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Modelling and characterization of piezoelectric 1-3 fibre composites

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Introduction

Ultrasonic transducers are widely used in modern medical, technical and industrial applications. In addition to medical diagnostic, ultrasonic methods were used for monitoring systems (bubble monitoring in dialysis machines), therapy and power ultrasonics. In the last years, ultrasonic technology conquers more and more new fields in engineering and industry. Ultrasonic transducers have a high potential for measurement and testing technology, non-destructive materials testing and different sensor applications.
The source of the ultrasonic sound wave in modern transducers is mostly a piezoelectric material transforming an alternating electrical field to a mechanical vibration. In dependence on the specific technical conditions and the measuring task the parameters of the ultrasonic transducer have to be varied in a wide range. The vibration mode and the resonance frequency depend on the geometry of the piezoelectric transducer. The band width and acoustic impedance can be influenced by the choice of an appropriate material. Single crystals are characterized by high quality factors and small band width. Piezoelectric ceramics are cost-efficient to produce and very good shapeable. Thin crystalline or ceramic films can be used for high frequency ultrasonic applications. Polymer and other organic materials, especially polymer foils are suitable for medical, air and underwater applications where low acoustic impedance is necessary.
Piezoelectric composite materials consisting of a piezoelectric active component and a piezoelectric passive matrix, usually epoxy resin or other polymers. Such composites combine the piezoelectric properties of the ceramics with the low density and softness of the polymer. They are characterized by their high electromechanical coupling coefficients, a low density and thus a low acoustic impedance. In dependence on the volume ratio of piezoelectric active material and the polymer matrix the acoustic properties of the composite can be varied in a wide range. An additional advantage over bulk ceramic materials is the very good formability. Polymer-ceramic-composites can be elastically deformed without damaging. Under slight heating composites can also be deformed plastically.

Preparation of conventional 1-3 composites

Ultrasonic transducers can be built on such called 1-3 composites. The description is applied to a two component system where the first component connects the boundary planes of the composite in one dimension and the second component is connected in all three dimensions. In the case of a piezoelectric 1-3 composite the first component is the piezoelectric active ceramic in the form of a rod or a fibre. The second component is the non-active polymer matrix where the rod is embedded.

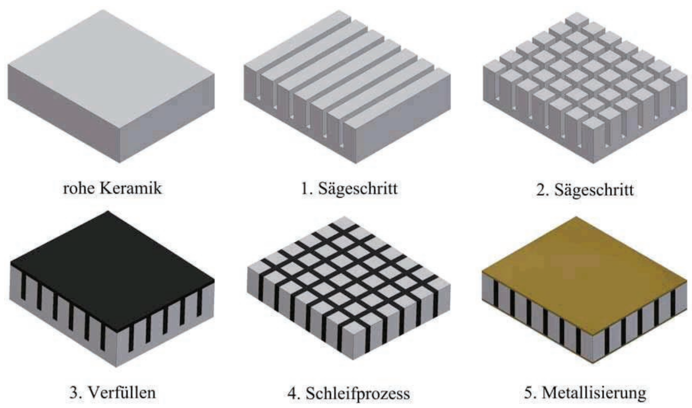

Figure 1: Preparation steps in the dice-and-fill-method (left, [Walther-09]), 1-3 composite before filling with polymer (right, Sonotec GmbH Halle, Germany)

The commercially mostly used preparation technology for 1-3 composites is the dice-and-fill-technique (Fig. 1, left). Thin parallel slice were sawed in a ceramic plate. The slices were performed some hundred micrometer deep, but not

