Development of the Fabrication Process and Characterization of Piezoelectric BaTiO$_3$/Epoxy Composite Used for Coated Ultrasonic Transducer Patterns in Structural Health Monitoring

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Abstract. Structural health monitoring (SHM) systems based on guided waves require a network of transducers to obtain on demand information about the conditions and performance of the structure or component being interrogated such that the occurrence of a tolerable damage can be reliably monitored. The damage detection can be achieved by monitoring a set of piezoelectric sensors over time, inferring the remaining useful life of the interrogated structure from the recorded data and programming the need of future structural maintenance actions. A desirable solution for the manufacturing and integration of the sensors to the host structure would be to get the transducer network ‘printed’ on the structure once the sensor pattern has been designed through modelling and simulation. In recent years, an important number of thin piezoelectric-polymer composites have been developed in order to obtain flexible materials to be used as transducers for the generation and detection of guided waves for different applications, including SHM systems.

In this paper the development of the fabrication process and the results of the characterization of a piezoelectric composite to be used as an ultrasonic transducer for damage sensing in a SHM system based on guided waves are presented. The composite consists of piezoelectric BaTiO$_3$ particles homogenously distributed in an epoxy resin matrix. A paste with solid content of up to 50 vol. % is prepared by the direct mechanical mixing of the piezoelectric particles in the epoxy matrix. Due to the ferroelectric properties of BaTiO$_3$, the polarization of the composite at high values of electric field is required before the characterization. For the characterization of the samples, the composite is manufactured in the form of a film. Two electrodes placed on both sides of the samples are required to measure the dielectric and electromechanical properties of the composite. The influence of the volume fraction of BaTiO$_3$ on the density and important electromechanical parameters of the piezoelectric composite are investigated. Variables of the fabrication process and conditions of the poling stage are adjusted to obtain a composite transducer with high density, low porosity and high values of the longitudinal piezoelectric coefficient ($d_{33}$).
1. Introduction

Non-destructive evaluation (NDE) methods are a reliable, efficient and economical approach to increase safety and reduce maintenance costs of structures. Besides detection and localization of damage in general, NDE techniques even allow for early damage detection without compromising the integrity of the structure considered. This early damage detection allows the repercussion of damages on the performance and operational life of the analysed structure or component to be assessed. This extension of NDE can also be considered as structural health monitoring (SHM) [1]. The monitoring technique considered here is based on guided waves, being an NDE method increasingly used for the inspection of thin-walled structures, currently also within the context of SHM. Some of the features of this technique include the possibility of inspecting entire cross sectional areas of structures, excellent sensitivity to multiple defect types often combined with high precision of identification and low energy consumption [2].

Guided waves can be generated and detected by different means, such as ultrasonic probes made of piezoelectric ceramics, piezoelectric wafer active sensor (PWAS) [3] or electromagnetic transducers. Piezoelectric polymeric materials are used for sensing strain, temperature and electronic charge/discharge. The manufacturing of poly(vinylidene fluoride) (PVDF) films is a cost effective and simple method and at the same time offers several possibilities for the application of electrodes [4]. Due to its flexibility and ability to be shaped and patterned with printed electrodes, PVDF is adequate for sensing structural vibrations in non-destructive applications. Despite the described properties and advantages of PVDF films, they are mainly used as sensors due to their weak driving force and piezoelectric constants [5].

One approach for realising piezoelectric materials is replacing a portion of the piezoceramic material with lightweight, flexible and non-piezoelectric polymers. The resulting density, acoustic impedance and dielectric constant will decrease when compared to a monolithic PWAS but is still higher than PVDF. However, by combining the best of the properties of both materials, the resulting composite can still become an improved transducer material [6]. Piezoelectric-polymer composites were first developed as transducers to achieve mechanical and electrical properties, which cannot often be obtained with single phase materials [7]. In recent years an important number of thin piezoelectric-polymer composites have been developed in order to obtain flexible materials to be used as transducers for the generation and detection of underwater acoustic signals, medical diagnostic systems and tactile sensors [8, 9, 10].

