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Research Article

Effect of Polymer-Ceramic Fibre Interphase Design on Coupling Factor in Low Fibre Volume Content Piezoelectric Composites

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In this work, we investigated different short molecule polymer coatings in piezoelectric ceramic-polymer composites with low fibre volume contents. Modifying the interphase between the piezoelectric PZT (lead zirconate titanate) fibre and the epoxy matrix thus enhances the electromechanical coupling factor for 1–3 ultrasound transducers with low fibre contents. It is known that the electromechanical coupling factor can be increased by precoating a ceramic fibre with a soft interlayer polymer [1-1-3]. In this paper, we investigate the so-called 1-1-1-3 composites composed of a ferroelectric ceramic fibre (core), a soft polymer layer (e.g., fatty acids, amides, waxes, or oils), an epoxy resin shell, and an epoxy resin matrix. Some soft polymer layers allowed the free movement of the ferroelectric fibres reducing blocking or clamping by the inactive polymeric matrix, resulting in higher electromechanical coupling factors (k_t) for composites with low fibre volume contents. Using an oil-based interlayer, the dielectric constant can be significantly increased. The lowest fibre push-out stress could be achieved with the paraffin interlayer; however, no correlation with the coupling factor could be observed.

1. Introduction

Ultrasound transducers consist of three main parts: active element, backing, and matching layer(s) where the active element, i.e., the piezoelectric material, converts electrical energy into ultrasonic energy. Piezoelectric 1-3 ceramic-polymer composites have been developed principally because their properties offer advantages, especially for sonar and medical ultrasonic imaging technologies of water and soft tissues (e.g., human skin), over those of bulk piezoelectric ceramics [1–4]. The advantages include relatively good acoustic matching between the transducer and the medium which allows a better acoustic wave interfacing with the subject.

In 1–3 composites, the electromechanical properties of transducers can be tailored by the volume content of the ferroelectric phase as well as their geometry. The acoustic impedance is coupled with the density of the transducer material; therefore, to reduce the acoustic impedance in 1–3 composites, the volume content of piezoelectric fibres has to be lower. Typically, this will result in mechanical clamping of the piezoelectric fibres by the inactive polymeric matrix.

The thickness and longitudinal coupling factors, k_t and k_{33}, respectively, express the coupling between an electric field (electrical polarisation) and mechanical vibrations in the same direction. It is known that 1–3 connectivity enhances the electromechanical coupling factor (k_t is the thickness mode); Chan et al. showed that, with doped bismuth sodium titanate 1–3 composites, k_t close to free ceramic rod values could be achieved with an active volume fraction of ~0.6 [5]. For a given piezoelectric material, k_{33} (longitudinal mode) is generally much higher than the k_t value. For discs or plates (diameter >> thickness), k_t is the thickness electromechanical coupling factor. For longitudinal vibration of a fibre, pillar, or cylinder (thickness >> diameter), the term k_{33} is used [6]. For 1–3 transducers, the term k_t is used because the diameter of the sensor is bigger than its thickness. Typically, a k_t value close to k_{33} of the active piezoelectric material can be expected because the coupling factor is a function of piezoelectric charge constant, permittivity, and stiffness. Some authors have started to use the expression effective electromechanical coupling factor ($k_{t.eff}$) for composite materials to avoid confusion [7]. It is said that k_{33} of 1–3 PZT composites are in

the range of 0.6–0.7, while k_t of PZT discs tends to be lower at between 0.4 and 0.5 [8]. For dice and fill ferroelectric composites, it was shown in the study by Kim et al. that the electromechanical coupling factor of 1-3 composites is typically lower than that of the equivalent bulk material and it can be improved by using an additional soft polymer coating (i.e., the interlayer is 1-1-3 composite) [9]. In the Kim et al. study, a soft epoxide was used as an interlayer material. According to our knowledge, the effect of different polymer interlayers on the coupling factor has not been discussed. Electromechanical properties of the piezoelectric fibre composites are highly dependent on the phase volume fraction of fibres and their arrangement [10]. By decreasing the volume fraction of the piezoelectric fibres in 3-1 composites, the electromechanical properties like d_{33} and d_t decrease because of the clamping effects of the nonactive polymer material [11, 12].