through the whole plate. After the first cut of a regular structure with parallel slices the sample is rotate by 90 degree. Than the sawing of parallel slices is repeated. In the result, a structure consisting of rectangular rods in a square arrangement is produced. High-tech sawing machines can perform slices with a thickness of down to 35 micrometer. The width of the rods can reduced up to 50 µm (Fig. 1, right). The problem at these very fine geometries is the brittleness of the ceramics. The finer the structure and deeper the slices are the higher the probability of cracks or damage of the rods. If the ceramic plate is moved by an angle of 60 degree between the sawing process steps structures with triangular cross-section can be prepared. In this case the rods are arranged with a hexagonal symmetry.
After the sawing process the rod structure is filled with a polymer. The hardening process is usually performed at higher temperature and in vacuum to avoid air bubbles in the matrix. Such bubbles often cause electrical breaktrough during the poling process and destroy the composite. In the next step, the ceramic ground plate is grinded down. Both sides are polished and electroded. Since the origin ceramic plate was mostly polarized, the poling process is not absolute necessary. Due to slightly depolarization of the ceramic by the mechanical treatment, the polarization of the composite can be optimized by applying a high electrical field.
The disadvantages of the dice-and-fill-technology are the high number of preparation steps and the high loss of ceramic material. In dependence on the volume fraction of ceramics in the final composition the loss by sawing and grinding is about 60-80 percent.
Another technology for 1-3 composites is the soft mold process [Gebhardt-00]. Here a master mold structured by microsystem technologies is used. Gebhardt et al. prepared an silicon master mold by Advanced Silicon Etch Process (ASET). Thus, rod arrays with user-defined forms and regular or arbitrary distribution in the matrix can be fabricated. From the silicon master mold soft plastic templates were taken which are reusable. The templates were filled with a ceramic slurry. After drying the ceramic green body can be demolded and sintered. The next steps are filling with polymer, grinding, polishing and electroding as well as by the dice-and-fill-technique. The 1-3 composites prepared by the soft mold process have to be necessarily polarized by applying a poling voltage.

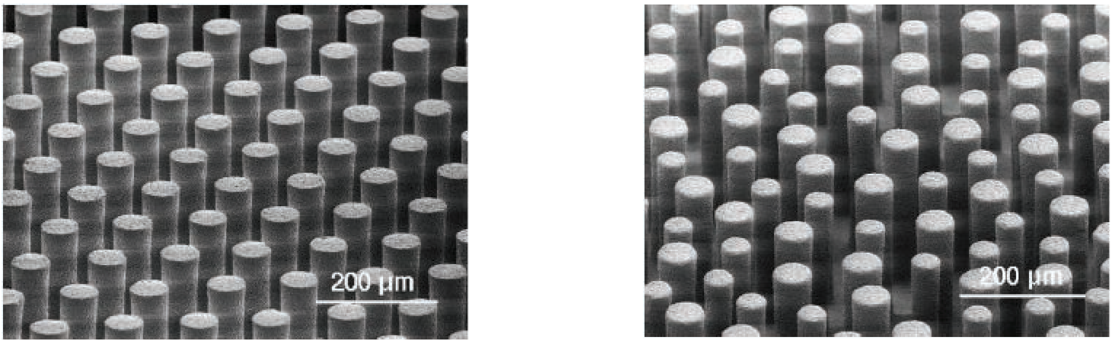

Figure 2: 1-3 composites (without polymers) prepared by the soft mold technique; cylindrical rods in a hexagonal arrangement (left), cylindrical rods with two different diameters in a non-regular arrangement (right) [Gebhardt-00]

Effective properties of 1-3 composites

The performance of ultrasonic transducers consisting of piezoelectric 1-3 composites depends on the effective material properties of the composites. The effective properties of a two component system can be classified in four groups. In the first case, the property of the composite is a linear combination of the properties of the components (sum-like property). The resulting value is always in the middle between the components values, for example the density. Anymore, the components can interact and the effective material coefficient of the composite is higher than the single values of the two phases (combination properties). One example is the coupling coefficient of the 1-3 composite, which can be higher in dependence on the volume ratio than the coupling coefficient of the piezoelectric ceramic inside, because the coupling coefficient is a combination of the effective piezoelectric, dielectric and mechanical coefficients of composite. Furthermore, these effective coefficients are themselves combination properties of the ceramic and polymer part.
The third kind of effective properties are values dependent on the symmetry. In dependence of the inner arrangement of the piezoelectric rods (square, hexagonal symmetry or random distribution) the effective properties like resonance frequencies can differ. Last but not least, composites can show new properties which don't have any of both components (product properties).
Here, we will present only a short overview about the most relevant effective parameters of 1-3 composites for ultrasonic applications. Analytical approximations for all effective material parameters were calculated by Smith and Auld, Chan and others [Smith-91, Smith-93, Chan-89].
The acoustic impedance plays an important role for the transmission of acoustic wave from one medium to an other. The smaller the difference of the acoustic impedance values is the better are the sending and/or receiving characteristics of the ultrasonic transducer. If there is a big impedance mismatch at the interface between transducer and medium, for instance from ceramics to air, the large part of the acoustic wave will be reflected at the interface. The effective acoustic impedance $Z_{a,eff}$ can be calculated from

