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New hybrid polymer nanocomposites for passive vibration damping by incorporation of carbon nanotubes and lead zirconate titanate particles

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A B S T R A C T

A new hybrid nanocomposite for vibration damping has been elaborated. Ferroelectric lead zirconate titanate particles and carbon nanotubes are dispersed simultaneously in an engineering semi-crystalline thermoplastic matrix by an extrusion processing. Ferroelectric particles have been made piezoelectric once incorporated into the polymer matrix through a poling step. The dynamic response of nanocomposites has been characterized by dynamic mechanical analysis and vibration test. The shear mechanical modulus exhibits an increase of the conservative and dissipative components after the poling step of nanocomposites. By vibration test, the first bending mode of the frequency response function has been followed and a significant damping inherent to poling is also recorded. These evolutions are heightened by the use of two constrained elastic layers. For the first time, a synergy between poled piezoelectric particles responsible for the transduction phenomena and conductive particles allowing a local dissipation of electric charges has been revealed by two complementary techniques for the improvement of the polymer damping.

1. Introduction

One of the most promising challenges of this decade is to bring new functionalities to lightweight structural materials [1]. Structural thermoplastic polymers are the best candidates to acquire new properties by incorporation of submicronic objects. Along this route, composites with complex formulations may be proposed according to the required application. At the same time, vibration reduction is constantly taken into consideration to increase lifetime of many structures in different industrial applications, such as space industry where improving instrument sensitivity as optical resolution is one of the main goal [2].

Active and passive vibration controls have been largely explored. In the case of active control [3], piezoelectric materials provide mechanical forces in phase opposition with the source vibrations. This system requires sensor feedback and control of commands which present a risk in term of reliability compared to passive devices. Most of the time, these materials are surface bonded or embedded in the host structure [4, 5]. The piezoelectric elements are usually integrated with an external shunted circuit [6,7]. When the host structure vibrates, the piezoelectric material is deformed and generates an electrical potential by a mechano-electrical transduction. Both vibration controls are heavy and bulky.

The idea is to integrate this passive macroscopic damping concept to the composite scale by proposing a light and integrated passive damping. By their ductility and ease to be processed, polymers are the best candidates to support this new functionality. A first patent has been submitted in 1991 [8] about the incorporation of graphite powder in a piezoelectric polymer for the elaboration of an anechoic coating. Later, Tanimoto [9] has proposed a composite made of several epoxy/carbon fibre layers with integrated lead zirconate titanate (PZT) particles between each of them. The originality of our work is to insert both piezoelectric and resistive elements to the polymer matrix. The first ones will ensure the mechano-electrical transduction and the second ones will locally dissipated the created charges.

This kind of material has been studied with an epoxy matrix by incorporating simultaneously PZT particles and carbon black or carbon nanotubes [10–12] but the synergy between electroactive particles and local conduction brought by conductive fillers for damping improvement has never been demonstrated.

Here, we report the elaboration and characterization of a hybrid nanocomposite for vibration reduction. Polyamide 11 (PA 11) is an engineering thermoplastic polymer and has been chosen as a model polymer. PZT particles and Carbon NanoTubes (CNTs) have been
respectively selected as piezoelectric and conductive fillers and have been introduced simultaneously into the polymer matrix. PZT particles are ferroelectric and need a poling step to become piezoelectric [13]. Before this step, dipoles exist within the PZT crystalline structure but without any particular orientation which leads to a quasi non-existent global polarization. The polarization allows an orientation of the PZT particle dipoles following the poling field direction. It makes appear a dipole at the particle scale. This step has been led on the nanocomposites i.e. PA 11/PZT and PA 11/PZT/CNT. For this last, the carbon nanotube volume fraction has been fixed below the electrical percolation threshold of CNTs to ensure a macroscopic insulator behaviour [14–17].