To improve the electroactive properties of 1-3 composites with low volume fraction of piezoelectric fibres, different organic additives have been investigated. Fibres have been precoated with a soft interlayer polymer as well as a soft epoxy outer layer. The motivation of this study was to combine the benefit of the soft polymer interlayer to reduce the clamping effect of the matrix with the benefit of the additional polymer shell to adjust the ferroelectric material volume ratio for different transducer applications by using fibre bundle processing [13]. The so-called 1-1-1-3 hybrids were composed of a ferroelectric ceramic core (fibre), an inner soft polymer layer (e.g., fatty acids, amides, waxes, or oils), an outer epoxy resin shell (interlayer), and the main stiff epoxy matrix (Figure 1). The inner soft polymer layer and the outer epoxy shell were expected to allow the free movement of the ferroelectric fibres reducing the blocking or clamping forces by the inactive polymeric matrix with a weak interphase, resulting in a higher electromechanical coupling factor [9, 14]. Using this approach, it is possible to use oil and other short molecular organic species to reduce the clamping effect and the polymer shell coating will help with the fabrication process. The interphase behavior was investigated by mechanical push-out experiments of the epoxy matrix (fibre push-out test). The purpose was to evaluate the matrix-fibre interaction, debonding energy [15], and correlation with the electromechanical coupling factor. The big advantage of fibre transducers against dice and fill composites is the realization of longer length/diameter ratios which result in a higher coupling factor and lower frequency ultrasonic devices [16].

2. Materials and Methods

Sintered soft PZT fibres ($\varnothing = 800\,\mu$m) supplied by Smart Materials Corp. were used for the fibre composite fabrication. The fibre composites were made by fibre bundle processing. Fibres are bundled together and fixed in a holder, and the free space in between the fibres is filled with epoxide resin [13]. Before bundling, a soft polymer layer and an outer epoxy resin shell were placed around the fibre by a dip coating process (DipMaster, Chemat Technology Inc., USA). For all dip coating procedures, parameters were constant:

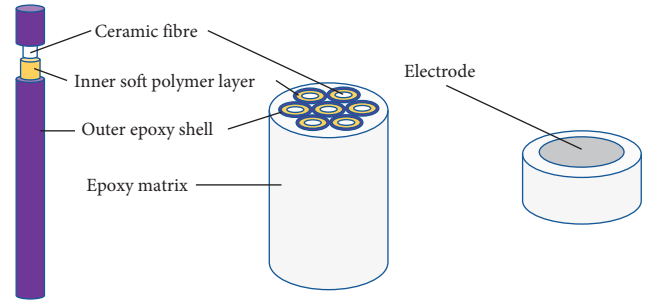


Figure 1: An illustration of the 1-1-1-3 hybrid showing the single fibre component on the left with the PZT fibre, a soft polymer interlayer to reduce the clamping effect, and an epoxide shell to control the fibre content in the transducer. On the left side, the PZT fibres embedded in an epoxy matrix and an electrode hybrid disc is shown.

immersion speed 200 mm/min, still time 30 s, dip coating depth of fibre 75 mm, and withdrawal speed 500 mm/min.

For the soft polymer layer, different kinds of polymers were selected. Two soft solid thermoplastic polymers (paraffin wax, Sigma-Aldrich 327212; stearic acid, Sigma-Aldrich 9636LJ), two oils (mineral oil, Sigma-Aldrich 330760; sunflower oil, Migros-M-classic sunflower oil), and one liquid low molecular weight polymer (polyethylene glycol 300, Sigma-Aldrich 81160) were investigated in this study. Paraffin and the oils do not bond well to the ceramic surface, while PEG and stearic acid are typically used as good interface layers (surfactants) to get good bonding between hydrophilic ceramic surfaces and hydrophobic polymer surfaces [17–19]. These materials were used to achieve the first soft polymer layer around the PZT fibre by the dip coating process with four layers applied. The two soft solid thermoplastic polymers were melted in order to carry out the dip coating. To stabilize the coating during further processing, a second coating (Beckopox EM 2120w/45WA; Cytec Solvay Grp.) was used. The PZT fibres were coated four times with the Beckopox EM 2120w/45WA and cured at 120°C for 15 min and at room temperature (paraffin and SA coating) overnight. The SEM analysis used to evaluate the interphase was performed on a Vega3 (TESCAN, Czech Republic) with the software used to determine the thickness of the different coatings being Imagic IMS Client. To investigate the effect of the coating of the soft polymer layer on the electromechanical properties, uncoated PZT fibres and PZT fibres with a second coating (Beckopox EM 2120w/45WA) were used for the later fibre composites.

