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PAPER

The effect of the intrinsic electrical matrix conductivity on the piezoelectric charge constant of piezoelectric composites

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Abstract

Polymer-piezoceramic composites have drawn a lot of attention for sensor and energy harvesting applications. Poling such materials can be difficult due to the electric field getting mostly distributed over the low dielectric constant matrix. During this process, the electrical matrix conductivity plays a vital role. This work shows how two different polymer materials, loaded with various piezoelectric ceramic fillers, have very different poling efficiencies simply due to their intrinsic matrix conductivity. It is shown how temperature increases the matrix conductivity, and hence, increases the piezoelectric charge constant of the composites. By choosing the proper matrix material under the proper conditions, piezoelectric composites can be poled at electric fields as low as 2 kV mm^{-1}, which is identical to that of bulk ceramic fillers. In addition, the matrix conductivity can be altered by aging the composites in a high humidity atmosphere, which can increase the piezoelectric charge constant in similar fashion. This is a simple method to increase the matrix conductivity, and hence the piezoelectric charge constant, without the need to add any conductive fillers into the composites, which increase complexity, and leads to an increased dielectric losses.

1. Introduction

Piezoelectric materials have the ability to convert mechanical energy into electrical energy, and vice versa. Because of this, these materials can act as actuators, sensors and energy harvesters [1–4]. It is therefore no surprise that these materials have drawn a lot of attention from researches in the field of smart sensors and renewable energy. Popular piezoelectric materials, due to their excellent values for the piezoelectric constants, are inorganic ceramics, such as the widely used lead zirconate titanate (PZT). However, these ceramics contain the substance Pb, and are therefore classified as a Substance of Very High Concern (SVHC) according to the European Community REACH regulation 1907/2006/EEC. Therefore, research is performed to find lead-free alternatives [5, 6]. Another drawback of these ceramic materials is their brittleness, which makes them susceptible to mechanical failure under large cyclic strains. This promotes the research into piezoelectric polymers, such as poly(vinylidine-fluoride) PVDF and its copolymers [7]. However, these have other disadvantages such as a limited curie temperature, T_c, high coercive field, and limited piezoelectric constants.

Piezoelectric composites combine a polymeric matrix with a piezoelectric ceramic filler [8–10]. The polymer matrix yields the mechanical flexibility, while the piezoelectric ceramic filler provides the piezoelectric effect. Since only a portion of the total volume fraction is the piezoelectric active filler, the piezoelectric charge constant, d_{33}, is generally lower compared to that of ceramics. Since d_{33} is accepted to be the figure of merit for actuator applications, composite actuators have a difficult time competing with ceramics. For sensor applications, on the other hand, the figure of merit is d_{33}/ε, where ε is the absolute dielectric constant, or permittivity. Here, composites have shown to have the upper hand due to their low value of ε [11–13]. For energy harvesting, with the figure of merit being ${d_{33}}^2/\varepsilon$, recent studies have shown that composites and ceramics can perform equally well [14, 15]. The composite systems referred to here are both highly flexible and lead-free. Their high piezoelectric constants are obtained due to the connectivity of the ceramic particles in the direction of applied stress.

An important parameter influencing the composite properties, is the choice of matrix and filler materials. To discuss the effect of various matrix and filler materials, random particulate composites are considered. These composites consist of isolated piezoelectric active particles embedded in a continuous polymer matrix. They are therefore also referred to as 0–3 composites, since the filler is continuous in zero dimensions while the matrix is in all three [16]. These have been investigated for a while already, and countless models have been proposed for modelling their piezoelectric constants [17]. Although the models can vary from one to another quite a lot, the general trends are agreed upon:

(i) By increasing the volume fraction of the filler, φ, both ε and d_{33} of the composite increase.

(ii) Increasing the bulk dielectric constant of the filler, ε_f, generally does not increase the ε of the composite. Note that this only applies to the case where ε_f is far greater than the dielectric constant of the matrix, ε_m, which in this field is nearly always true. Therefore, ε of the composite is dominated by ε_m.

(iii) The d_{33} of the composite depends on the mismatch between ε_m and ε_f. The smaller the mismatch, although it is generally rather large, the higher the d_{33} of the composite.

These three statements are true assuming that the piezoelectric composites are fully poled. However, poling these kind of composites can be tricky, since most of the applied electric field gets lost in the polymer matrix. Therefore, another important parameter to consider is the matrix conductivity, σ_m.

Earlier work has already shown that the matrix conductivity plays an important role [10]. Increasing the matrix conductivity does not increase the maximum achievable d_{33}, but does decrease the electric field required to fully pole the piezoelectric composites. Various studies have shown that by adding a third conductive phase into the polymer matrix this required electric field indeed decreases [10, 18, 19]. However, by introducing a conductive phase into the composites, the dielectric loss, $\tan(\delta)$, typically increases. Therefore, ideally, one would gain the benefit of the increased matrix conductivity only during poling, while during operation the matrix conductivity is low again, maintaining a low dielectric loss. This can be achieved by considering the conductivity of polymers at elevated temperatures. Generally, the conductivity of polymers increases with increasing temperature, although the exact magnitude strongly depends on the chosen polymer system.

In this work, two different polymers are chosen to act as matrix materials in piezoelectric composites, being an epoxy and a polyurethane (PU) polymer. The two polymers have a nearly identical value of ε_m, meaning that, when making piezoelectric composites out of them, their maximum value of d_{33} is nearly identical as well. Both have increased conductivity at elevated temperatures, although to a different extent. It is shown that the higher conductivity polymer reaches its maximum d_{33} already at low electric fields, while the other one does not reach it at all. To make sure that this phenomenon is matrix material independent, three different filler materials are embedded in the polymers, yielding six different composite systems. The filler materials used are $BaTiO_3$ (BT), $K_{0.485}Na_{0.485}Li_{0.03}NbO3$ (KNLN) and PZT-5A4 (PZT). The obtained d_{33} values are compared to Jayasundere's model [20, 21]. This model is chosen because it includes both the dielectric constant and the piezoelectric charge constant, does not have any supposed fitting parameters, and includes interactions between neighboring particles. The following equations are used to calculate Jayasundere's ε and d_{33}:

$$\varepsilon = \frac{\varepsilon_m(1-\varphi) + \varepsilon_f\gamma}{(1-\varphi)+\gamma} \tag{1}$$

$$\gamma = \frac{3\varepsilon_m\varphi}{2\varepsilon_m + \varepsilon_f}\left(1 + 3\varphi\frac{\varepsilon_f - \varepsilon_m}{2\varepsilon_m + \varepsilon_f}\right) \tag{2}$$

$$d_{33} = \left(1 + \frac{3\varphi\varepsilon_f}{2\varepsilon_m + \varepsilon_f}\right)\frac{\varepsilon}{\varepsilon_f}d_{33f} \tag{3}$$

In here, φ is the filler volume fraction and d_{33f} is the d_{33} of the filler material.