Thanks to dynamic mechanical analysis (DMA) and vibration tests, both complex shear mechanical modulus and vibration amplitude at the resonance frequency of the sample will be followed. To bring proofs about efficiency of a transduction-local dissipation phenomenon on the composite damping properties, the composite poling state is considered as the determining factor. In the non-piezoelectric state, PZT particles are not able to convert mechanical vibrations into an electrical potential while in the piezoelectric state, piezoelectric fillers will ensure the mechano-electrical conversion. By this way, for a same particle concentration, the PA 11/PZT/CNT composite will be or not piezoelectric; therefore, the influence of particle introduction on damping properties is eliminated. This way to proceed is original and may be revealing to show the real synergy between piezoelectric and conductive fillers for vibration damping.

Constrained viscoelastic layer [18–20] also called sandwich structure [21,22] is widely used for vibration reduction. To increase shearing stresses into the nanocomposites and highlight the transduction–local dissipation phenomenon, a sandwich configuration will be experimented. It would lead to promote damping by using synergy between piezoelectric and conductive particles.

2. Experimental procedure

2.1. Materials

Polyamide 11, the polymer matrix, is provided as a powder (30 μm) by Arkema (France). It is an engineering semi-crystalline thermoplastic polymer which is chosen for its good mechanical properties: its tensile modulus is about 1 GPa with a glass transition temperature and an melting point of 46 °C and 189 °C respectively. Thermal degradation of the polymer operates at 436 °C. PA 11 will be studied in its non-piezoelectric state.

Lead zirconate titanate (Pb(Zr$_{0.52}$Ti$_{0.48}$)$_2$O$_3$), also called PZT, is well known for its high ferroelectric properties at the morphotropic phase boundary due to the coexistence of the tetragonal and rhombohedral crystalline phases [23,24]. PZT particles have been provided by Ferroperm (Denmark) with a mean diameter of 900 nm. Bulk ceramic exhibits a Curie temperature of 235 °C and a piezoelectric coefficient $d_{33}$ of 575 pC·N$^{-1}$ (given by the manufacturer in the bulky state). Its coercive field is about 5–10 kV·mm$^{-1}$ [25]. X-ray diffraction measurements have been previously led on these inorganic fillers [26,27]. By this analysis technique, PZT fillers have shown ferroelectric properties meaning that they will acquire the piezoelectric characteristic after a poling step.

Carbon nanotubes have been synthesized by catalytic chemical vapour deposition by Marion Technology (France) and are mostly double-walled (80 wt.%). They are characterized by a high aspect ratio (length over diameter) of 10$^2$–10$^4$ [28].

2.2. Nanocomposite processing

For the study of PA 11/PZT and PA 11/PZT/CNT composites, PZT particle volume fraction was fixed at 30% in volume with the intention of minimising the number of studied parameters and ensuring the best compromise between high electroactive properties and preserved mechanical properties. It has to be noticed that the nanocomposites must be necessary insulator to be poled. In a previous work, the electrical conductivity of PA 11/PZT/CNT composites was studied [29]. It was shown that for a CNT concentration of 0.2 vol.%, the PA 11/PZT 30 vol.%/CNT 0.2 vol.% is still insulator with an electrical conductivity within the thickness of 1.9 · 10$^{-12}$ S·m$^{-1}$. For higher concentrations, this threshold is reached and hybrid composites become conductive making impossible any poling step. In that way, the poling step required to orient PZT dipoles and make PZT particles piezoelectric as well as nanocomposites [30,31] is characterized by a continuous electric field of 5 kV·mm$^{-1}$ applied during 15 min at 80 °C. This procedure was applied to pole nanocomposites whether PA 11/PZT or PA 11/PZT/CNT.

PA 11/PZT and PA 11/PZT/CNT composites are elaborated by extrusion with a twin screw extruder (Minilab II from Haake). This method consists in introducing fillers in the polymer matrix in a molten state. Three parameters govern the extrusion process: mixing temperature, mixing time and screw rotation speed. These values were optimized in a previous work for PA 11/CNT composites [32]. The nanocomposites are elaborated by ensuring the best particle dispersion in the polymer matrix, and are respectively: 210 °C, 15 min and 30 rpm. After the extrusion step, composites are hot pressed at 210 °C in order to achieve sample in a parallelepiped shape. Fig. 1 shows a scanning electron microscopy image of the PA 11/PZT 30 vol.%/CNT 0.2 vol.% composite using the backscattered electron detection. At a micronic scale, PZT particles and carbon nanotubes are well dispersed in the polymer matrix and they do not present particular affinities between themselves.