Intrinsically piezoelectric polymers, such as PVDF and its copolymers, represent an interesting choice as a matrix for piezoelectric composites due to its good electromechanical coefficients and high conductivity. However, issues remain to be dealt with, such as the necessity of a high electric field to pole them and poor thermal stability [10]. Another suitable candidate for the polymeric matrix in piezoelectric composites is the epoxy resin, which is used in many applications due to its good mechanical and electrical properties, ease of manufacturing and low cost.

This paper aims at the development of the fabrication process and characterization of a BaTiO$_3$/epoxy resin piezoelectric composite to be used as an ultrasonic transducer for damage sensing in a SHM system based on guided waves.
2. Materials and Methods

2.1 Materials

The BaTiO$_3$ used in this study is a commercially available powder (Inframat advanced materials, USA). It was characterized as a material having an average particle size of 700 nm (reported by the manufacturer), $\varepsilon_r$ of 771 and a specific surface area of 1.8 m$^2$/g [12]. The polymer used is an epoxy resin (Araldite MY750) with low viscosity (Hunstman, Belgium) hardened with sufficient amounts of isophorone diamine (Fluka, Germany).

2.2 Composite Elaboration

The BaTiO$_3$ powder, with volume fractions in the range of 10 - 60 vol. %, and the epoxy resin were mixed manually for 10 min. Afterwards, the system was put in an ultrasound bath for 30 min. A sufficient amount of hardener (mass ratio epoxy resin/diamine = 7/2) was then added to the system and it was mixed in a speed mixer (Hanschild Engineering, Model DAC 600.2 VAC-P) in vacuum for 10 min at 2350 rpm. The mixture was directly poured into silicone moulds and was subsequently pre-cured in a furnace at 50 $^\circ$C for 1 h and cured at 100 $^\circ$C for 1 h. The composites were moulded to obtain discs with a diameter of 15 mm and a thickness of 1 mm. For the measurement of the piezoelectric properties, circular gold electrodes were sputtered (JEOL Model JFC 1300) on both sides of the composites.

The sputtering conditions, made in Ar plasma, were 300 s, 30 mA, 5 kV, 10 Pa. As a preliminary step for the poling of the composites, the influence of the applied voltage, poling temperature and time on the $d_{33}$ of the 30 vol. % BaTiO$_3$/epoxy composite was analysed. The poling of the samples with electrodes was performed by applying a dc voltage of up to 10 kV (Heinzinge 10 kV power supply) at different temperatures for up to 1 h in a silicone oil bath to ensure uniform heating and to avoid instantaneous sample breakdown initiated by external flashover. Once the optimal experimental conditions were found, they were applied to the poling of the remaining formulations.

2.3 Composite Characterization

The microstructure of the fracture surface of the composites and the particle distribution in the polymeric matrix were analysed by scanning electron microscopy (SEM) (Quanta Model 400 FEG). The density of the samples was measured by gas pycnometry (Micromeritics Model Accu Pyc 1330) and compared to the relative density calculated by the rule of mixtures

$$\rho_c = \rho_f \phi_f + \rho_m \phi_m$$  \hspace{1cm} Eq. 1

where $\rho_c$, $\rho_f$, $\rho_m$ are the density of the composite, filler and matrix and $\phi_f$, $\phi_m$ the volume fraction of the filler and matrix, respectively. The frequency dependency of the relative permittivity ($\varepsilon_r$) of the composites was analysed by impedance spectroscopy (Agilent Model 4284A) in a frequency range of $10^2$ - $10^6$ Hz, measurements were done at room temperature. The relative permittivity was calculated from the capacitance according to

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 A}$$  \hspace{1cm} Eq. 2
where $C$ is the capacitance, $d$ the thickness of sample, $A$ the electrode surface area and $\varepsilon_0$ the permittivity of free space ($\varepsilon_0 = 8.854 \times 10^{-12}$ F/m). The longitudinal piezoelectric coefficient ($d_{33}$) was measured by a $d_{33}$-meter (Sinocera Model S5865) at a fixed frequency of 110 Hz.