2. Fabrication of 0–3 particulate composites

The starting powders are fine $BaTiO_3$ (BT) (obtained from Sigma Aldrich), pre-calcined $K_{0.485}Na_{0.485}Li_{0.03}NbO3$ (KNLN) (obtained from CeramTec, Ruabon, UK) and green PZT-5A4 (PZT) (obtained from CeramTec, Ruabon, UK). All the powders are calcined to obtain single phase materials. The BT is calcined at 900 °C for 2 h (heating rate of 2 °C $\min^{-1}$), the KNLN at 925 °C for 10 h (heating rate of 1 °C $\min^{-1}$) and the PZT at 1150 °C for 1 h (heating rate of 2 °C $\min^{-1}$) [13, 22]. After calcination, the powders are milled in a

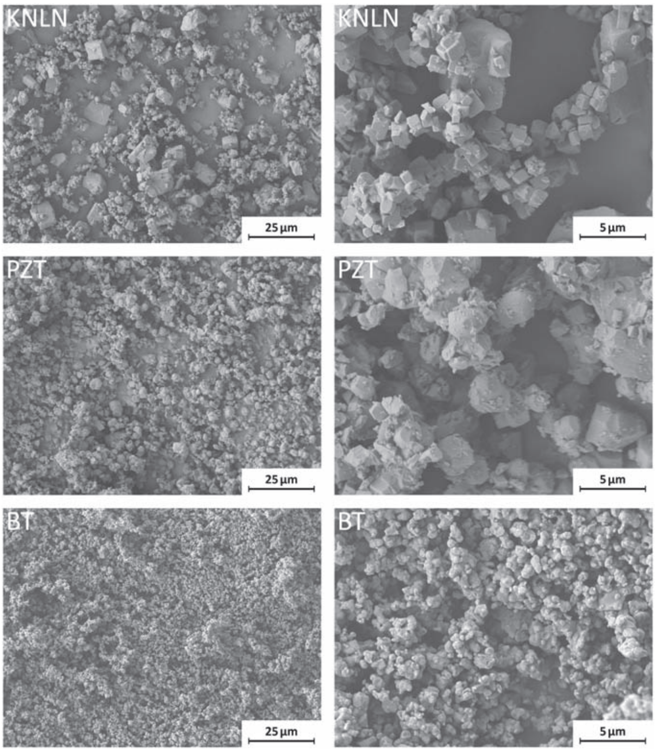

Figure 1. SEM micrographs of calcined KNLN particles, PZT particles and BT particles, at a 1000× (left) and 5000× (right) magnification.

Table 1. Filler and matrix material properties.

Material	Function	ε [−]	d_{33}[pC N^{-1}]	Reference
KNLN	Filler	360	125	[23, 24]
PZT	Filler	1850	460	[25]
BT	Filler	1800	190	[4]
Epoxy	Matrix	3.4	—	[26]
PU	Matrix	3.3	—	[27]

planetary ball mill (Retsch PM100, Aartselaar, Belgium) for 1 h at 150 rpm using 10 mm yttria-stabilized ZrO_2 balls immersed in cyclohexane. Finally, the powder is dried in a furnace. From scanning electron microscope (SEM) (JEOL, JSM-7500F, Nieuw Vennep, the Netherlands) micrographs, shown in figure 1, an estimate of the particle size is made. The BT particles are slightly smaller, while the PZT are slightly bigger, and KNLN has a couple of big particles. All filler particles are in the range of 0.5–5.0 μm. Typical properties of the powders involved are shown in table 1.

All three types of filler particles are mixed into epoxy (Epotek epoxy 302–3 M, Epoxy Technology Inc.) and PU (Crystal Clear 202, Smooth-on Inc.), yielding six different types of composite systems. The nearly identical value of ε_m of the two polymer matrices are given in table 1 as well. The nearly identical value is chosen on purpose, to make sure that their theoretical maximum value of d_{33}, after making composites out of them, is nearly identical as well. The filler particles are added to the polymer matrix in various volume fractions (30, 40, 50 and 60 vol%) and mixed using a planetary speed mixer (DAC 150 FVZ, Hauschild, Germany). In order to fabricate disk shaped composite pellets, the obtained mixture is poured into prefabricated holes punched into a Teflon sheet. Note that the higher volume fraction mixtures do not flow, and therefore could not be poured. These are forced in the holes using a spatula instead. The Teflon sheet is covered on both sides with two other Teflon sheets, without any punched holes, and clamped between two steel plates. While being clamped, the composite slurries are cured at 120 °C for 2 h. This temperature is slightly higher compared to the manufacturer's recommended curing temperature to prevent any ageing or further curing effects during the poling process. Nine composites are manufactured per materials set. However, due to the high volume fraction composites being more difficult to successfully produce, some break during processing. Due to this, at least five out of the nine samples produced were successfully measured.

After curing, gold electrodes are sputtered through a shadow mask on both sides of the composites with a sputter coater (Quorum Q300T, East Sussex, UK). The final step is poling, which provides the composites with their piezoelectric charge constant. Poling is performed in a silicon oil bath, providing control over poling field, time and temperature. The applied electric field is chosen to be as high as possible while having the lowest possible chance of getting short circuits, ruining the samples. The DC electric field is therefore set to 8.5, 8.0, 7.5 and 7.0 kV mm^{-1} for the 30, 40, 50 and 60 vol% composites, respectively. As for the poling time, it has been shown before that only relatively short periods are required to successfully pole composites [15, 28]. Therefore, all composites are poled for only 5 min. The maximum temperature to pole at is the minimum of the following three temperatures: the T_c of the ceramic filler, the temperature at which the polymer matrix starts to be too conductive, and the temperature at which the polymer matrix starts to degrade. Both the epoxy and PU matrix are able to withstand temperatures of over 150 °C. However, at temperature above 120 °C epoxy starts to become too conductive. This means that at temperatures above 120 °C a relatively high current starts to flow through the sample, which will significantly reduce the poling efficiency, and potentially destroys the samples. Therefore, the poling temperature is set to this maximum of 120 °C. In addition, the BT filler particles have a T_c of 120 °C. Poling near the T_c requires the electric field to stay applied until the temperature has dropped to at least half the T_c to prevent depolarization from occurring. Therefore, for all BT composites, after the 5 min of poling time at 120 °C, the temperature is lowered to below 50 °C before the electric field is switched off.