2.3. Dynamic mechanical techniques

2.3.1. Sample geometry

The sample characterization is realised on two configurations. The first one is a bulk sample. The second one is a sandwich beam, studied in order to increase shear stresses into the composite through a constraining layer [33] and enhance piezoelectric transduction. For this, a 0.4 mm layer of the nanocomposite is constrained between two 0.1 mm aluminium layers for DMA measurements and between a 0.5 mm stainless steel layer and a 0.1 mm aluminium foil for vibration tests. The adhesion forces between PA 11 and the metallic layers are strong enough to avoid the use of an adhesive. Sample geometry for both configurations and both dynamic techniques are specified in Fig. 2.

2.3.2. Dynamic mechanical analysis

Dynamic mechanical analysis was performed on an ARES (Advanced Rheometric Expansion System) strain controlled rheometer (TA Instruments) in the torsional rectangular mode within the material linear
elasticity range (0.1% strain for bulk configuration and 0.03% strain for sandwich configuration). This technique allowed us to measure the complex shear modulus $G^*(\omega, T)$:

$$G^*(\omega, T) = G'(\omega, T) + iG''(\omega, T)$$

(1)

$G'$, $G''$ and $\tan\delta = G''/G'$ are the conservative modulus, the dissipative modulus and the loss factor respectively. They were measured as a function of the temperature from $-10$ to $120$ °C at $3$ °C·min$^{-1}$ and at an angular frequency of $1$ rad·s$^{-1}$.

2.3.3. Vibration test

An electrodynamic shaker was employed for damping measurements. In the case of the bulk configuration, the cantilever beam was directly fixed to the shaker by one of its end as pictured in Fig. 3. For the sandwich configuration, the stainless steel plate was the fastened part.

An impedance head, linked to the shaker, allowed us to control the imposed acceleration to the beam by a closed loop control. The displacement (or the speed) was measured, thanks to a laser vibrometer at the 4/5 of the free part of the beam. The frequency response function (FRF) is defined as the ratio of the response (speed in m·s$^{-1}$) over the excitation (acceleration in g with $1$ g = $10$ m·s$^{-2}$) as a function of frequency. The FRF was used to follow the dynamic behaviour of the samples at the first bending mode. The “MIMO Sweep and Step Sinus” module of the LMS Test Lab software was employed to measure the dynamic response of the sample.

3. Results and discussions

3.1. Dynamic mechanical analysis in torsional mode

3.1.1. Influence of the sandwich configuration on the polymer matrix

Sandwich configuration is often used for enhancing shear stress into specimen. The sandwich is formed by adding to the vibrating structure (here, the metallic beam) the nanocomposite layer and setting a metallic constraining layer. When the system flexes during vibration, shear deformation occurs in the damping layer rather than extension with no constraining layer. It increases the energy dissipation and the observation of vibration damping would be optimized.

The influence of two elastic aluminium layers on the PA 11 mechanical behaviour is analysed. Fig. 4 compares the conservative and dissipative shear moduli of neat PA 11 in bulk and sandwich configurations, at $1$ rad·s$^{-1}$. The elastic layers induce an increase of the conservative modulus (Fig. 4(a)); aluminium foils govern the assembly mechanical modulus. Shear stresses brought to PA 11 by the metallic layers lead to an intensification of the polymer mechanical relaxations. Regarding dissipative modulus evolution (Fig. 4(b)), the sandwich configuration exhibits higher dissipation values than the bulk one. The level of strain in the polymer layer is locally raised by the presence of elastic substrates.
and the molecular mobility in a viscous environment dissipates this additional mechanical energy. Above the primary mechanical relaxation, dissipative modulus stays high and keeps on increasing with temperature: energy dissipation is promoted with the enhancement of polymer molecular mobility.