### 3. Results and Discussion

The composite density values calculated by the rule of mixtures and the experimental values as function of the filler volume fraction are presented in Fig. 1. For the calculation of the theoretical values by the rule of mixtures, $\rho_f$ and $\rho_m$ are taken to be $6.02$ g/cm$^3$ and $1.14$ g/cm$^3$ respectively. The increment of the amount of filler leads to an increment of the composite density. For volume fractions up to 30 vol. %, the experimental values are approximately 90 % of the theoretical values. For higher volume fractions (40 - 60 vol. %) the experimental values represent approximately 75 % of the theoretical values.

It is well known that the properties of composite materials largely depend on its homogeneity. SEM images were performed to assess the degree of dispersion of the filler particles and to study the interaction between filler and matrix by means of analysing the interface. SEM images of the fracture surface of the composites are shown in Fig. 2. In the composites with 20 vol. % and 30 vol. % of BaTiO$_3$ the particles are dispersed and distributed homogenously in the epoxy matrix (Fig. 2(a), (b)). For higher amounts of filler, the dispersion of the particles is not efficient, resulting in the formation of agglomerates. The presence of residual porosity is also observed (Fig. 2(c), (d)). With respect to the interface, independently of the volume fraction of the filler, the formation of an interface with weak interaction between ceramic filler and polymeric matrix is observed, as evidenced by the debonding of the particles from the matrix. Taking this into account, the higher discrepancy between the theoretical and experimental density values for composites with high volume fraction of filler (40 - 60 vol. %) shown in Fig. 1 could be explained by the presence of air voids in the composites.

The electrical properties of composite materials show different trends when compared to the pure constituent phases [13]. Several mixing rules were developed to describe the relative permittivity of a system consisting of two immiscible phases. The Maxwell-Garnett model [14] considers the dielectric permittivity arising from spherical fillers dispersed in a continuous medium.

**Fig. 1.** Comparison between the theoretical density obtained by the rule of mixtures and the experimental density of the composites.
The Maxwell-Garnett equation can be expressed in several forms, one of those shown in Eq. 4

\[
\varepsilon_c = \varepsilon_m \left[ 1 + \frac{\eta \phi_f (\varepsilon_f - \varepsilon_m)}{(1 - \phi_f)(\varepsilon_f - \varepsilon_m) + \eta \varepsilon_m} \right]
\]

where \( \varepsilon_c, \varepsilon_m \) and \( \varepsilon_f \) are the relative permittivity of the composite, matrix and filler, respectively, \( \phi_f \) is the filler volume fraction and \( \eta \) is a shape factor, which takes into account the geometry of the filler. \( \eta \) takes a value of 3 in the case of spherical particles.

For low filler concentrations, due to the large distance between the particles, the interaction between them is weak and therefore is neglected by the Maxwell-Garnett model. Moreover, this model is only valid for low concentrations of filler [8]. At higher filler concentrations, the spontaneous polarization of the particles becomes significant because the distance between them is extremely short. Moreover, the electrical field arising from the induced dipoles is no longer negligible when calculating the field generated locally in the matrix. On the basis of this observation, Jayasundere and Smith [13] developed a more realistic mixing rule. This model considers the electric field of a dielectric sphere embedded in a continuous dielectric medium and takes into account the polarization of adjacent particles. The equation of the Jayasundere and Smith model is shown in Eq. 5.

\[
\varepsilon_c = \frac{\varepsilon_m \phi_m + \varepsilon_f \phi_f \left[ \frac{3\varepsilon_m}{2\varepsilon_m + \varepsilon_f} \right] \left[ 1 + 3\phi_f \frac{\varepsilon_f - \varepsilon_m}{2\varepsilon_m + \varepsilon_f} \right]}{\phi_m + \phi_f \left[ \frac{3\varepsilon_m}{2\varepsilon_m + \varepsilon_f} \right] \left[ 1 + 3\phi_f \frac{\varepsilon_f - \varepsilon_m}{2\varepsilon_m + \varepsilon_f} \right]}
\]

The relative permittivity of the composites compared to the values predicted by the Maxwell-Garnett model and Jayasundere-Smith model as a function of the volume fraction of filler is shown in Fig. 3. For the calculation of the theoretical values, \( \varepsilon_m \) and \( \varepsilon_f \) are taken to be 6.8 and 771, respectively. Measurements were done at room temperature at a frequency of 1 kHz. It is observed that the values of \( \varepsilon_r \) increase with the volume fraction of filler.
Fig. 3. Relative permittivity $\varepsilon_r$ of the composites compared to the Jayasundere-Smith Model and Maxwell-Garnett Model. Measurements were done at room temperature at a frequency of 1 kHz.