The composites are aged for at least 24 h at room temperature after poling before measuring the piezoelectric constants. The piezoelectric charge constant, d_{33}, is measured with a Berlincourt-type piezometer on poled capacitors (PM300, Piezotest, London, UK). Rounded anvils are used with a radius of 16 mm. A static force of 10 N is applied, under a 0.25 N peak-to-peak sinusoidal excitation at 110 Hz. We note that the extracted value of d_{33} depends on the boundary conditions, such as the sample aspect ratio [29]. Here all measurements have been performed under identical conditions using 1 mm thick piezoelectric disks with a radius of 12 mm. Therefore the extracted values of d_{33} can be directly compared, resulting in a reliable material comparison. The capacitance and dielectric loss are measured at 1 kHz and 1 V with a LCR meter (Agilent 4263B, Santa Clara, CA, USA). The relative dielectric constant, ε_r, measured under zero stress, was derived from the capacitance. The density of the composites is measured using an Archimedes setup, using distilled water as the liquid medium. The conductivity of the composites and polymer matrix materials is measured using a Broadband Dielectric Spectrometer (BDS) (Novocontrol Alpha Analyzer, Montabaur, Germany). Finally, the polarization is also measured using hysteresis measurements (Radiant Precision RT66c, Albuquerque, USA).

3. Results and discussion

3.1. Dielectric constant

The relative dielectric constant of the composites, ε_r, is measured as a function of volume fraction, matrix material and filler material. The results are shown in figure 2. The epoxy composites are given in blue (figure 2(a)), while the PU composites are given in red (figure 2(b)). Meanwhile, the three different fillers are given in different shades of blue and red, with different symbols. Jayasundere's model is included with the dashed lines. Note that only two dashed lines are visible since two of them, the PZT and BT line, closely overlap each other. This happens due to their similar value of ε_f.

From the figure it can be seen that, in general, the experimental values get near the theoretical prediction. This is especially true or PZT (square data points), which almost perfectly fits the curve. This can be attributed to the homogenous particle size, as shown in figure 1. In the case of KNLN, the experimental data is slightly higher compared to the predicted curve. Again consulting figure 1, this can be explained due to the few larger particles, slightly increasing the dielectric constant. Finally, in the case of BT, the experimental values are clearly higher than predicted, by about a factor of two. Again, this can be explained by considering their particle size. Figure 1 shows slightly smaller particles for BT. Smaller particles are more susceptible to static attractions, which in turn agglomerates the particles in the polymer matrix. These agglomerations can increase the dielectric constant, likely due to the lower amount of filler-matrix interfaces. It can also be seen from the experimental data that at a volume fraction of 60% the dielectric constant of the BT composites suddenly decreases. Due to the agglomerations, it is harder to achieve fully dense composites at higher volume fractions. This is confirmed from the composites densities measured using Archimedes principle, shown in figure 3. In all cases the density is lower at a volume fraction of 60%, although the extent of this is clearly more profound for the BT composites. This decreased density has a serious impact on the dielectric constant.

From figure 2, it can be confirmed that ε_r is independent of ε_f, which is agreed upon by various analytical dielectric models [17]. It is therefore concluded that, for the composites with good homogeneity, the experimental data fits Jayasundere's model almost perfectly.

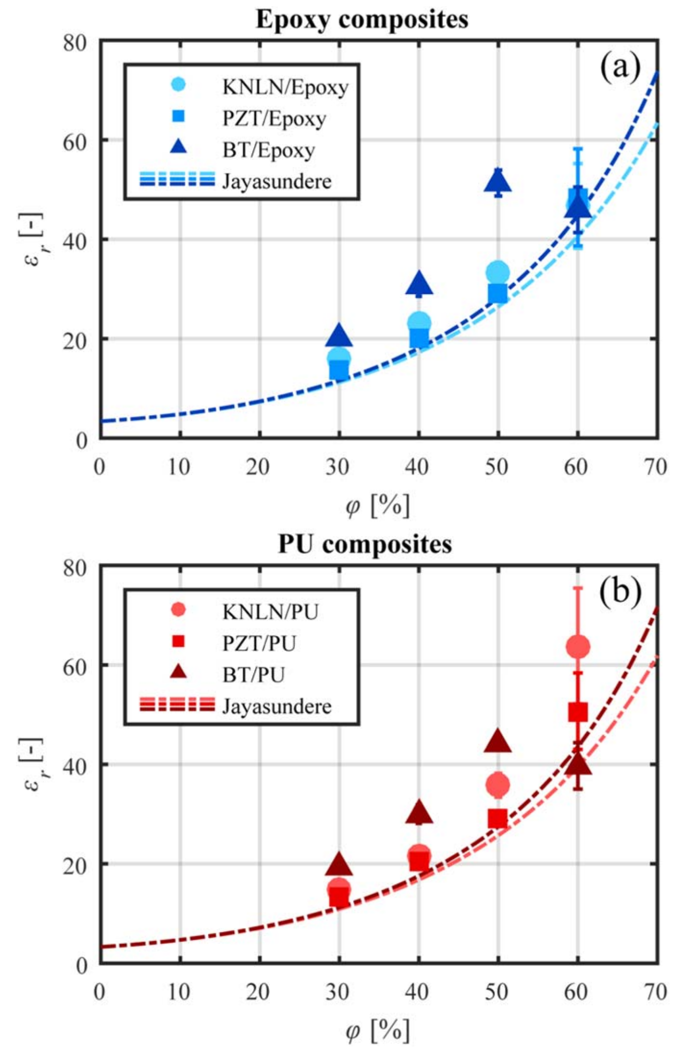

Figure 2. Composite relative dielectric constant, ε_r, versus filler volume fraction, φ, of (a) epoxy composites and (b) PU composites. The three different filler materials, KNLN, PZT and BT, are given in different shades of blue and red, with different symbols. The dashed lines are obtained from Jayasundere's model. Note that only two dashed lines are visible since two of them, the PZT and BT line, closely overlap each other. This happens due to their similar value of ε_f.

3.2. Piezoelectric charge constant

The piezoelectric charge constants of the composites, d_{33}, is measured as a function of volume fraction, matrix material and filler material. The results are shown in figure 4. The epoxy composites are given in blue (figure 4(a)), while the PU composites are given in red (figure 4(b)). Meanwhile, the three different fillers are given in different shades of blue and red, with different symbols. Jayasundere's model is included with the dashed lines.

The first thing to notice from figure 4 is that the predicted trends are correct; KNLN composites indeed have the highest d_{33} values, followed by the PZT composites, while the BT composites have the lowest d_{33}. This is agreed upon by Jayasundere's model, and can simply be explained by the better d_{33f}/ε_f values of the ceramic filler materials, which are 0.35, 0.25 and 0.11 for KNLN, PZT and BT, respectively. Taking a closer look at figure 4(a), it can be seen that the experimental data of the epoxy composites generally lies quite close to Jayasundere's prediction. This is especially true for a volume fraction of 40%–50%. At lower volume fractions Jayasundere slightly underestimates, while at higher volume fractions it overestimates. The overestimation at higher volume fractions can be caused due to the decreasing density trend with increasing volume fraction, as was shown earlier on in figure 3. Taking a look at the PU composites, shown in figure 4(b), a completely different behavior is observed. Since ε_m of epoxy and PU is almost identical, the d_{33} of the composites should be identical as well. Still, in all cases, the experimental d_{33} values of the PU composites are lower than that predicted by Jayasundere's model. Still the same trends are observed as is seen with epoxy composites, just with lower d_{33} values.

