Journal of the European Ceramic Society **19** (1999) 1289–1293

0955-2219/99/$ - see front matter
PII: S0955-2219(98)00422-1

Finescaled Piezoelectric 1–3 Composites: Properties and Modeling

R. Steinhausen,[a] T. Hauke,[a]* W. Seifert,[a] H. Beige,[a] W. Watzka,[b] S. Seifert,[b] D. Sporn,[b] S. Starke[c] and A. Schönecker[c]

[a]Martin-Luther-Universität, Halle-Wittenberg, FB Physik, EP II, Friedeman-Bach-Platz 6, 06108 Halle/S., Germany
[b]Fraunhofer-Institut für Silicatforschung, Würzburg, Germany
[c]Fraunhofer-Institut für Keramische Technologien und Sinterwerkstoffe, Dresden, Germany

Abstract

Composites consisting of fine, unidirectional ordered piezoelectric fibers in a polymer matrix offer a series of commercially relevant applications. Making use of PZT fibers with diameters in the range of 10–50 μm improved functional properties of such 1–3 composites are expected, stimulating the development of advanced ultrasonic transducers. The present paper reports on the preparation of 1–3 composites with different volume fractions of PZT(53/47) fibers and the characterization of their dielectric and piezoelectric properties. The experimental data were compared with results of finite element method modeling and parallel circuit modeling. © 1999 Elsevier Science Limited. All rights reserved

Keywords: finite element method, composites, fibers, piezoelectric properties, PZT.

1 Introduction

1–3 composites of piezoelectric rods embedded in a passive polymer matrix show superior properties for ultrasonic transducer applications compared to single phase PZT materials. They combine a high coupling coefficient, low acoustic impedance, low mechanical quality, minimized lateral mode coupling and an intermediate dielectric constant.[1] Improved functional properties like a higher bandwidth can be expected by a further down-scaling of the diameter of the piezoactive rods.

This challenge can be realized by making use of sol–gel derived PZT-fibers with diameters ranging from 10 to 50 μm. Measurements of the dielectric and piezoelectric properties of single fibers are difficult to perform due to the fact that the fibers are very thin and therefore not easy to handle. However, by comparing the properties of 1–3 composites prepared with these fibers with results obtained by theoretical modeling one can calculate the properties of the fibers.

In this paper the experimental data of the quasi-static dielectric and piezoelectric properties of such 1–3 composites are presented. The results are compared to those of a finite element method (FEM) modeling as well as to those of a parallel circuit model. From the different models, the piezoelectric and dielectric coefficients of a single fiber are obtained.

2 Experimental Setup and Basic Modeling Considerations

2.1 Composite preparation and optical microscopy

Thin PZT(53/47)-fibers with diameters between 10 and 50 μm were prepared by a sol–gel route and subsequent thermal treatment as described in Ref 2. For composite preparation the PZT fibers were carefully aligned and infiltrated with an epoxy resin. In order to avoid bubbles and thus to minimize the possibility of an electrical breakdown the resin was degassed during preparation.

Curing was carried out under pressure. According to the applied pressure, the fiber content in the composite was adjusted to 25, 50 and 65 vol%. From optical micrographs a statistical distribution of the fibers was found for composites with a low fiber content of about 25 vol%, whereas the fibers were regular arranged in samples with fiber contents of 50 and 65 vol%. Figure 1 shows typical micrographs of composites with a fiber content of 25 and 65 vol%, respectively.

*To whom correspondence should be addressed. Fax: +49-345-552-7158; e-mail: hauke@physik.uni-halle.de