$$Z_{a,eff} = \rho_{eff} c^{D}_{33,eff}$$

where ρ_{eff} – the effective density and $c^D_{33,eff}$ – the effective elastic stiffness of the composite parallel to the polarization direction measured at constant dielectric displacement D.
The effective density is a linear combination of the component's density. The weighting factor is the volume fraction of the ceramic in the composite. The effective elastic stiffness is calculated by a more complex formula and depends not only on the elastic coefficients and the volume fraction but also on the piezoelectric and dielectric coefficients of both components. However, in a first approximation the resulting acoustic impedance depends linear on the volume fraction of the ceramic part in the composite (Fig 3, left). Thus, the relatively high acoustic impedance of a bulk ceramic can be reduced to values closer to the impedance values of biological materials or water.
The second important parameter of ultrasonic transducer materials is the electromechanical coupling coefficient. It can be regarded as a quantity for the effectiveness of transformation from the electrical energy driving the transducer to the mechanical energy of the generated sound wave in the sending mode or vice versa in the receiving mode. The coupling coefficient depends on the vibration mode of the sample. The thickness or longitudinal mode of a cylinder is named k_{33} or longitudinal coupling factor. This vibration mode has the lowest frequency of all resonances of a cylinder. The coupling coefficient k_{33} for commercial PZT ceramics is about 0.65 – 0.7. However, the thickness should be at least three times the lateral width (diameter). Thus, for this geometry the resonance frequencies are quite low connected to the relatively big thickness. For high frequency applications in the MHz region the thickness resonance of thin disc or thin films is excited. In this case the coupling coefficient is named k_t or thickness coupling factor. The typical values of k_t of ceramic discs are about 0.4 – 0.5, much lower than the longitudinal factor k_{33}. The reason is the lateral clamping of the disc in the thickness mode resonance. The lateral resonances occur at lower frequencies which results to a suppression of the lateral vibrations at higher frequencies.
The main idea of 1-3 composites is the combination of the high longitudinal coupling factor k_{33} of small cylinders and the high resonance frequencies of a thin disc. The polymer matrix plays the role of a holder for these very fine structured ceramic rods. It should be relatively soft to allow free vibrations of the piezoelectric ceramics in the lateral dimension. Additionally, the soft polymer will be deformed at the surface by the piezoelectric displacement of the ceramic part. Both effects result in a higher electromechanical deformation of the composite and a higher coupling coefficient in comparison with a bulk ceramic disc. The thickness coupling factor of 1-3 composites are in the range of 0.6 - 0.7.
The thickness coupling factor k_t depends like all other effective parameters on the volume fraction of the ceramic part in the composite (see Fig. 3, right). The maximum values were obtained between 20 and 80 percent of ceramics in the composite. It can be calculated using the material parameters

$$\frac{k_t^2}{1-k_t^2}=\frac{h_{33}^2\epsilon_{33}^S}{c_{33}^E}$$

where ε^S_{33} the dielectric permittivity measured at constant strain, c^E_{33} – the elastic stiffness measured at constant electric field and $h_{33} = \delta T_3/\delta D_3$ is the piezoelectric coefficient. T_3 is here the mechanical stress in z-direction (thickness of the composite) and D_3 – the dielectric displacement. All indices are in the Voigt's notation (xx – 1, yy – 2, …, xy – 6). All these material parameters are the effective parameters of the composite and strongly depend on the volume fraction. More in detail this is described by Smith and Auld [Smith-91].

