a) The SEM image of the nanosalar morphology of the CB/PVDF compound at a CB weight ratio of 8wt%, and (b) Fabricated CB/PVDF sensors of 120 and 350 Ω, respectively. The electrical wires in (b) were attached on the electrodes made of conductive silver paste

Figure 2: Experimental set-up for the measurement of dynamic responses on a cantilever GFRP beam subject to mass attachment

Figure 3: Time-domain strain signals measured by the CB/PVDF sensor and the metal foil strain gauges, respectively, under vibration frequencies of (a) 20 Hz and (b) 20kHz. All the presented signals were treated by 30 times of averaging in time domain

Figure 4: FRFs constructed by using the CB/PVDF sensor and the laser scanning vibrometer, respectively, on the GFRP beam without mass attachment. The frequency ranges are (a) from 0 to 500Hz, and (b) from 500 to 2200Hz, respectively. All the signals were treated by 30 times of averaging in frequency domain

Figure 5: FRFs constructed by using the CB/PVDF sensor subject to two cases of mass attachment within frequency ranges (a) from 0 to 500Hz, and (b) from 500 to 2200Hz, respectively, by referring to FRF measured without mass attachment as the baseline signal. All the signals were treated by 30 times of averaging in frequency domain.

Figure 6: Experimental set-up for the measurement of dynamic strains on a cantilever aluminum beam subject to a crack with varied depths.

Figure 7: FRFs constructed by using the CB/PVDF composite sensor and the laser scanning vibrometer, respectively, under the undamaged state of the beam within a frequency range from 0 to 1200 Hz. All the signals were treated by 30 times of averaging in frequency domain

Figure 8: FRFs constructed within 0 to 1200Hz by using the CB/PVDF sensor under different crack depths, corresponding to $\beta = 0.3$ and 0.5, respectively, with FRF measured under the intact state of the beam as a reference. All the signals were treated by 30 times of averaging in frequency domain.

Tables

Table 1 Specific coordinate values in the setup of Experiment I

	CB/PVDF	Laser beam	Strain gauges	Excitation point	Mass Loc. 1	Mass Loc. 2
x [mm]	20	20	20	190	60	110

Table 2 Specific coordinate values in the setup of Experiment II

	CB/PVDF	Laser beam	Excitation point	Crack
x [mm]	20	20	420	80

Table 3 The values and relative variations of the five-order natural frequencies subject to different crack depths

Mode	Intact	$\beta = 0.1$		$\beta = 0.3$		$\beta = 0.5$	
	Freq.[Hz]	Freq.[Hz]	Var.[%]	Freq.[Hz]	Var.[%]	Freq.[Hz]	Var.[%]
1	16.63	16.5	-0.78	16	-3.79	16	-3.79
2	111	110.8	-0.18	110.3	-0.63	110.8*	-0.18
3	322	321.9	-0.03	320.3	-0.53	319.4	-0.81
4	635.8	635.8	0	630	-0.91	624.4	-1.79
5	1059	1057	-0.19	1052.5	-0.61	1036	-2.17

*An abnormal value of natural frequency showing an increase compared to its previous value