To understand why PU composites have a lower d_{33}, a more detailed poling study is performed, measuring the d_{33} of the composites versus the DC electric poling field. All composites are poled at 120 °C for 5 min. Only the BT composites, due to the low T_c of the ceramic filler, are cooled down to below 50 °C before the electric field

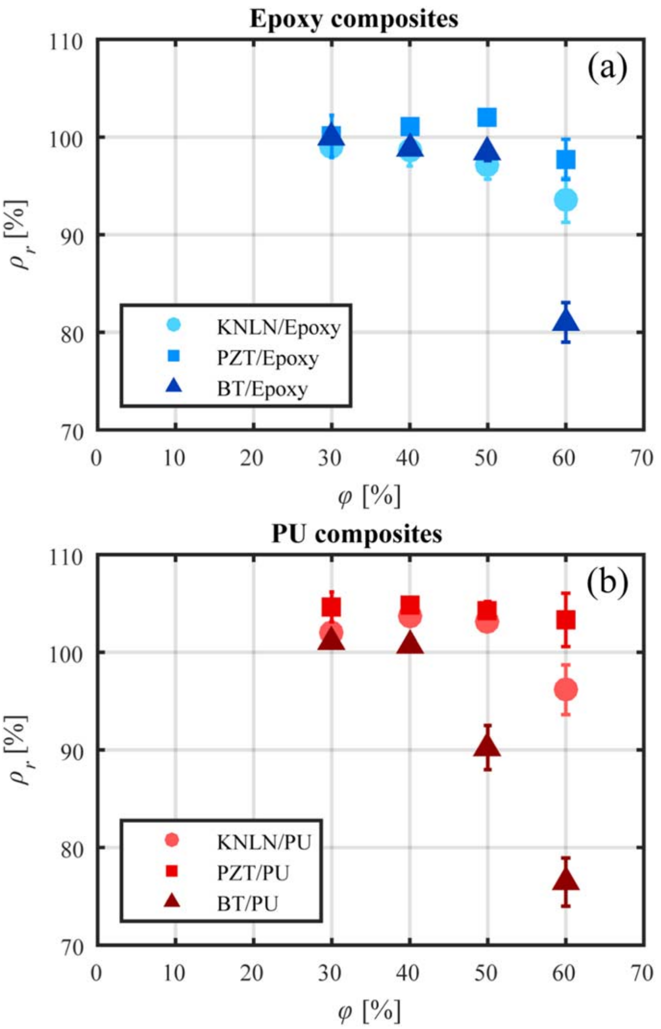

Figure 3. Composite relative density, ρ_r, versus filler volume fraction, φ, of (a) epoxy composites and (b) PU composites. The three different filler materials, KNLN, PZT and BT, are given in different shades of blue and red, with different symbols.

is removed. The electric field is varied from 1 to 8 kV mm^{-1}. The results are shown in figure 5. In all cases, at 1 kV mm^{-1} no d_{33} is found, which makes sense since this is not enough to pole the ceramic fillers themselves. All epoxy composites, shown in figure 5(a), show a plateau at higher voltages, meaning the maximum possible d_{33} is achieved for these composites. In the case of PU however, shown in figure 5(b), none of the composites seem to reach their maximum value. This seems to indicate, that by simply increasing the electric field more, their maximum would be reached. This theoretical maximum of the PU composites, should, according to Jayasundere's model, have similar values to the epoxy composites. However, in this case it proved to be difficult to reach higher fields, since above 8 kV mm^{-1} the composites suffered from dielectric breakdown. Therefore, no results above this voltage can be shown here.

It has been shown before, that to reduce the required voltage to fully pole piezoelectric composites, one could increase the conductivity of the matrix material [10]. Therefore, the conductivity of the matrix materials is measured using BDS. The results are shown in figure 6. Since poling is performed with a DC electric field, the bulk DC conductivity needs to be determined. Normally, the AC conductivity decreases as frequency decreases, and finally reaches a plateau at low frequencies. This plateau can be considered as the DC conductivity [30]. At room temperature, no such plateau is observed. The AC conductivities of both the epoxy and PU matrix look nearly identical. At the poling temperature, however, both matrix materials do show the DC conductivity plateau. Here it can be seen that epoxy reaches a DC conductivity which is two orders of magnitude larger than PU. This explains why the epoxy composites pole at much lower voltages compared to the PU composites.

3.3. Hysteresis loop measurements

To validate the d_{33} values obtained through the conventional DC contact poling, polarization hysteresis measurements have been performed on the composites. The results are shown in figure 7, where once again all the epoxy composites are given in blue, while all PU composites are given in red. All the measurements are

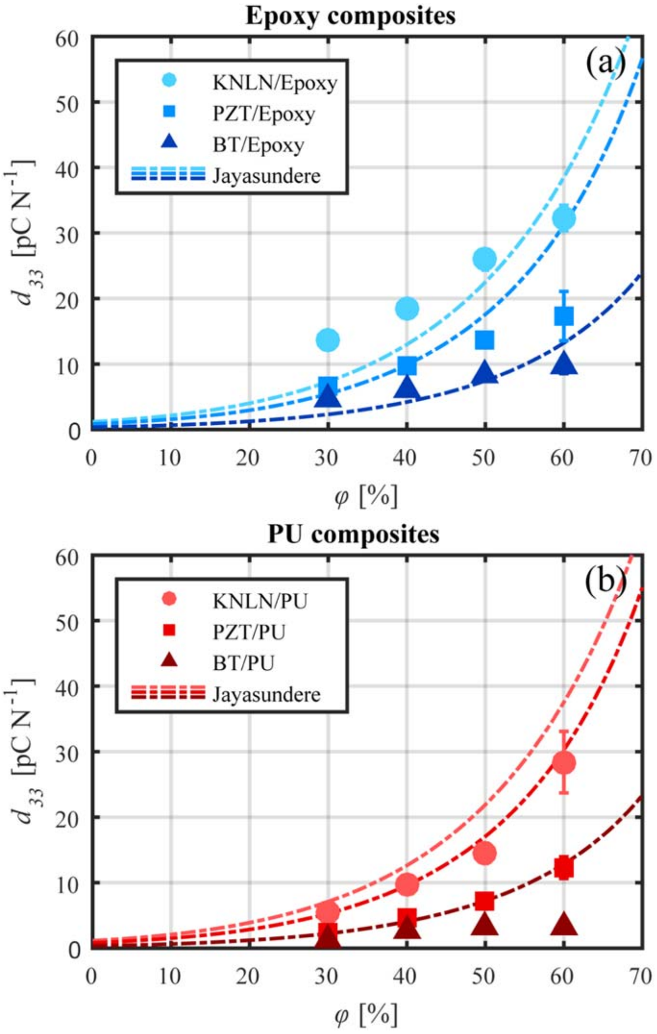

Figure 4. Composite piezoelectric charge constant, d_{33}, versus filler volume fraction, φ, of (a) epoxy composites and (b) PU composites. The three different filler materials, KNLN, PZT and BT, are given in different shades of blue and red, with different symbols. The dashed lines are obtained from Jayasundere's model.

performed at the same temperature as the conventional DC contact poling of 120 °C. The same trends are obtained, giving higher polarizations for epoxy composites over PU composites, and higher polarizations for KNLN over PZT and BT. The main difference between conventional DC contact poling and the hysteresis measurements is time. Where the conventional method lasted for 5 min, the total hysteresis time is in the order of seconds, or even less, depending on the frequency. Generally, longer times give higher polarization values. However, from this figure it is hard to judge whether the polarization actually increases, since the loops show a high leakage current at low frequencies.