The coated and uncoated PZT fibres were embedded into a 2-part epoxy resin (Specifix resin + Specifix 20 curing agent, Struers ApS, Denmark). Seven fibres were closely held together and placed in an enclosed plastic holder, and the main resin matrix (Specifix) was poured in and allowed to cure overnight.

Seven-millimeter-thick disc sections were cut to make the 1-1-1-3 hybrid ceramic polymer. These were ground down and polished on either surface to a general thickness of ~5 mm. Ag epoxy paste (Electrodag 5915, Acheson Colloids Co.) electrodes ($\varnothing = 5$ mm) were screen printed onto each

side of the samples. The active area of the various discs (measured by removing the electrode and measuring the distance from the central fibre to the edges of the surrounding fibres; varying from 0.046 to 0.072 cm^2) had a fibre volume fraction between 30 and 60%.

The electrical poling of the 1-1-1-3 hybrid polymer ceramic was carried out using a ChargeMaster CM5-60 (Simco Ion, Switzerland), with samples fully submerged in silicone oil at room temperature. A poling field of 3 kV/mm was applied for 30 minutes to each sample at room temperature. Impedance measurements on ceramic-polymer composites determined the electromechanical coupling factors and the electrical permittivity. The electromechanical coupling factor of the composites was measured using an impedance gain/phase analyser, SI1260 (Solartron Analytical, UK). 3-disc samples were used to determine the electrical characteristics of each material under observation. The parameter used to determine the electromechanical coupling factor was the EIS setup from 0.2 Hz to 1 MHz with a voltage bias of 0 V to 0.5 V. Electrical impedance, phase angle, and capacitance were measured, and the relative permittivity at 1 kHz was calculated.

The electromechanical characteristics of single-coated fibres were measured to observe the effect of the epoxy polymer coating on ferroelectric properties, with a novel piece of equipment (FerroFib) developed from collaboration between Empa and aixACCT System GmbH [20, 21]. A full description of sample fabrication is described in detail in [22, 23]. The fibres were poled for 5 min at room temperature under an applied electric field starting at 2.5 kV/mm. PE and SE loops as a function of the applied electric field were recorded at 0.1 Hz. The small signal properties (d_{33}) were measured at 10 Hz. The reported results for the large signal response (i.e., SE and PE loops) and the small signal response (i.e., d_{33}, $\tan\delta$ and e_r) are averages of three fibres with the standard deviation.

Fibre push-out tests were carried out on 1-1-1-3 composites. 10 mm long coated and uncoated fibres were placed in a ~1–2 mm thick epoxy resin disc with a diameter of 10 mm (Figure 2(a)). Testing was carried out on a Zwick/Roell Z005 (Zwick/Roell Grp., Germany) (Figure 2(b)). Push-out stress (or shear strength) was calculated by dividing the force at failure to the surface of the fibre-matrix interphase. The results are an average of 3 samples each.

The formula used to calculate the push-out stress was

$$\sigma = \frac{F}{h * \pi * d^2/4}, \quad (1)$$

where σ is the push-out stress, F is the applied force, h is the height of the epoxy in contact with the fibre, and d is the fibre diameter.

3. Results and Discussion

Figure 3 shows a cross-sectional image and SEM trace of the 1-1-1-3 hybrid disc.

Kim et al. suggested that a stiff matrix polymer may have the effect of curtailing the piezoelectric properties of rod composite ceramics. To investigate this effect of the epoxy coating (Beckopox EM 2120w/45WA), an epoxy shell interlayer was used to enable free movement of the ferroelectric fibres, thus reducing the blocking or clamping forces that may result from the stiff inactive epoxy matrix [9, 14]. PZT fibres were dip coated with 4 layers of the outer epoxy shell (Beckopox EM 2120w/45WA) to achieve a shell thickness of ~30 μm; electromechanical measurements were carried out to investigate how coating would affect the electromechanical behavior of single fibres (Figure 4). For the epoxide shell thickness of 30 μm on a 800-μm fibre, the fibre volume will be 86.5 vol.%. Based on calculations of Nelson et al., the clamping effect of the polymeric shell can be neglected [11], in agreement with our results.

The graphs in Figure 4 show no significant difference between the ferroelectric results of coated and uncoated fibres. This was confirmed by the small signal data of the coated and uncoated fibres (Table 1).