3.1.2. Mechanical modulus of the hybrid nanocomposite upon polarization

The synergy between the piezoelectricity of PZT and the local electrical conduction of CNTs within the polyamide matrix is explored. It is reminded that the CNT concentration is below the electrical percolation threshold of these conductive fillers meaning that the hybrid composite is macroscopically insulator. For this purpose, comparative studies of piezoelectric and non-piezoelectric PA 11/PZT/CNT nanocomposites have been performed.

3.1.2.1. Shear conservative modulus. Fig. 5 presents the shear conservative modulus $G'$ as a function of temperature for neat PA 11 and PA 11/PZT/CNT 0.2 vol.% nanocomposite in piezoelectric and non-piezoelectric states. The vitreous and the rubbery plateaus are identified from $-10$ to $20 \, ^\circ C$ and from $50$ to $120 \, ^\circ C$ respectively. The introduction of PZT at 30 vol.% and carbon nanotubes at 0.2 vol.% leads to an increase of the matrix conservative modulus. This is mainly attributed to the high modulus of the ceramic spherical particles which have been added at a relatively high concentration level. Accordingly, Tsantzalis has shown an increase of the storage modulus of an epoxy matrix by the introduction of carbon nanofibres but also upon the dispersion of PZT particles at 4 vol.% [34]. In accord with Suhr's work [35], it has been demonstrated on bulk samples (not presented in this work) that CNT addition (0.2% in volume) also induces an increase of the conservative modulus but in a low ratio compared to the effect of PZT particles (30% in volume).

The original finding of this work is the raise of the conservative modulus upon poling: $G'$ of the PA 11/PZT/CNT nanocomposite increases by 14% on the vitreous plateau and by 3% on the rubbery plateau after poling. After the poling process, PZT particles and then the hybrid nanocomposite becomes piezoelectric and acquires the ability to convert mechanical vibrations into electrical charges. It results in an increase of the $G'$ modulus attributed to a stiffening of the polymer matrix at the particle scale. Dipoles of the poled PZT particles interact with the polymer ones leading to an interfacial polarization which may create residual stress at polymer/PZT interfaces. With a PZT filler concentration of 30% in volume, this local stress modification is visible at the macroscopic scale. Without CNT (not presented here), the raise in $G'$ value due to polarization is not observable anymore. Charges created by PZT particles under the mechanical stress are trapped at polymer/PZT interface and the transduction mechanism is unsustainable. Consequently, the interactions between poled PZT particles and polyamide macromolecular chains are frozen and any modification of the mechanical modulus appears under dynamic solicitation.

The raise of the conservative modulus of the hybrid nanocomposite after polarization is more pronounced on the vitreous plateau than on the rubbery one. Below the primary mechanical relaxation, the polymer is rigidified and the mechanical strain is transmitted more efficiently to the PZT particles. PZT crystalline structure undergoes a higher strain which induces a higher created charge density at their surface.

3.1.2.2. Shear dissipative modulus. The dissipative modulus $G''$ of neat PA 11 and PA 11/PZT/CNT 0.2 vol.% nanocomposite in piezoelectric and non-piezoelectric states versus temperature are reported in Fig. 6. The primary relaxation mode labelled $\alpha_1$ is observed around 48 °C and is associated with the mechanical manifestation of the polyamide 11 glass transition. The introduction of 30 vol.% of PZT spherical particles and 0.2% of CNTs in the neat polymer matrix results in an increase of the dissipative modulus. This observation is ascribed to a friction phenomenon appearing at the polymer/filler interfaces: it is designated in the literature by the stick-slip mechanism [36]. It is interesting to note that several authors have shown an enhancement of the dissipative part of the polymer mechanical properties by the introduction of carbon nanotubes [37,38]. By friction, some additional damping is brought to the polymer.
However, since our work is dedicated to highlight the synergy between piezoelectric and conductive fillers for damping improvement, we will focus on the analysis of this piezoelectric based concept which may offer higher electromechanical coefficient. Above the \( \alpha \) relaxation, the dissipative modulus of the hybrid composites stays high compared to neat PA 11. The molecular mobility increases when the polymer is in the rubbery state leading to additional dissipation energy at polymer/filler interfaces.