This result is due to the increasing contribution of the BaTiO$_3$ particles to the electric properties of the composite since BaTiO$_3$ has a substantially higher value of $\varepsilon_r$ to that of the epoxy matrix. For a volume fraction of 60 vol. %, an increment of a factor of 3.5 is obtained when compared to pure epoxy, achieving a value of 23.8. As expected, the experimental results behave as predicted by the Maxwell-Garnett model for low concentrations of filler, such as up to 20 vol. %. The Jayasundere-Smith model fits the experimental data well for a filler volume fraction of up to 40 vol. %. For higher concentrations, a discrepancy between the experimental data and the predicted values is observed. This discrepancy for high concentrations of filler (50 - 60 vol. %) could be explained by the presence of air voids in the composites, as seen in Fig 2. It is well known that the presence of porosity has a detrimental effect on the electrical properties of composites because of the low value of $\varepsilon_r$ of air. The porosity is also expected to reduce the contact surface between composite and electrodes, therefore leading to low values of $\varepsilon_r$.

The frequency dependence at room temperature of $\varepsilon_r$ is shown in Fig. 4. It is possible to observe that the $\varepsilon_r$ values decrease following roughly the same profile with the increment of the frequency, independently of the volume fraction of filler.

Fig. 4. Frequency dependence of the relative permittivity ($\varepsilon_r$) of the composites as a function of the filler volume fraction.
Composites containing ferroelectric or conducting particles generally show this frequency dispersion phenomenon, which in turn is due to the polarization of the composites [15]. In ceramic/polymer composites two main polarizations are observed, spontaneous and interfacial polarization. The spontaneous polarization arises from the interaction between adjacent particles, whilst the interfacial polarization is produced by the dissociation of mobile charges under an electric field producing positive and negative space charges in the bulk of the composite or at the interfaces between the ceramic particles and the polymeric matrix [16].

At low frequencies, high values of $\varepsilon_r$ are obtained since the induced dipoles can follow up with the changes of electric field. However, at high frequencies, some dipoles can no longer contribute to the permittivity. The interfacial polarization, which takes place at low frequencies ($< 1$ MHz), lags gradually behind with the increasing frequency due to the mismatching between the rate of orientation of the dipoles and the alternating electric filed, resulting in the frequency dispersion observed in Fig. 4.

To induce the piezoelectricity in the ceramic phase of the composites an electric field was applied to the composites. This induced the alignment of the dipoles with the direction of the applied electric field. It is well known that the poling conditions have a major influence on the $d_{33}$ of composites. Therefore, in order to understand the influence of these parameters (poling time, voltage and temperature) on the $d_{33}$, a preliminary study was done with the 30 vol. % BaTiO$_3$/epoxy composite. The results of this optimization process are presented in Fig. 5.

The influence of the poling time on the $d_{33}$ of the composite is shown if Fig 5(a). For this measurement the applied voltage and the poling temperature were set to be 10 kV and 75 °C, respectively. The value of $d_{33}$ increases from 3.1 pC/N to 3.7 pC/N when the poling time is increased from 15 min to 30 min. This value remains constant when the poling time is extended to 60 min. Given this result, the poling time of the succeeding tests was set to be 30 min. In Fig. 5(b) it is possible to observe that higher values of electric field applied leads to higher values of $d_{33}$, independently of the poling temperature. The poling temperature has also a major influence on the $d_{33}$ values. Considering the results obtained for 10 kV, a maximum value of 3.7 pC/N is obtain at 75 °C. At 100 °C a drop in the $d_{33}$ values is observed, resulting in a value of 2.8 pC/N. This result could be explained as follows; at 75 °C the $T_g$ of the epoxy matrix is reached, which is found to be in the 60 – 70 °C range. At this temperature the high mobility of the induced dipoles increases the polarization of the ceramic particles, which in turn increases the permittivity and consequently the $d_{33}$ values.