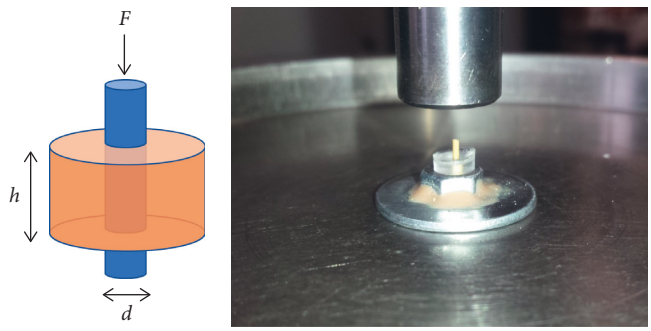
The large and small signal results in Table 1 indicate that the outer epoxy resin coating (Beckopox EM 2120w/45WA) has no significant effect on the electromechanical properties. It is worthwhile mentioning that, with the thickness of such a coating, the fibre content and therefore the active piezoelectric phase in 1–3 fibre-polymer composites can be tailored easily. Due to the reduction in the piezoceramic phase by using shell technology, an added advantage is that the acoustic impedance can be adjusted to the application.

The coating thickness of the various interphase materials (Figure 5(a)) was measured by using an optical microscope. The different soft polymer interlayer materials affected the coating of the epoxide shell. However, a trend between the coating thickness and the fibre content was observed. A thinner coating thickness will result in a higher fibre content in the 1–3 composite.

The thickness of the inner soft polymer materials (PEG 300, stearic acid, two different oils, and paraffin wax) was measured, and it was observed that the coatings were solid at room temperature (i.e., paraffin wax and stearic acid) and required elevated temperatures in order to apply them and displayed some of the highest coating thicknesses. The PEG 300 also displayed a higher coating thickness which relates to its higher viscosity with respect to the oils used in this study. The coating thickness of the oils was quite small (i.e., ~1 μm) likely due to the low viscosity.

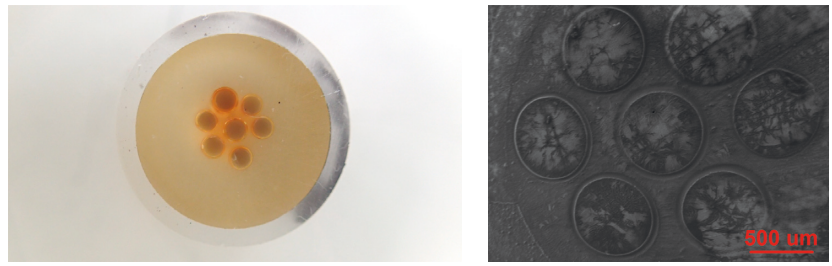
The effect of the soft inner polymer materials (PEG300, stearic acid, two different oils, and paraffin wax) on the relative permittivity of 1-1-1-3 composites was examined by impedance spectroscopy at 1 kHz to make comparisons. The samples named "uncoated" have PZT fibres embedded in the epoxy matrix (1–3 composite), while the samples named "epoxide only" are fibres coated only with the epoxide shell before embedding them into the epoxy matrix (1-1-3 composite).

It is well known that increasing ceramic volume fraction increases the relative permittivity in 1–3 composites [24]. However, in this study, a significant increase in the relative permittivity by coating the fibres with all the soft polymers, except paraffin wax, was observed. Similar results have been reported by Kim et al. where increased coating with a soft polymer on all surfaces of ceramic pillars resulted in a higher dielectric constant [9].



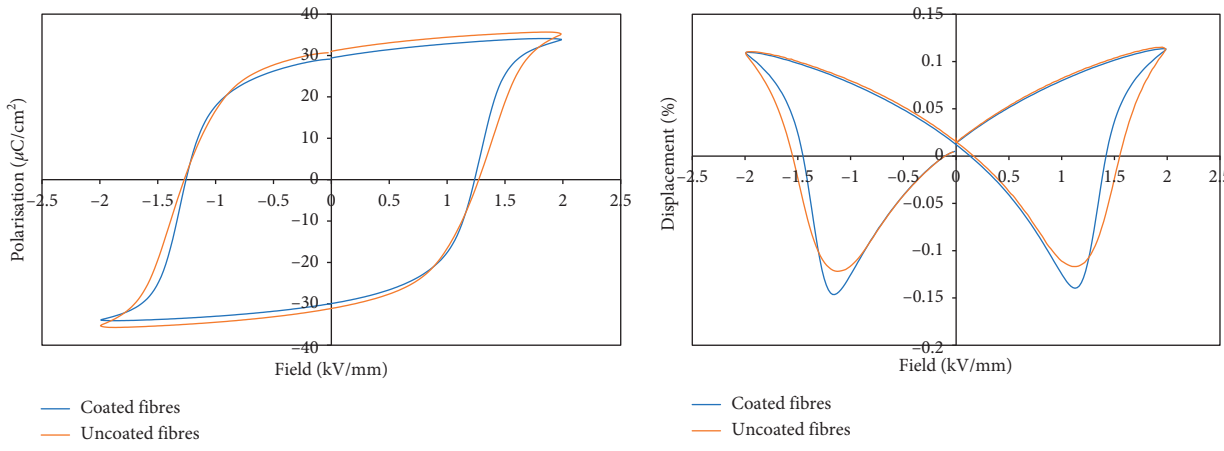
(a) (b)