Regarding the influence of the poling step on the PA 11/PZT/CNT composite, an enhancement of the dissipative part of the polymer appears. At the maximum of the \( \alpha \) relaxation peak, an increase of the dissipative modulus of 29.2% is observed after polarization. The poled PZT particles create, with CNTs, a synergy that results in an increase of the dissipative modulus. Piezoelectric fillers convert the mechanical deformation into additional interfacial polarization which is dissipated through CNTs by Joule effect.

3.1.2.3. Loss factor. The loss factor of neat PA 11 and PA 11/PZT/CNT 0.2 vol.% nanocomposite in piezoelectric and non-piezoelectric states versus temperature is pointed out in Fig. 7.

At the maximum of the \( \alpha \) relaxation peak, the loss factor of the hybrid PA 11/PZT/CNT composite increases within the range of 20% upon polarization, showing the contribution of the transduction–local dissipation phenomenon on the material damping properties. The loss factor \( \tan \delta \) represents the ratio of the dissipative modulus over the conservative one. Below 65 °C, the increase of the conservative modulus due to synergy between piezoelectric PZT particles and CNTs remains more important than the raise of the dissipative modulus: the loss modulus of the hybrid composite is lower than neat PA 11 one. Above 65 °C, the loss factor of the piezoelectric composite becomes higher than the neat PA 11 one due to a large increase of the dissipative modulus.

The challenge of this new field of material is to increase the dissipative part by keeping a high mechanical modulus for structural application. Obtained results offer promising possibilities regarding the incorporation of submicronic piezoelectric fillers with carbon nanotubes into polymer matrix to improve the damping of any polymeric based materials.

3.2. Vibration test under bending solicitation

3.2.1. Influence of the excitation level on bulk and sandwich configurations

Fig. 8 presents the evolution of the frequency response function (FRF) of neat PA 11 in bulk and sandwich configurations. The FRF corresponds to the velocity of the sample (i.e. displacement) normalised to the imposed base acceleration at a given frequency.

Either in a bulk or sandwich configuration, the amplitude of the resonance peak decreases when the imposed acceleration increases. For an excitation of 5 g, this phenomenon is amplified. Regarding bulk results (Fig. 8(a)), calculations have shown that the matrix is still in the viscoelastic domain and does not reach the yield point in this range of acceleration. The influence of excitation levels is attributed to a viscoelastic dissipation phenomenon inherent to the polymer strain. Fig. 8(b) shows that the stiffening brought by the metallic layers induces a shift of the resonance peak to higher frequencies. In this configuration, an asymmetry of the resonance peak appears and gets more important when the excitation level increases. For an excitation level of 5 g, the FRF is strongly modified and the peak's shape highlights a nonlinear behaviour, characterized by a flattening and a softening effect. This result is explained by large shear stresses existing in the sandwich configuration. The dissipative component of the sample is strongly dependent of the excitation level.

3.2.2. Synergy between piezoelectric and conductive fillers

Fig. 9 compares the FRF of neat PA 11 (as reference) and PA 11/PZT 30 vol.%/CNT 0.2 vol.% hybrid nanocomposite in piezoelectric and non-piezoelectric states for two imposed accelerations (0.1 and 0.5 g). Only the lowest excitation levels are applied to the materials in order to avoid a highly nonlinear behaviour in the nanocomposite.

The resonance peak shifts towards lower frequencies when PZT particles and CNTs are introduced in PA 11: the tensile modulus and the density of neat polymer are modified. The polarization of the hybrid nanocomposite results in a decrease of the FRF amplitude: for an excitation level of 0.1 g, the amplitude drops from 0.97 m s\(^{-1}\) g to 0.6 m s\(^{-1}\) g, corresponding to a decrease of 40%. For an excitation level of 0.5 g, the amplitude is divided by two. PZT particles need to be piezoelectric to convert mechanical vibrations into an electrical potential; CNTs dissipate the created charges by Joule effect. The damping ratio of the polymer matrix is improved thanks to the synergy between the piezoelectric PZT particles and the CNTs.