To understand the nature of the leakiness, hysteresis measurements of a PZT-5A4 ceramic disk are considered, shown in figure 8. Here it can be seen, that by decreasing the frequency from 30 to 3 Hz, a big increase in polarization is observed. Decreasing it further to about 1 Hz, does not increase the polarization any further. This means that there is a minimum amount of time required for the dipoles to align. When this time is reached, all dipoles have aligned, and maximum polarization has been reached. Here, however, the loop does not become leaky, as was seen with the composites. This can be explained by considering the equivalent circuit diagram of a piezoelectric material which is exposed to an AC electric field, as shown in figure 9(a). When the frequency decreases, the impedance, Z, increases. Meanwhile, the resistance, R, which is frequency independent, stays the same. Since the applied voltage chooses the path of least resistance, the electric field starts to run more through the resistor R as the frequency continues to decrease. This means that the piezoelectric material starts to exhibit more resistive losses. A typical resistor loop is shown in figure 9(b), showing a very leaky loop. If the electric field runs mostly through the capacitor Z, a ferroelectric loop will be measured, with its typical shape also shown in figure 9(b). Now PZT-5A4, as shown in figure 8, does not show a leaky loop at low frequencies due to its higher capacitance. Generally, the capacitance of ceramics is about one or two orders of magnitude higher

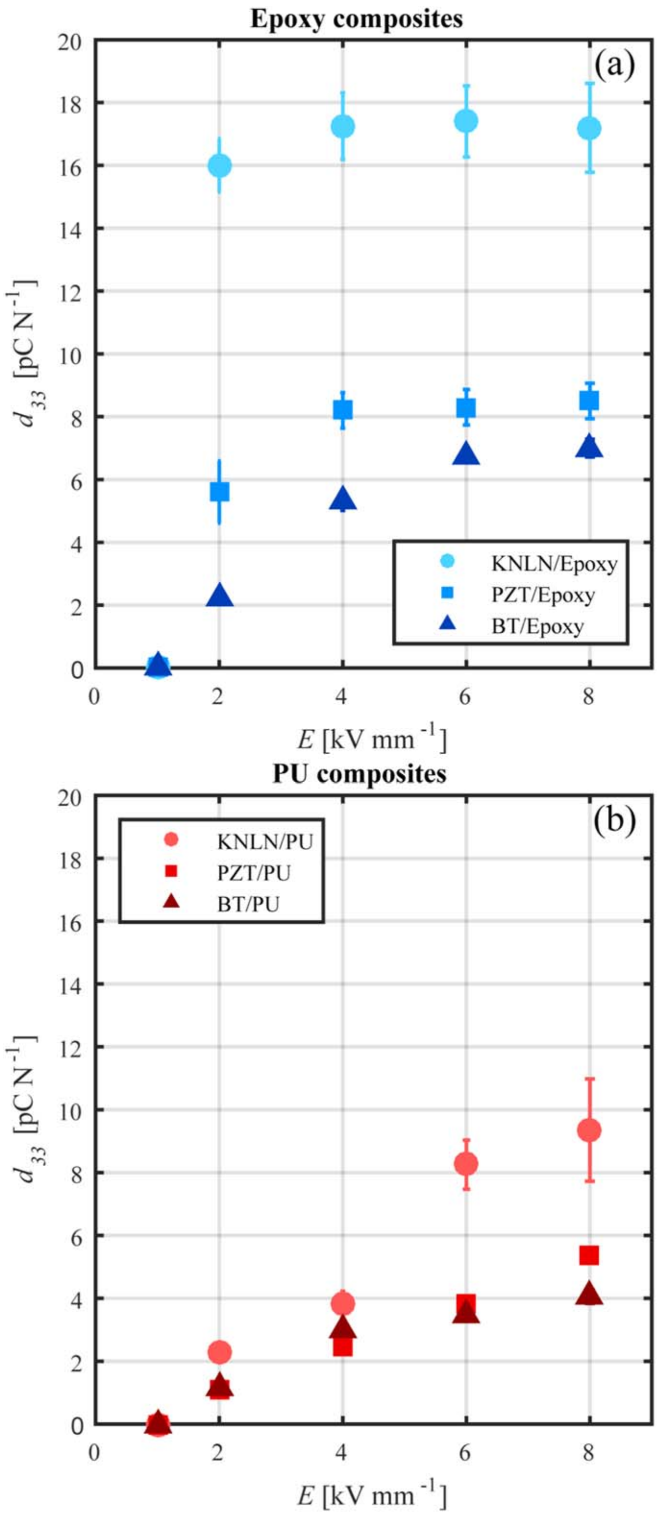

Figure 5. Composite piezoelectric charge constant, d_{33}, versus DC electric poling field, E, of (a) epoxy composites and (b) PU composites. All composites are poled for 5 min at 120 °C. Due to its low T_c, only the BT composites are cooled down to below 50 °C before the poling field is removed. The three different filler materials, KNLN, PZT and BT, are given in different shades of blue and red, with different symbols.

compared to composites, meaning that Z will be one or two orders of magnitude lower. Therefore, the frequency at which composites start to show leaky loops is also orders of magnitude higher compared to ceramics.