Figure 2: (a) An illustration of the push-out test sample; h is the thickness of the epoxy resin disc and d is the diameter of the fibre. 10 mm long fibres were embedded into the epoxy disc with a diameter of 10 mm. (b) Mounted sample in the test rig prior to push-out test.



(a) (b)

Figure 3: A cross-sectional (a) image and (b) SEM trace of the 1-1-1-3 hybrid device.



(a) (b)

Figure 4: The average (a) polarization evolution (PE) loop and (b) the strain evolution (SE) loop results from 3 fibres, each tested with no significant differences in the ferroelectric properties between fibres coated with the interlayer polymer (Beckopox EM 2120w/45WA) and the uncoated fibres.

Table 1: (a) The small signal dielectric and piezoelectric data and (b) the large signal ferroelectric data of the coated and uncoated PZT fibres.

	(a)			(b)			
	d_{33} (pC/N)	tanδ (%)	ε_{33}^{T}	E_c (kV/mm)	S (%)	P_{r+} (μC/cm^2)	P_{r-} (μC/cm^2)
Uncoated fibres	**250** ± 9	**10** ± 2	**1315** ± 163	**1.26** ± 0.07	**0.24** ± 0.03	**31** ± 2.0	**-31** ± 2.0
Coated fibres	**239** ± 16	**11** ± 7	**1359** ± 221	**1.24** ± 0.04	**0.27** ± 0.04	**29** ± 1.0	**-30** ± 0.6

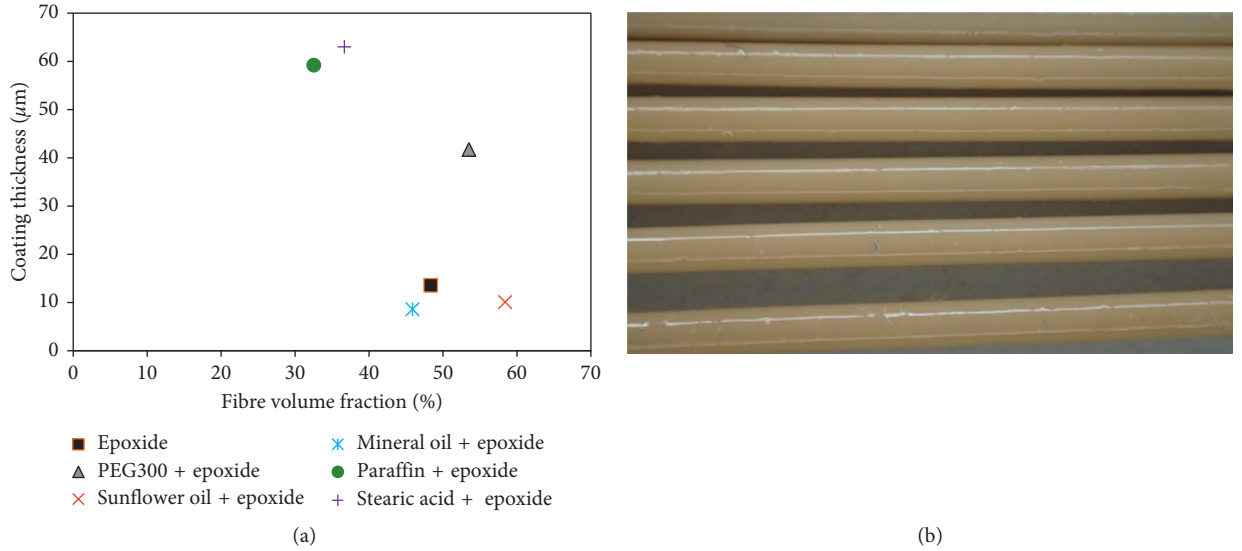


FIGURE 5: (a) The coating thicknesses of the various coatings used and the resultant fibre volume fractions and (b) an image of a homogeneous coating with sunflower oil.