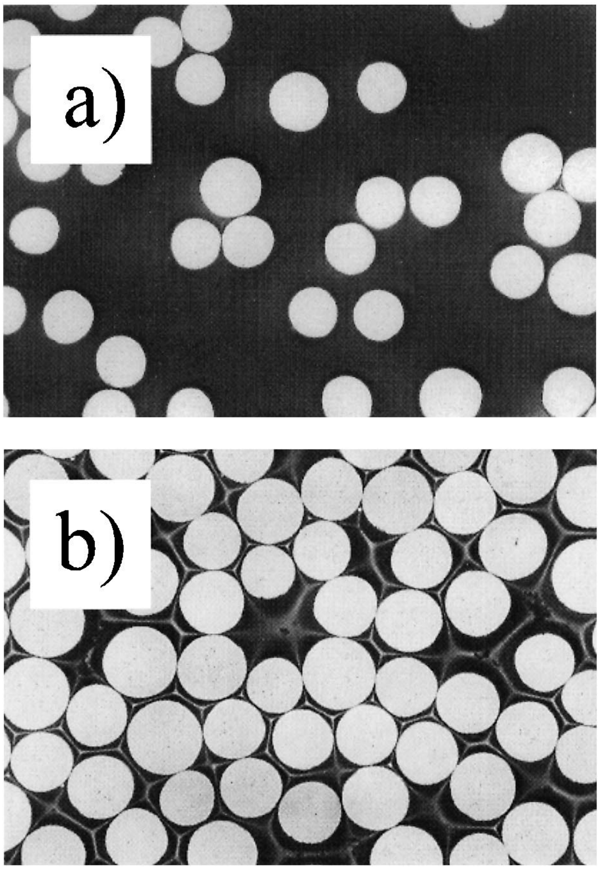

Fig. 1. Optical micrographs of samples with (a) 25 vol% fiber content; (b) 65 vol% fiber content.

After curing composite slices 0·5–1 mm in thickness were cut in the way that the fiber axis was directed perpendicular to the composite surface. The samples were ground and subsequently electroded with gold. Poling was done in oil at 80°C for 2 h with approximately 5·5 kV mm^{-1}. The poling field was kept constant during cooling to 50°C.[3]

2.2 Measurement equipment

For measurements of the piezoelectric moduli an equipment based on a capacitive detector was used.[4] The samples were placed between two rods, one of them freely movable. The other end of the movable rod carries one plate of an air capacitor, which is a component of a HF resonance circuit. Thus a change of the sample thickness results in a change of the capacity of the capacitor and finally in a frequency modulation of the HF circuit. After demodulation a voltage proportial to the strain of the sample is available. A quartz connected mechanically in series with the sample is used for calibration and for accurate measurement of the piezoelectric moduli by a compensation technique.

2.3 Basic modeling considerations

The FEM package ANSYS 5·3 was used for modeling the composite properties. The modeling was restricted to the quasistatic properties. Therefore the boundary conditions were set to laterally non clamped. For the material parameters of the PZT-fibers a data set of bulk material with the same composition was used[5] with $d_{33,\mathrm{free}} = 272$ pm/V and $c_{11}{}^{E} = 132$ GPa. For all calculations an electric field strength of 1 kV mm^{-1} was applied to the samples.

In order to investigate the influence of the fiber arrangement on the composite properties three different model structures were applied. The regular arrangement of fibers was described with a square and a hexagonal unit cell, whereas for the statistical distribution a structure with six randomly arranged fibers was assumed. The models of the hexagonal and the statistical distribution are shown in Fig. 2 for a fiber content of 50 vol%.

From FEM modeling the effective piezoelectric moduli $d_{33,\mathrm{eff}}$ and $d_{31,\mathrm{eff}}$ of the composites were calculated. The strains S_1 and S_3 were derived by averaging the dilatation of all nodes at the surfaces and dividing by the applied electric field strength.

3 Results

3.1 Results of the modeling

In Figs 3 and 4 the effective piezoelectric moduli $d_{33,\mathrm{eff}}$ and $d_{31,\mathrm{eff}}$ of the composites in dependence on the fiber content are shown. The results are in good agreement with data reported by other authors.[6,7] The piezoelectric moduli rise with increasing fiber content. $d_{33,\mathrm{free}}$ of a composite with a fiber content of 25 vol% already reaches 75% of the value of a single fiber.

Apparently the quasistatic properties are only slightly influenced by the fiber arrangement. For example, $d_{33,\mathrm{free}} = 251$, 250 and 246 pm/V were obtained for the square, the hexagonal and the statistically arranged fibers, respectively. However, the fiber arrangement becomes more important in the dynamic mode, when resonance coupling between the different modes occurs.[8]

Although it is possible to determine the effective permittivity ϵ_{eff} by FEM modeling, the simple parallel circuit model was additionally used. The capacity of the composite is assumed to be the sum of the capacities of the fibers and of the epoxy matrix. Therefore the dielectric permittivity of the fibers ϵ_{fib} can be calculated directly from the known permittivity of the epoxy ϵ_{ep} and the measured effective permittivity ϵ_{eff} of the composite:

$$\epsilon_{\mathrm{fib}} = \frac{\epsilon_{\mathrm{eff}} - \epsilon_{\mathrm{ep}} V_{\mathrm{ep}}}{V_{\mathrm{fib}}} \tag{1}$$

where V_{ep} and V_{fib} are the volume fractions of the epoxy and the fibers, respectively.