Due to this issue, it becomes clear that it is challenging to accurately measure the polarization of composites such as the ones shown in this work. On the one hand one needs longer times, or lower frequencies, in order to reach the threshold at which all the dipoles had enough time to polarize. On the other hand, one needs high

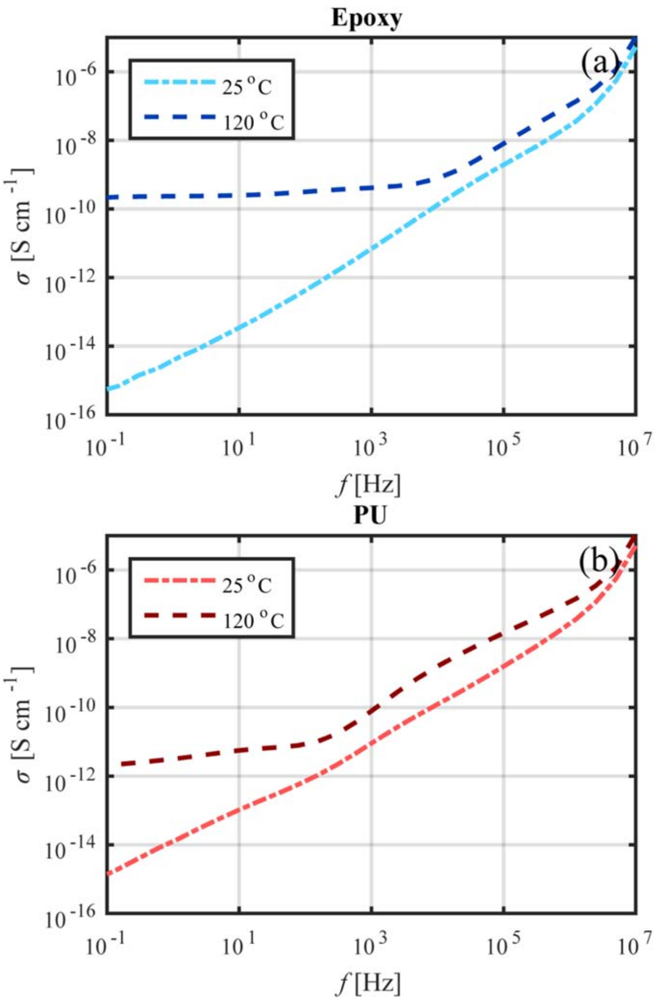

Figure 6. Polymer matrix conductivity, σ, as a function of frequency, *f*, for the (a) epoxy matrix and (b) PU matrix. Measurements are both performed at room temperature and the poling temperature of 120 °C.

frequencies, or shorter times, to prevent the applied electric field from leaking away in the resistive part of the material.

An estimation of the corresponding d_{33} to the hysteresis loops can be made using figure 8. The remnant polarization of the PZT is about 30 μC N^{-1}, which results in a d_{33} of about 400 pC N^{-1}. Applying this to the PZT/epoxy and PZT/PU composites from figures 7(c) and (d), the remnant polarizations of about 1.5 and 0.5 μC N^{-1}, obtained from the 30 Hz non-leaky loop, scale to a d_{33} of about 20 and 7 pC N^{-1}, respectively. Comparing this to the actual d_{33} values given in figure 4, the PZT/epoxy composites have a slightly lower d_{33} while the PZT/PU composites have exactly the same as is estimated from the hysteresis measurements. This means that the 30 Hz polarization measurements appear to be quite correct.

3.4. The effect of humidity

A well-known problem of the KNN based system, is its moisture sensitivity [23]. Absorbed moisture in this ceramic filler causes the dielectric loss, tan(δ), to increase rapidly, making it problematic to use this piezoelectric ceramic in applications. A polymer matrix around the ceramic filler can solve, or mitigate, this issue. Using BDS, the dielectric loss of KNLN/Epoxy and KNLN/PU composites is measured versus aging time after drying the samples in a furnace at 100 °C for 2 h. The aging itself is simply performed in laboratory conditions, which generally means a humidity of about 40%–60%, and a temperature of about 22 °C. The results are presented in figure 10. As a comparison, the grey lines indicate bulk KNLN ceramic. It can be seen that epoxy protects the KNLN quite well, while the tan(δ) of the KNLN/PU composite is almost identical to that of bulk KNLN after one week of aging. This indicates that the PU matrix is able to absorb moisture, while epoxy barely does so, even after one year of time.

Although the moisture absorbing capabilities of the PU matrix is a clear disadvantage when using KNLN as a filler material, when using another filler such as PZT it becomes a completely different story. PZT is not moisture