It is recognized that dielectric liquids are often used in high-voltage capacitors to help prevent corona discharge and increase capacitance [25]; thus, a hypothesis for this phenomenon is that the soft polymers being less viscous than the epoxide materials at the time of dip coating are able to better coat the rough surface of the ceramic forming an air-tight coating. This enhances the insulation capability of these materials when compared to the epoxide polymers and thus enabling more capacitive ability within the ceramic, resulting in high relative permittivity. It is worthwhile mentioning that the epoxide shell layer on the 1-1-3 composite also displayed a limited effect on the dielectric constant in comparison to the 1–3 composite (Figure 6).

The electromechanical properties of piezoelectric materials depend on their piezoelectric, dielectric, and elastic constants. The measurement of these constants can be achieved by resonator measurements on specifically shaped and oriented samples, provided the theory for the mode of motion of that sample is known. The measurements involve the determination of the electrical impedance of the resonator as a function of frequency. It is necessary to measure the resonance and antiresonance frequencies (Figure 7), the capacitance, and the dissipation factor away from the resonance range to obtain the information required to find the material constants [26].

Some of the resonance-antiresonance frequency responses in Figure 7 displayed the defects that are contained within the fibres, resulting in several minor peaks and reduced magnitudes of impedance (|Z|) [27].

Using the formula from the IEEE standard on piezoelectricity [26], the electromechanical coupling factor can be obtained from the series resonance frequency (f_s) and the parallel resonance frequency (f_p) measured using impedance spectroscopy:

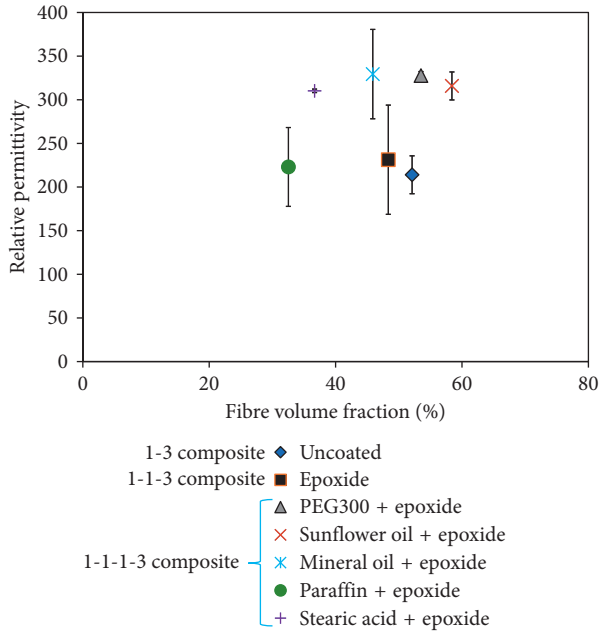


FIGURE 6: The relative permittivity (ε_{33}^{T}) of 1–3, 1-1-3, and 1-1-1-3 PZT-based composite discs against the fibre volume fraction based on Equation (1).

$$k_t^2 = \left(\frac{\pi}{2}\right)\left(\frac{f_m}{f_n}\right)\tan\left[\left(\frac{\pi}{2}\right)\left(\frac{f_n - f_m}{f_n}\right)\right], \quad (2)$$

where k_t^2 is the electromechanical coupling constant in the thickness mode, squared; f_m is the minimum impedance frequency; and f_n is the maximum impedance frequency. The resonance frequency (f_r) which approximates to the series resonance frequency (f_s) which also further

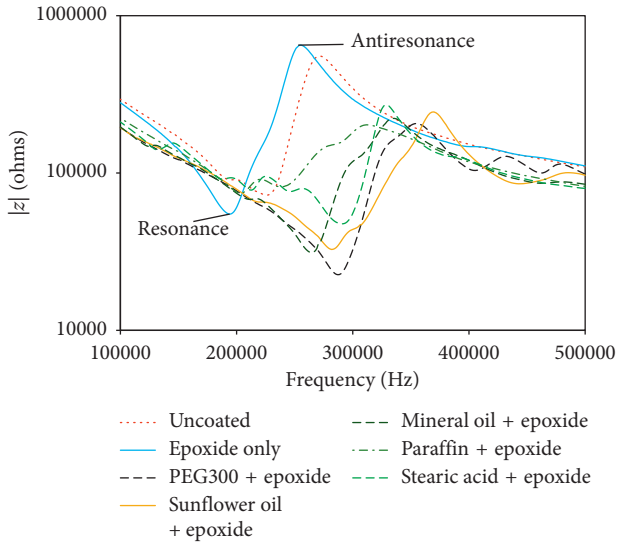


FIGURE 7: The Bode plot of the frequency response of the 1–3, 1-1-3, and 1-1-1-3 PZT-based composite discs.