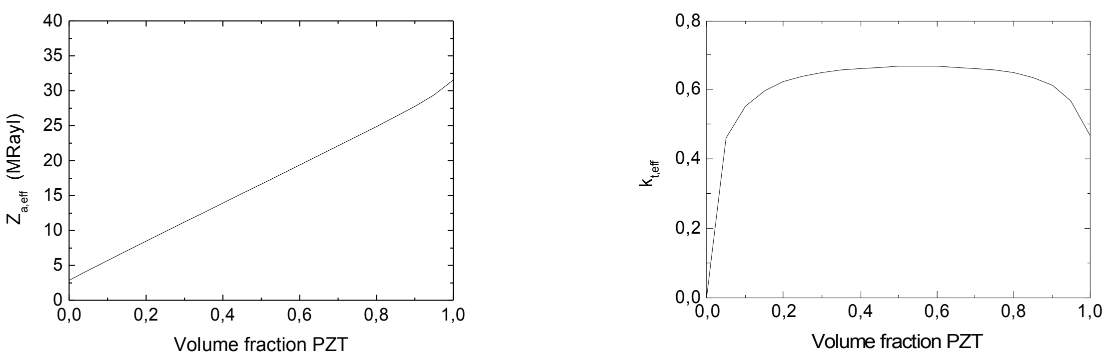

Figure 3: Acoustic impedance (left) and coupling coefficient k_t (right) of 1-3 composites in dependence on the volume fraction of ceramics

For the analytical calculation of all effective material coefficients of the composite is based on the effective medium theory. Thus, the inner structure and the geometry of the ceramic rods do not play a role for this static approximation. However, the dynamic properties show an influence of the internal structure of the composite. If the composite is exited by an external electrical field, resonance effects occur not only in dependences on the geometry of the composite sample. Furthermore, due to the periodicity of the rows of rods additional resonances can be observed in the impedance spectrum. The wave length of this lateral wave is connected with the distance between the

neighbouring rods. The resonance frequency results than consequentially from the sound velocity, i.e. from the effective elastic coefficient of the polymer-ceramic-composite in the propagation direction of the acoustic wave. The coupling coefficient of the thickness resonance is noticeably reduced if the resonance frequency of this lateral acoustic wave is in the near of the thickness resonance. The lateral spacing at the dice process should be chosen so fine, that the spurious lateral resonances are far away from the working resonance of the transducer. The higher the desired ultrasonic frequency is the finer the internal structure should be. Here technological limitations arise. Deep saw cuts are more complicated the thinner the rods are. In commercial composites the aspect ratio of the rods (width-to-height-ratio) is usually 1:5 till 1:6 [Sonotec].
Composites produced with the dice-and-fill-technique consist of rectangular rods in a square arrangement. In the impedance spectrum two spurious resonances can be observed connected to a acoustic wave parallel to the edges of the rod (saw cuts) and diagonal to them, respectively. In Fig. 4 the impedance spectra of different 1-3 composites with different internal symmetries are shown. The lower the volume fraction of the composite the larger is the distance between the rods. Thus, the wave length of the spurious lateral resonances increases, and the resonance frequency shifts to lower values. In Fig. 4 (left) it shown that there is overlap of the thickness resonance f_t and the resonance of the first lateral mode f_{l1} for the composite with lower volume fraction.
Using the soft mold technique rod arrays with cylindrical rods in a hexagonal arrangement can be prepared. Here, at the same volume fraction and the same aspect ratio of the rods the first spurious resonance frequency is obtained at higher frequencies than for a square arrangement (compare samples C and F). In the impedance spectrum of composite consisting of cylinders with two different diameters and a non-regular arrangement (Fig. 2, right) the spurious resonances are smooth and nearly vanished (sample I).

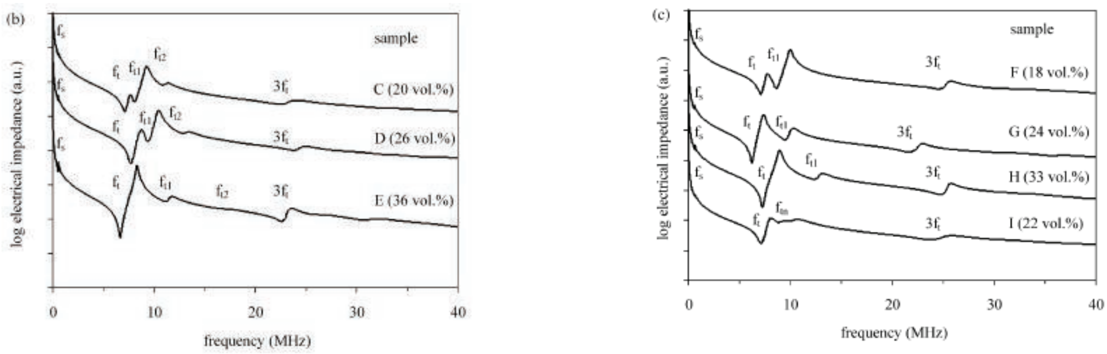

Abb. 4: Impedance spectra of 1-3 composites with different internal structures: square rods in a square arrangement (left, C-E), cylindrical rods in a hexagonal (F-H) or non-regular (I) arrangement (right) [Gebhardt-03]