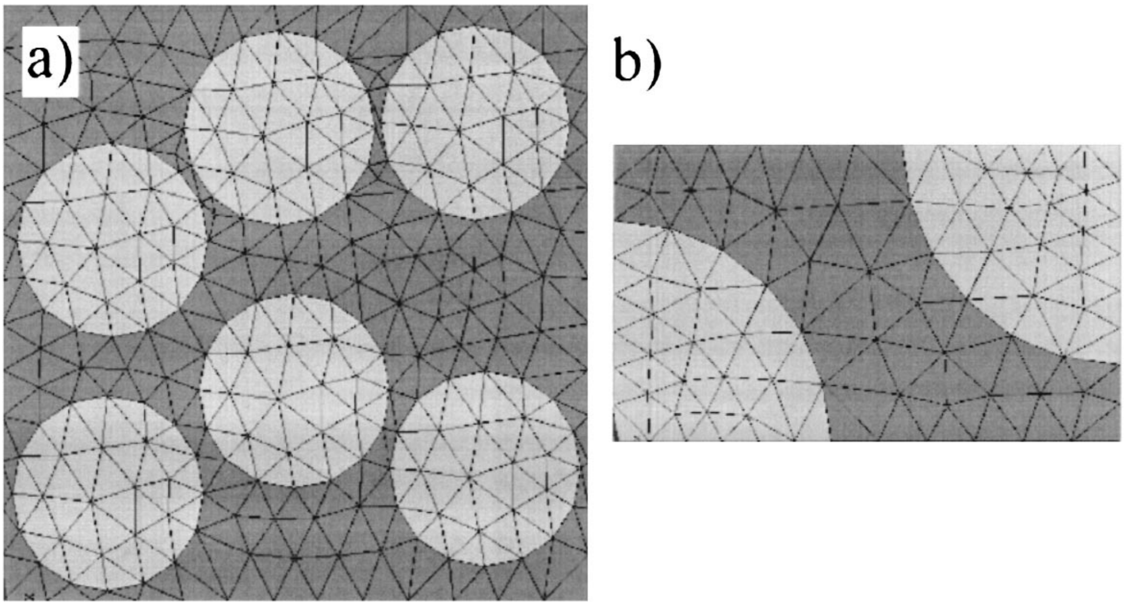

Fig. 2. Model structures used for the FEM (50 vol% fiber content): (a) structure for a statistically distributed fiber arrangement; (b) unit cell for the hexagonal fiber arrangement.

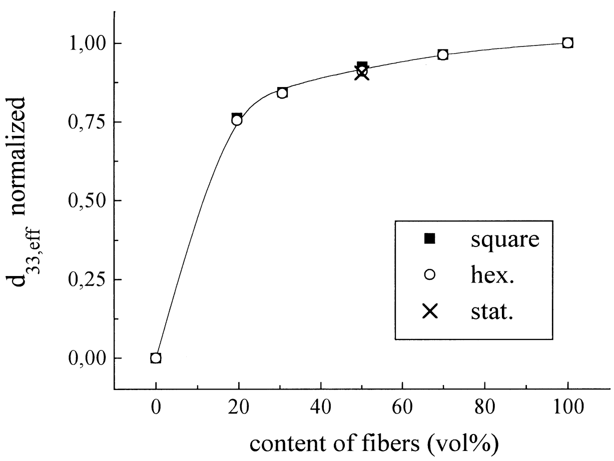

Fig. 3. Effective piezoelectric coefficients $d_{33,\mathrm{eff}}$ of the composite from the modeling, the data are normalized to the piezoelectric modulus of the fiber.