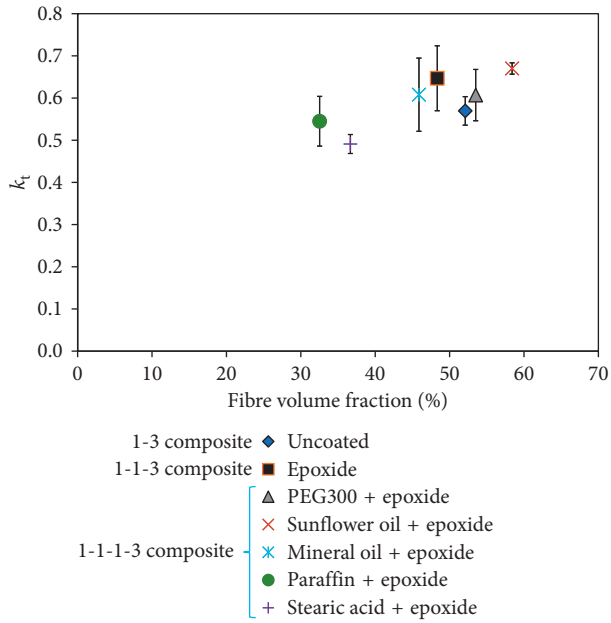


FIGURE 8: The electromechanical coupling factor (k_t) of 1-1-1-3 PZT-based composite discs with fibres dip coated in various soft polymers against the fibre volume fraction.

approximates to f_m was measured and used for the calculation of k_t. Similarly, the antiresonance frequency (f_a) approximates to the parallel resonance frequency (f_p) which also approximates to f_n was used to calculate k_t. Figure 8 shows the average electromechanical coupling factor results for 1-1-1-3 PZT composites.

Based on our results, we can see the effect of the coating on the coupling factor k_t. Generally, we observe an increase in k_t as the fibre volume fraction increased, which has already been reported by Gebhardt et al., Steinhausen et al., and Madhusudana *et al.* [7, 8, 28]. It has been demonstrated by these authors that, between 50 and 65 vol.%, k_t is constant and not effected by the fibre volume fraction.

The k_t results of the soft polymer materials that were solid at room temperature (i.e., paraffin wax and stearic acid) are in good agreement with the values for low fibre volume fraction calculated and analyzed by Madhusudana *et al.* [28]. With the paraffin interlayer, we could achieve a k_t of 0.55 for a composite with 0.33 fibre volume content, which is lower in comparison to the value which has been reported by Gebhardt et al. [7]. The use of mineral oil and PEG 300 (both liquid at room temperature) did not significantly increase the measured k_t, in comparison to 1-1-3 and 1–3 composite. The sunflower oil-based composite disc samples had the highest fibre volume fraction and also allowed the free movement of the ferroelectric fibres reducing the blocking or clamping forces by the inactive epoxy matrix, resulting in a higher k_t [9, 14], with respect to the uncoated samples.

To get a better understanding on the clamping effect on the electromechanical results, a fibre push-out test was used to analyze the strength of the interface between the fibre and the matrix. Figure 9(a) shows the fibre push-out test deformation graph of representative single fibres for different samples. Equation (1) was applied to the measured samples and the fibre push-out stress calculated from the peak force. Figure 9(b) shows the correlation between the fibre push-out stress and the electromechanical coupling factor with the knowledge that the two tests occurred on vastly different energy scales. The soft polymers were expected to lower the interaction of the fibre surface with the epoxy resin matrix which will result in debonding at lower energies when compared to 1-3 and 1-1-3 composite materials.

The epoxide (1-1-3 composite) and the soft coating with PEG300 displayed a stronger clamping effect when compared to the 1-3 composite (i.e., the uncoated fibres). As expected, the other samples displayed lower push-out stress. This is also in contrast to the results of the epoxide resin-coated fibres shown in Figure 4 and Table 1. It seems that the clamping effect is not dominated by the mechanical interaction between the fibre and the matrix, as reported by Nelson et al. [11]. These results confirm Madhusudana *et al.* results that the widely used Smith model [29] has some limitations and does not cover the effective material properties of piezoceramic-polymer composites.