Fig. 10 compares the decrease of the resonance peak amplitude due to polarization for composites loaded in PZT particles. Three parameters are studied: the imposed base acceleration, the sample configuration (bulk or sandwich) and the influence of CNT presence (PA 11/PZT and PA 11/PZT/CNT composites). Due to the high asymmetry of sample response in sandwich configuration, the damping ratio was not able to be estimated with usual software. The decrease of the resonance peak amplitude has been chosen as an image of the damping factor since it represents the vibration amplitude measured at one point of the cantilever beam.

For bulk composites, the amplitude of the imposed base acceleration has no influence on the contribution of the poling step. The influence of
CNT presence on the bulk composite response is also studied. Without CNTs, only a 5% decrease of the peak amplitude with the poling step is observed whereas a 13% decrease is noticed when CNTs are introduced in the polymer matrix at the same time than piezoelectric particles. The damping ability of the composite becomes significant when PZT particles are coupled with carbon nanotubes. Piezoelectric PZT fillers need to be associated to local conduction for avoiding a piezoelectric saturation: inorganic particles convert the energy of the mechanical vibrations into electrical charges and CNTs allow the evacuation of these charges by local conduction. For PA 11/PZT composites, the charges created by PZT under vibrations are trapped at polymer/PZT interface and the transduction mechanism is unsustainable: as a consequence, no additional damping is observable.

For an imposed acceleration of 0.5 g, the sandwich configuration presents a decrease of the resonance peak amplitude after polarization three to four times greater than the bulk configuration. Shear stresses brought by the sandwich configuration leads to a better efficiency of the mechano-electrical conversion by piezoelectric PZT particles: PZT crystalline structure undergoes an intense strain which induces a higher created charge density at their surface. The sandwich configuration has shown its efficiency to enhance the synergy between transduction and local dissipation that promote damping into polymer/PZT/CNT nanocomposites.

4. Conclusion

A new hybrid nanocomposite for vibration damping has been elaborated. For this, ferroelectric PZT particles and CNTs have been dispersed simultaneously in a semi-crystalline thermoplastic matrix, polyamide 11. The molten way, i.e. extrusion, has been used as an industrial dispersion process. The damping properties of nanocomposites have been evaluated by dynamic mechanical analysis and vibration test. The originality of this work stems from an experimental comparison of the same composite (PA 11/PZT 30 vol.%/CNT 0.2 vol.%) which has undergone or not a poling step for damping improvement. For same PZT and CNT concentration, the composite becomes able to convert mechanical vibrations into an electrical potential. Moreover, the carbon nanotubes do not constitute a conductive network and the transduction-dissipation phenomenon at the heart of this work is based on local dissipation through CNTs by Joule effect.

To enhance shear stress and promote the mechano-electrical transduction of PZT particles into hybrid nanocomposites, a sandwich configuration has been adopted. The dynamic mechanical analyses have highlighted an increase of the conservative and dissipative shear
modulus after a poling step only in case of PA 11/PZT/CNT 0.2 vol.% CNTs are required since this phenomenon is not observed in case of PA 11/PZT nanocomposite. The polarization of the hybrid composite making PZT particles able to insure the transduction mechanism has revealed a 20% improvement of the composite loss factor.

Regarding vibration test, the sandwich configuration has shown a particular behaviour with a resonance peak which becomes asymmetric at high excitation levels. This asymmetry, characterizing a softening and a flattening effect, has been correlated to an intrinsic dissipation mechanism of the polymer matrix. Furthermore, the amplitude of the first resonance peak of neat PA 11, representative of its damping ratio, is divided by two when poled PZT particles and CNTs are introduced simultaneously in the polymer matrix. By poiling PZT particles and making them piezoelectric, they acquire the ability to convert mechanical vibrations into electrical charges. It has been noticed that the vibration damping effect is consistent only when piezoelectric particles are coupled to conductive fillers. In that case, the transduction mechanism keeps being efficient because a saturation of the piezoelectric effect is avoided.

This work has revealed for the first time the real efficiency of a damping brought by the synergy of piezoelectric particles and conductive fillers. Using two different submicronic fillers allows realising the transduction–local dissipation coupling required for persistent vibration damping. An experimental set-up through a sandwich configuration has shown its ability to highlight the transduction–local dissipation phenomenon for integrated vibration damping in polymeric systems.

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