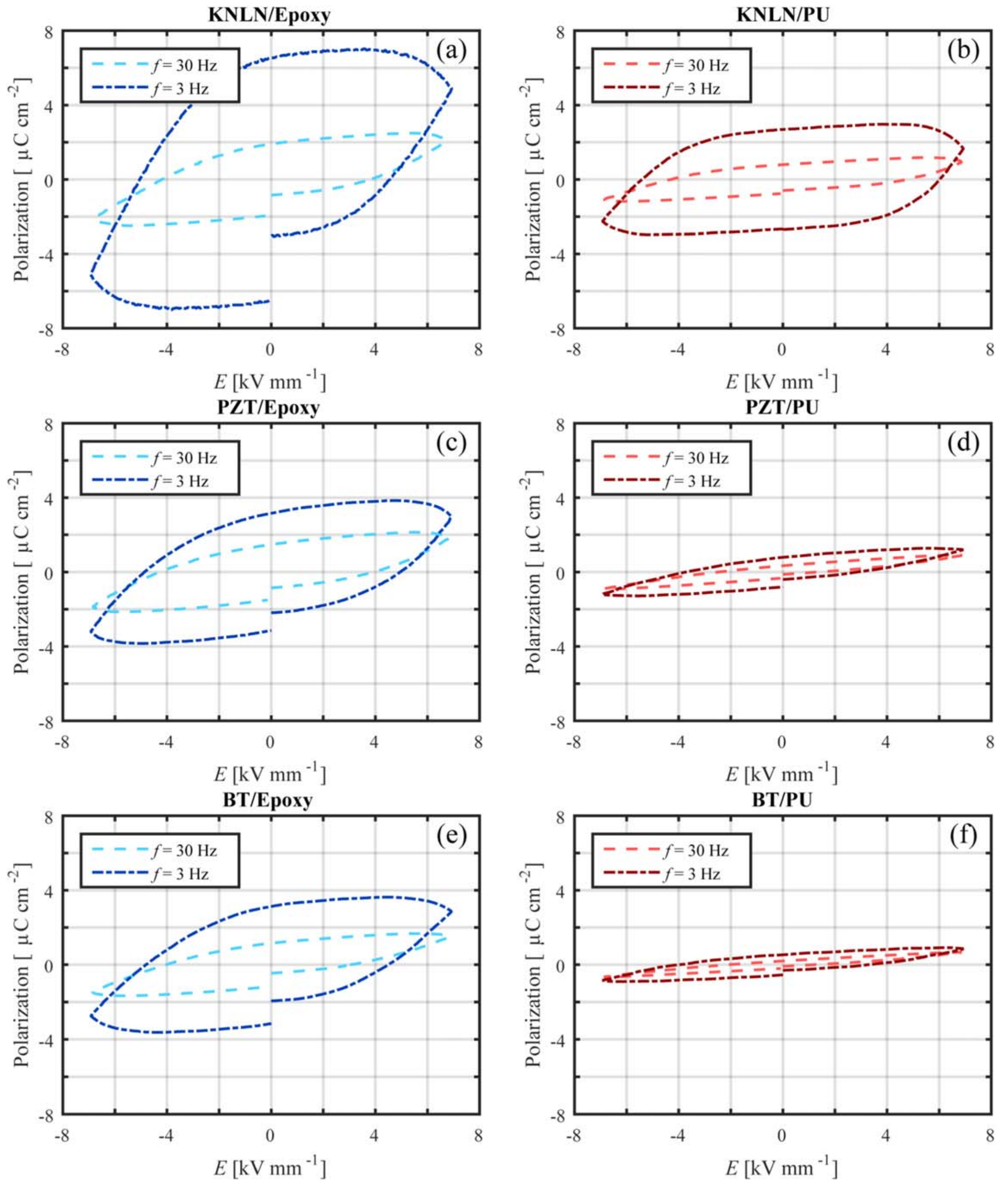

Figure 7. Hysteresis loops of (a) KNLN/epoxy, (b) KNLN/PU, (c) PZT/epoxy, (d) PZT/PU, (e) BT/epoxy and f) BT/PU composites, all containing 50 volume percent ceramic filler, varying the applied AC electric field frequency. All measurements are performed at the poling temperature of 120 °C.

sensitive, and therefore does not suffer the consequences KNLN does when in contact with a humid matrix. Actually, in the case of PZT, it turns out that the humidity sensitivity of PU can be used to our advantage. By increasing the humidity of the matrix, the matrix conductivity increases. To see the extent of this increased conductivity, the conductivity of PZT/Epoxy and PZT/PU composites is measured at ambient conditions, including a measurement where the PZT/PU is aged in a high humidity (humidity of about 90%) atmosphere for a week. The results are shown in figure 11. From figure 11(b) it can be seen that at room temperature, the difference in conductivity between the ambient and high humidity aged PZT/PU composites is barely noticeable. At the poling temperature, however, almost one order of magnitude increased conductivity is found. Comparing to figure 11(a), the conductivity is still one order of magnitude lower than that of PZT/Epoxy. Still, this increased humidity in PZT/PU, which in turn increases the conductivity, could increase the poling efficiency, and therefore, the composite its d_{33}.

After aging the PZT/PU composites for a week in different humidity environments, they are poled using the same poling parameters as before, being a DC electric field of 8 kV mm^{-1}, for 5 min time, at 120 °C. The

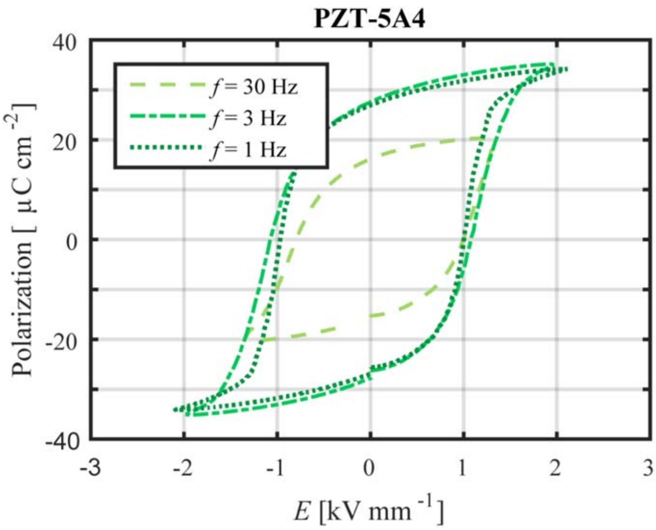

Figure 8. Hysteresis loop of PZT-5A4 ceramics, varying the applied AC electric field frequency.

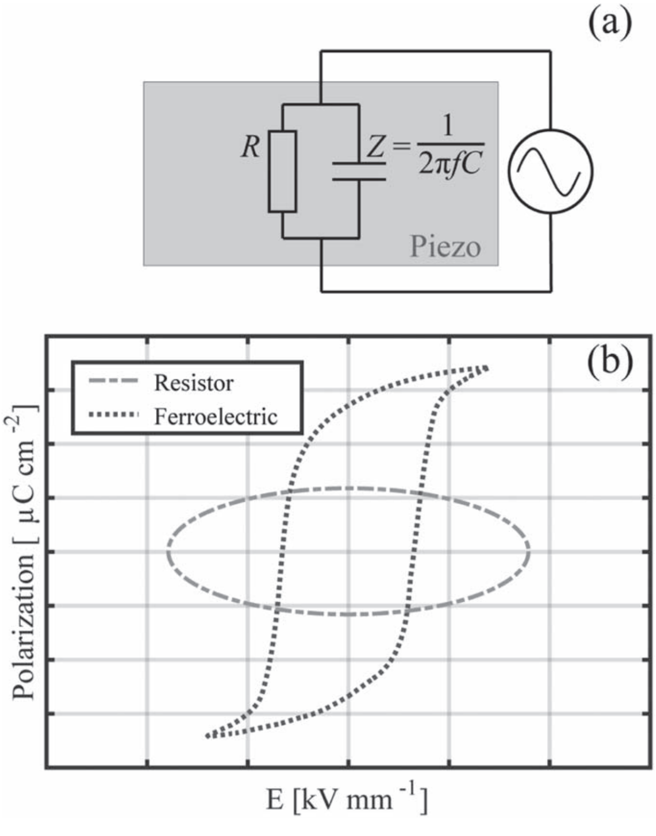

Figure 9. (a) Equivalent circuit diagram of a piezoelectric material exposed to an AC electric field is applied. (b) Typical hysteresis loops of a resistor and a ferroelectric [31].

obtained values for d_{33} are shown in figure 12. A clear trend is found where d_{33} increases with humidity in which the composites are aged. This can be attributed to the increased conductivity of the polymer matrix due to the presence of moisture. Consulting the 40 volume percent PZT composites from figure 4, the PZT/epoxy composites reach a d_{33} of about 10 pC N^{-1}, which is still slightly higher compared to the 8 pC N^{-1} reached by the PZT/PU aged in high humidity conditions. This means that the PZT/PU composites are still not fully poled, which again can be attributed due to the slightly lower matrix conductivity of the PU composites shown in figure 11.