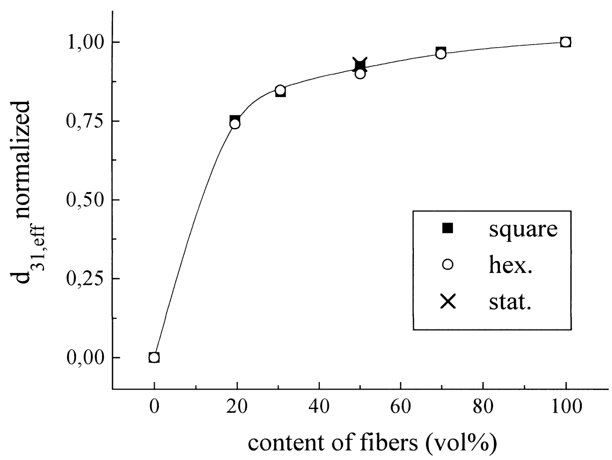

Fig. 4. Effective piezoelectric coefficients $d_{31,\mathrm{eff}}$ of the composite from the modeling, the data are normalized to the piezoelectric modulus of the fiber.

In order to prove the accuracy of this approach, the values from the FEM modeling were compared with values of the parallel circuit model. From eqn (1) an effective permittivity of 577 for a composite with 50 vol% fiber content was calculated with $\epsilon_{33,\mathrm{fib}}{}^{\mathrm{T}} = 1149$, $\epsilon_{\mathrm{ep}}{}^{\mathrm{T}} = 4{\cdot}5$,[5] whereas from FEM modeling permittivities of 585, 586 and 581 for the statistical, the hexagonal and the square fiber arrangement were obtained, respectively. As a result, the error by using the parallel circuit approximation seems to be about 2%.

3.2 Experimental results

In Fig. 5 the effective permittivity $\epsilon_{\mathrm{r,eff}}{}^{\mathrm{T}}$ before poling and the permittivity $\epsilon_{\mathrm{r,fib}}{}^{\mathrm{T}}$ calculated by eqn (1) in dependence on the fiber content are shown. Contrary to the parallel circuit model $\epsilon_{\mathrm{r,eff}}{}^{\mathrm{T}}$ increases with increasing fiber content of the composites only up to a fiber content of 50 vol% and decreases again with a further increase in the fiber content. $\epsilon_{\mathrm{r,fib}}{}^{\mathrm{T}}$ has nearly the same value of 800 for composites with a fiber content of 25 and 50 vol%, whereas $\epsilon_{\mathrm{r,fib}}{}^{\mathrm{T}} = 600$ is distinctly smaller for the composite with 65 vol% fiber content.

Figure 6 shows the dependence of $\epsilon_{33,\mathrm{eff}}{}^{\mathrm{T}}$ and $\epsilon_{33,\mathrm{fib}}{}^{\mathrm{T}}$ on the fiber content after poling. Similar to the observations from PZT bulk ceramics with rhombohedral structure, for all composites a drop in the dielectric permittivity was observed after poling. The maximum drop occurred in samples with a fiber content of 25 vol%. As a consequence, the maximum dielectric permittivity after poling was found for composites with 50 vol% fiber content. The dielectric permittivity of this composite

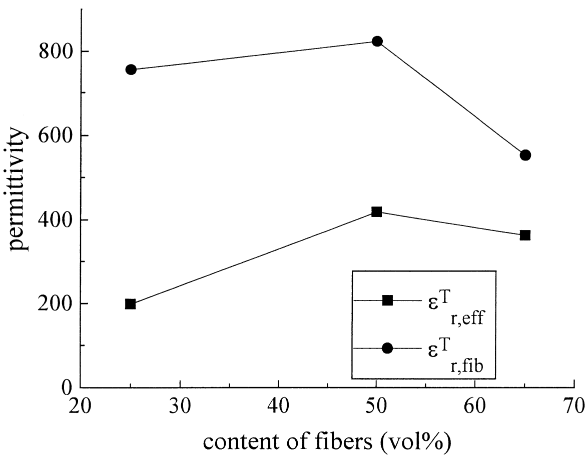

Fig. 5. Dependence of the permittivity measured at 10 kHz on the fiber content before poling.