4. Conclusion

PZT fibres were used to fabricate 1-1-1-3 composites which contained PZT fibres coated with a soft polymer layer to provide a physically weak bond and an epoxy shell which reduced the clamping effect of the epoxide matrix. Both interlayers were applied by the dip coating process including thermal crosslinking of the epoxide shell with a layer thickness of ~30 μm. It is worthwhile mentioning that the layer thickness of the epoxide shell can be adjusted to achieve optimal fibre content for the ultrasonic application. As expected, a trend between the coating thickness and the fibre content was observed. A thinner coating thickness will result in a higher fibre content in the 1–3 composite.

The additional soft polymer coatings appeared to insulate the ceramic, enabling higher relative permittivity

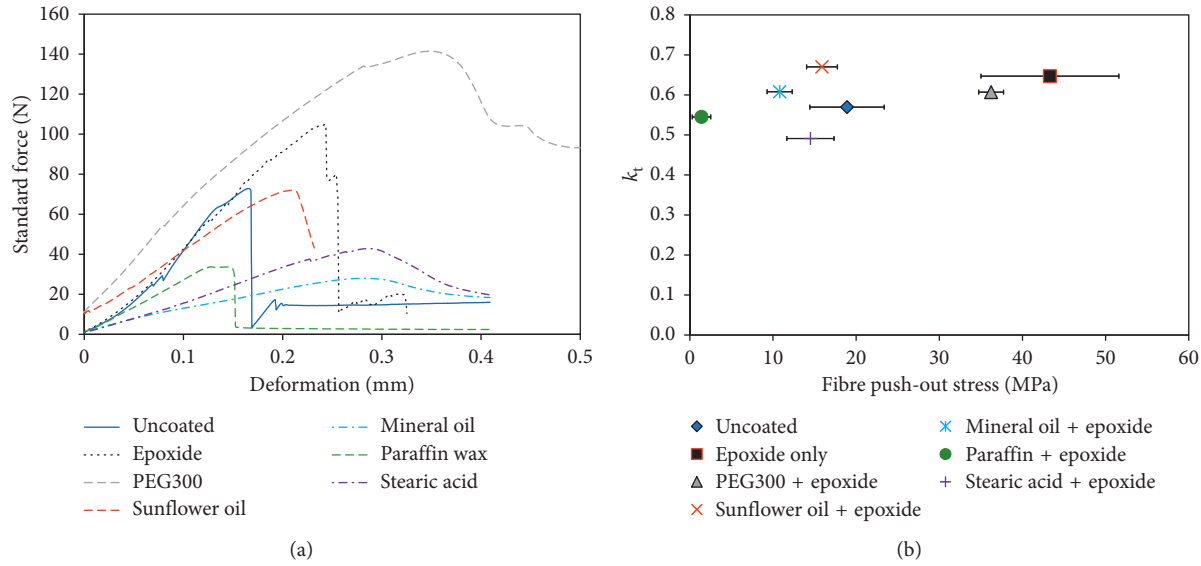


FIGURE 9: (a) The fibre push-out force and deformation graphs for representative single fibres and (b) the fibre push-out test results vs the electromechanical coupling factor (k_t) for the PZT-based composite fibres and discs with fibres dip coated in various soft polymers.

values to be recorded compared to the uncoated fibres in the 1–3 composites. Despite differences in the fibre volume fraction, some coatings had beneficial effects on the electromechanical coupling factor (k_t) compared to uncoated composites. The composite with the sunflower oil coating revealed a coupling factor (k_t) of 0.67.

A significant increase in the relative permittivity by coating the fibres with all the soft polymers, except paraffin wax (with no increase in ceramic quantity), was observed. Relative permittivity over 300 was achieved for fibres coated with mineral oil, sunflower oil, PEG, and stearic acid. An increase in k_t was achieved by designing the surface of the fibres using small organic molecule structures, i.e., sliding agents (e.g., oils). The fibre push-out test displayed the different levels of clamping strength that each coating material had on the fibres. The sample with the paraffin coating reduced the interfacial strength to almost zero. Mineral oil, stearic acid, and sunflower oil reduced the interfacial strength significantly, while PEG coating did not influence the strength. However, this did not correlate with k_t as this was mainly affected by additional factors.

Our paper shows that coating of fibres for 1-1-1-3 composites is important and significantly influences the electromechanical and dielectric properties. The fibre composites with a thin layer of sunflower oil showed promising changes compared to the composites with uncoated fibres.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

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