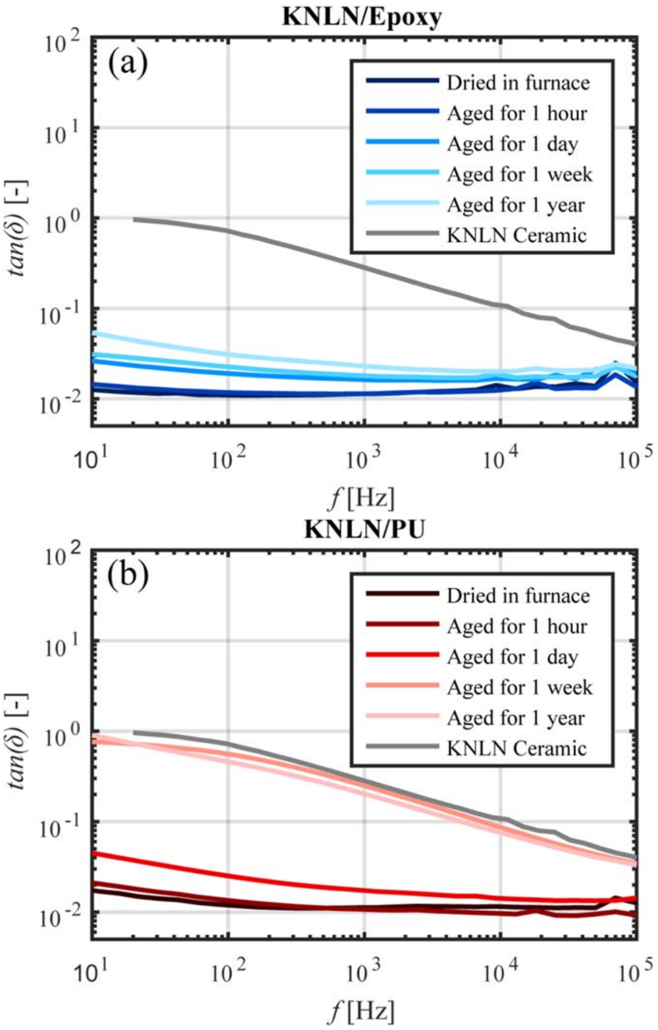

Figure 10. Dielectric loss, tan(δ), versus frequency, f, of (a) KNLN/Epoxy composites and (b) KNLN/PU composites.

Note that this trick can only be achieved using ceramic fillers which are themselves insensitive to moisture, in combination with a polymer matrix which is able to absorb moisture. This makes it able to increase the matrix conductivity, while keeping the tan(δ) low enough to still be able to apply an electric field without causing shorts.

4. Conclusions

Various polymer-piezoceramic granulate composites, consisting of piezoelectric ceramic filler particles randomly distributed in a polymer matrix, are fabricated. Typically, piezoelectric composites can be difficult to fully pole due to applied electric field getting mostly distributed over the low dielectric constant matrix. Therefore, the electrical matrix conductivity plays a vital role.

It has been shown that the matrix conductivity increases by increasing the temperature, making it essential for these composites to be poled at elevated temperatures. The conductivity of the epoxy matrix used in this work strongly reacts to the increased temperature, making it possible to fully pole these composites at low electric fields. Both conventional contact poling, lasting 5 min, and hysteresis measurements, lasting in the range of seconds, show the same trends. During hysteresis measurements leaky loops are observed when increasing the measurement time. Composites show this behavior, in contrast to most other piezoelectric materials, due to their low capacitance.

The conductivity of the PU matrix used in this work reacts in a less pronounced manner to an increased temperature, making it harder to fully pole composites with this type of matrix. The PU matrix is however able to absorb moisture. By doing this on purpose, by aging the PU composites in a high humidity environment, the composite conductivity can be increased by about one order of magnitude. This increased conductivity leads to an increased poling efficiency, which in turn increases d_{33}.

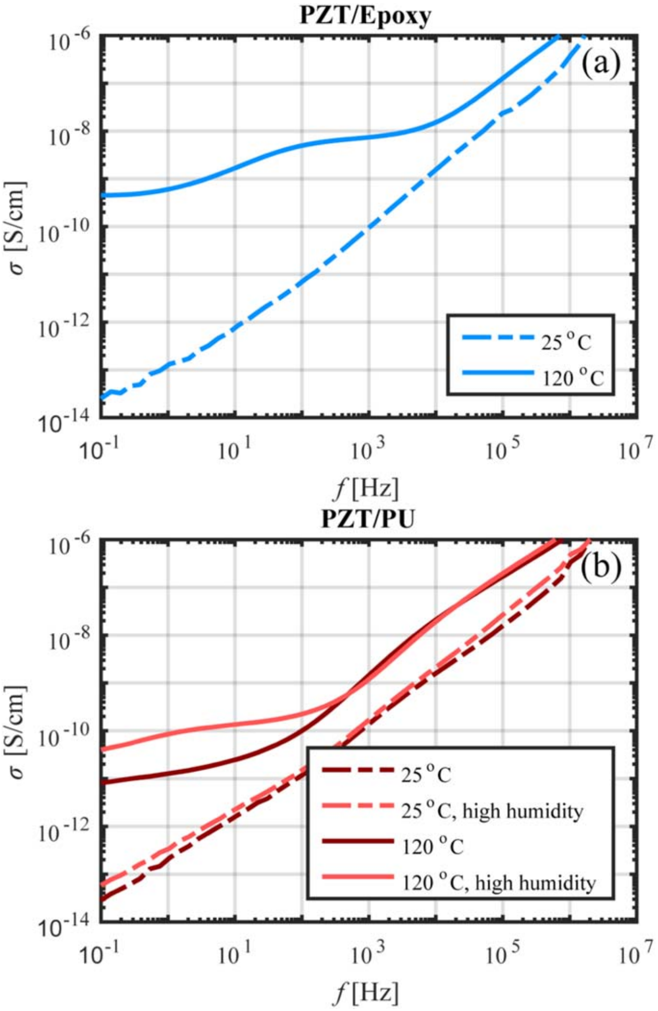

Figure 11. Composite conductivity, σ, as a function of frequency, f, for (a) PZT/Epoxy and (b) PZT/PU composites, with a volume fraction of 50%. Measurements are both performed at room temperature and the poling temperature of 120 °C.

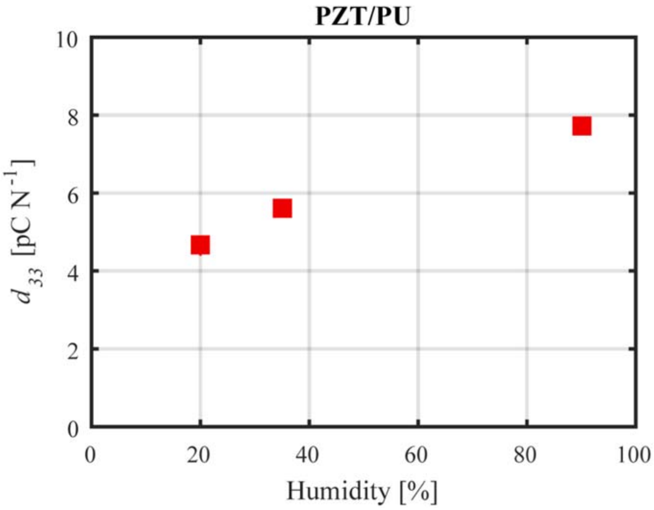

Figure 12. Piezoelectric charge constant, d_{33}, of 40 volume percent PZT/PU composites as a function of the humidity in which the composites are aged at for a week.

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