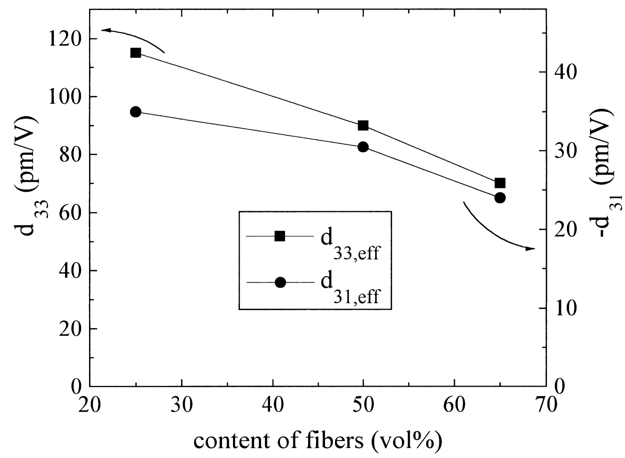

Fig. 7. Dependence of the piezoelectric moduli on the fiber content.

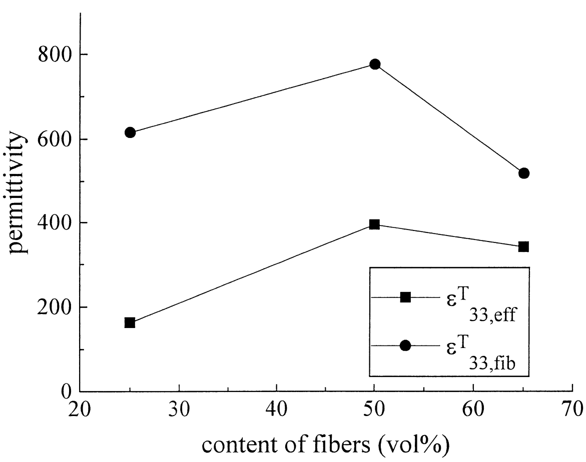

Fig. 6. Dependence of the permittivity measured at 10 kHz on the fiber content.

was of about 780 and was lower than the value reported for bulk ceramics.

Figure 7 shows the piezoelectric moduli $d_{33,\mathrm{eff}}$ and $d_{31,\mathrm{eff}}$ measured at 130 Hz in dependence on the fiber content. Contrary to the modeling $d_{33,\mathrm{eff}}$ decreases from 120 pm/V for composites with 25 vol% fiber content down to 70 pm/V for composites with 65 vol% fiber content. The same tendency is found for $d_{31,\mathrm{eff}}$, which decreases from −35 down to −24 pm/V. Both piezoelectric moduli are smaller than the values expected from modeling.

4 Discussion

In order to explain the differences between the modeling and the experimental data the structure of the composites has been investigated by optical microscopy. Therefore the composites were cut and polished along the longitudinal direction of the fibers. It was found that in composites with a fiber content of 50 and 65 vol% some of the fibers were broken. This was due to the applied pressure during composite preparation. The amount of broken fibers was low for composites with 50 vol% PZT, but relatively high for composites with 65 vol% PZT. Composites with 25 vol% PZT showed almost no damaged fibers.

For a better understanding of the influence of fiber fragments on the dielectric properties of a 1–3 composite, a simple model for a broken fiber embedded in a polymer was considered.

It consists of a series circuit of the capacities of the fiber fragments and the polymer between. Assuming the space charges to be absent, the component D_3 of the dielectric displacement within the composite is regarded to be constant. From the condition

$$\epsilon_{33,\mathrm{fib}} E_{3,\mathrm{fib}} = \epsilon_{\mathrm{ep}}, E_{3,\mathrm{ep}} \tag{2}$$

one can see that the electric field strength in the fiber fragments $E_{3,\mathrm{fib}}$ is significantly smaller than in an undamaged fiber due to the low dielectric constant of the epoxy resin.

Therefore broken fibers may affect the properties of the composite in two ways. Taking into account the reduced electric field strength, the broken fibers can only be partially poled without reaching the saturation field strength. This effect seems to be valid for composites with a fiber content of 50 and 65 vol%. A confirmation of this assumption seems to be the fact that the sample with the lowest fiber content showed the highest drop in ${\epsilon_{33,\mathrm{fib}}}^{\mathrm{T}}$ after poling. That means this composite contained the highest volume fraction of active material.