![Fig. 5. Influence of the poling conditions on the $d_{33}$ values of the 30 vol. % BaTiO$_3$/epoxy composite, (a) poling time, (b) electric voltage and poling temperature.](image-url)
At 100 °C the mobility of the dipoles increases further but the temperature is getting close to the Curie temperature of BaTiO$_3$, which is 120 °C. At this temperature the ferroelectric properties of BaTiO$_3$ are reduced. The overall combination of these two phenomena leads to the reduction of the $d_{33}$ values. Given the results obtained, the best poling conditions are 30 min, 10 kV and 75 °C. These conditions were applied in the poling of the remaining formulations.

The accurate knowledge of the piezoelectric coefficients is essential to understand the behaviour of piezoelectric materials. The piezoelectric coefficient ($d_{33}$) is defined as the electric polarization generated in a material per unit mechanical stress applied to it. Yamada [17] developed a model able to describe $d_{33}$ of a binary system consisting of a polymeric matrix and piezoelectric particles. This model is also suitable for composites with high volume fractions of filler. The model contemplates ellipsoid particles embedded in a dielectric continuous medium. The piezoelectricity of the binary system is considered to be caused by the piezoelectric particles. The longitudinal piezoelectric coefficient of the composite ($d_c$) is given by Eq. 6, where $\phi_f$ is the volume fraction of filler, $\theta$ the poling ratio, $G$ the local field coefficient and $d_f$ the longitudinal piezoelectric coefficient of the piezoelectric particles, which was set to be 190 pN/C. The value of $G$ is given by Eq. 7

$$d_c = \phi_f \cdot \theta \cdot G \cdot d_f$$  \[\text{Eq. 6}\]

$$G = \frac{\eta \varepsilon_c}{\eta \varepsilon_c + \varepsilon_f - \varepsilon_c}$$  \[\text{Eq. 7}\]

where $\eta$ is the shape factor, $\varepsilon_c$ and $\varepsilon_f$ are the relative permittivity of the composite and filler, respectively. It is assumed that the piezoelectric particles exist in the continuous medium with the relative permittivity $\varepsilon_c$. The comparison of the experimental data with the Yamada model is represented in Fig. 6. There is a good agreement for composites with volume fractions of the filler up to 30 vol. %, where values of $d_{33}$ are slightly superior to those predicted by the model. However, for a further increment of the filler amount there is a discrepancy where the values of $d_{33}$ obtained are lower than those predicted by the model. As observed in previous results, the presence of air voids has a negative effect on the density and relative permittivity of the composites, leading also to low values of $d_{33}$.

![Graph showing comparison of experimental data with Yamada model for $d_{33}$ values of composites.](image)

**Fig. 6.** Comparison of the experimental data with the Yamada model for $d_{33}$ values of the composites.
4. Conclusions

BaTiO$_3$/epoxy composites were fabricated and physical and electromechanical properties were measured aiming at the application as piezoelectric sensors to detect guided waves as a part of a structural health monitoring system to detect damage. The proposed fabrication process for the piezoelectric sensor was based on the direct mechanical mixing of filler and matrix phases, the process led to a homogenous dispersion and distribution of the filler in the matrix. A weak interfacial interaction between particles and matrix was observed in SEM images. For volume fractions of filler up to 30 vol. %, the density obtained resulted to be 90 % of the theoretical density. The values of the electromechanical properties, relative permittivity and longitudinal piezoelectric constant, obtained for volume fractions of filler up to 40 vol. % were in agreement with the theoretical models. The addition of higher amounts of filler led to particle agglomeration and formation of air voids in the composites, as demonstrated by SEM images. The presence of air voids showed to be detrimental for the density and electromechanical properties of the composites, leading to discrepancies with respect to the theoretical models. The combination of electromechanical properties of the composite, acceptable values of relative permittivity and longitudinal piezoelectric constant, and mechanical properties make this material attractive for transducer and sensors applications. It is highly likely that improving the mixing stage of the phase components of the composite will reduce the presence of air voids, thus increasing the electromechanical and mechanical properties of the composite.

References