As a second reason, the dielectric and piezoelectric properties are also reduced by damaged fibers, even when the fibers are considered to be completely poled.[9] Thus the decrease of the effective permittivity as well as the piezoelectric moduli with increasing fiber amount is caused by fractures as well as by incomplete poling.

Since there were almost no damaged fibers in composites with 25 vol% PZT, the piezoelectric coefficients $d_{33,\mathrm{fib}}$ and $d_{31,\mathrm{fib}}$ of a single fiber can be calculated by FEM modeling. The effective piezoelectric modulus of a composite with 25 vol% fiber content was found to be of about 80% of the value of a single fiber. That means the piezoelectric modulus of a single fiber should be at least $d_{33,\mathrm{fib}} = 150$ pm/V and $d_{31,\mathrm{fib}} = -44$ pm/V. These values are 55 and 38%, respectively, of the values reported for bulk ceramics.[4]

5 Summary

Fine PZT fibers are expected to have a great impact on new 1–3 composites for broadband ultrasonic transducers in the frequency range > 10 MHz. 1 – 3 composites with different volume fractions of sol–gel derived PZT fibers had been prepared and their dielectric and piezoelectric properties were measured.

The permittivity of the fibers $\epsilon_{r,\mathrm{fib}}$ and $\epsilon_{33,\mathrm{fib}}{}^{T}$ as well as the piezoelectric moduli $d_{33,\mathrm{fib}}$ and $d_{31,\mathrm{fib}}$ have been calculated using FEM modeling and the parallel circuit approach. So far, the fibers show a permittivity of $\epsilon_{r,\mathrm{fib}} = 800$. The piezoelectric moduli were calculated to $d_{33,\mathrm{fib}} = 150$ pm/V and $d_{31,\mathrm{fib}} = -44$ pm/V, which is about 50% of the values reported for bulk materials. FEM modeling has shown that the quasistatic piezoelectric and dielectric coefficients of the composites were only slightly influenced by the fiber arrangement.

The differences between the modeling results and experimental data were caused by broken fibers arising during composite processing. For a better understanding of the correlations between the preparation conditions of PZT fibers and 1–3 composites on their dielectric and piezoelectric properties the preparation procedures will be further optimized.

Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft.

References

1. Safari, A., Janas, V. F. and Bandyopadhyay, A., Development of fine-scale piezoelectric composites for transducers. *AIChE Journ.*, 1997, **11A**(43), 2849–2856.
2. Glaubitt, W., Watzka, W., Scholz, H. and Sporn, D., Sol–gel processing of functional and structural ceramic oxide fibers. *J. Sol–Gel Sci. Technol.*, 1997, **8**, 29–33.
3. Watzka, W., Seifert, S., Scholz, H., Sporn, D., Schönecker, A. and Seffner, L., Dielectric and ferroelectric properties of 1–3 composites containing thin PZT-fibers. Proc. of 10th Int. Symp. Appl. Ferroel. ISAF '96, 1996, **2**, 569–572.
4. Sorge, G., Hauke, T. and Klee, M., Electromechanical properties of thin ferroelectric $PbZr_{0.53}Ti_{0.47}O_3$-layers. *Ferroelectrics*, 1995, **163**, 77–88.
5. Boucher, D., Lagier, M. and Maerfeld, C., Computation of the vibrational modes for piezoelectric array transducers using a mixed finite element-perturbation method. *IEEE Trans. on Son. and Ultrason.*, 1981, **28**(5), 318–330.
6. Dunn, M. L. and Taya, M., Micromechanics predictions of the effective electroelastic moduli of piezoelectric composites. *Int. J. of Solids and Structures*, 1993, **30**(2), 161–175.
7. Chan, H. L. W. and Unsworth, J., Simple model for piezoelectric ceramic/polymer 1–3 composites used in ultrasonic transducer applications. *IEEE Trans. Son. and Ultrason.*, 1989, **36**(4), 434–441.
8. Smith, W. A., Shaulov, A. and Auld, B., Design of piezocomposites for ultrasonic transducers. *Ferroelectrics*, 1989, **91**, 155–162.
9. Levin, V. M., The effective properties of piezoactive matrix composite materials. *J. Appl. Mathematics and Mechanics*, 1996, **60**(2), 309–317.