Fibre composites

The disadvantages of dice-and-fill-composites are the relatively high number of preparation steps and the huge loss of ceramic material by the sawing process. The final composite contains only 20 to 50 % of the initial piezoelectric ceramics. Both problems can be overcome by using piezoelectric ceramic fibres for the composite preparation. Such thin fibres with diameters of some hundreds of micrometer till down to 10 µm can be prepared by different technologies. The fibres are embedded in a polymer matrix. The composite have to be polished, electroded and polarized.
Fibres have in principle an unlimited aspect ratio. Thus, thick composites for ultrasonic applications in the kHz range can be prepared very easily. The setting of a definite volume fraction of the fibres in the composite is more complicated. Also the control of a relatively homogeneous distribution of the fibres and avoid of agglomerations is difficult to handle. On the one hand, a irregular or random arrangement of the fibres prevents the generation of the spurious lateral resonances due to the lack of a periodic structure. On the other hand, the volume fraction of ceramics is not homogeneous in the whole composite.
In the literature different technologies for fibre preparation are described. Commercially available processes are the ALCERU process [Meister-03], the viscous suspension spinning process VSSP [Cass-91] and the fibre extrusion technology [Strock-99]. All these three methods started from a previously prepared ceramic powder, usually PZT. The powder is dispersed in water and then mixed with cellulose or viscose in the ALCERU and VSSP method, respectively, or compounded with a thermoplastic material (extrusion method). The fibres were formed by an extrusion process. The organic or thermoplastic were removed by specific methods, and subsequently the fibres were sintered. Using these methods ceramic fibres with diameters of 30-80 µm can be prepared. Other methods use the sol-gel process or electrospinning and other spinning technologies for fibre preparation, but they are not commercially available [Heiber-09].
In contrast to dice-and-fill-composites the ceramic single fibres were embedded in the polymer matrix in a non-poled state. The polarization process is performed only after hardening of the polymer. Thus, the fibres are slightly mechanical clamped by the surrounding material and the polarisation can be reduced, especially at lower volume fractions of fibres [Hauke-01].
Since the fibres can be extruded in principle with any length composites with an infinite aspect ratio of the ceramic part can be prepared. Furthermore, the preparation steps are reduced because the time-consuming sawing process is not applicable. Certainly, the fibre preparation is more difficult than bulk ceramic processing. But there is not a

material loss like from dicing. This can compensate the more expensive fibre preparation costs.
Unfortunately, the effective properties of piezoelectric fibre composites for ultrasonic applications are often not so good than expected. In Fig. 5 (left) the coupling coefficient k_t of 1-3 composites with embedded undoped PZT fibres are shown [Steinhausen-01]. The volume fraction of the fibres is about 20 vol%. The influence of the volume fraction of the fibres is negligible (see also Fig. 3, right). The highest values are obtained at composites consisting of fibres at the morphotropic phase boundary of PZT (Zr content of 53 %). In Fig. 5 (right) the piezoelectric coefficient is shown in dependence on the Zr content. The value d_{33}= 127 pm/V of these fibres is much smaller than the value of comparable undoped bulk PZT (d_{33}=270 pm/V). The coefficients were recalculated from the measured effective composite data. In this method of determination for the fibre parameter the polymer matrix plays the role of a sample holder. The mechanical clamping of the fibres by the polymer is considered in this linear theory. However, the local deviation of the volume fraction of fibres could not be included in the calculation. Thus, a lot of single measurements and a statistical analysis are necessary to determine an average value for the fibre badge.
The relatively high effort for the composite preparation is an other problem in fibre characteristics by this method. Furthermore, the elastic properties of the polymer have to be known very exactly at the measurement frequency. It is well known that polymers show a large dispersion in their elastic properties.

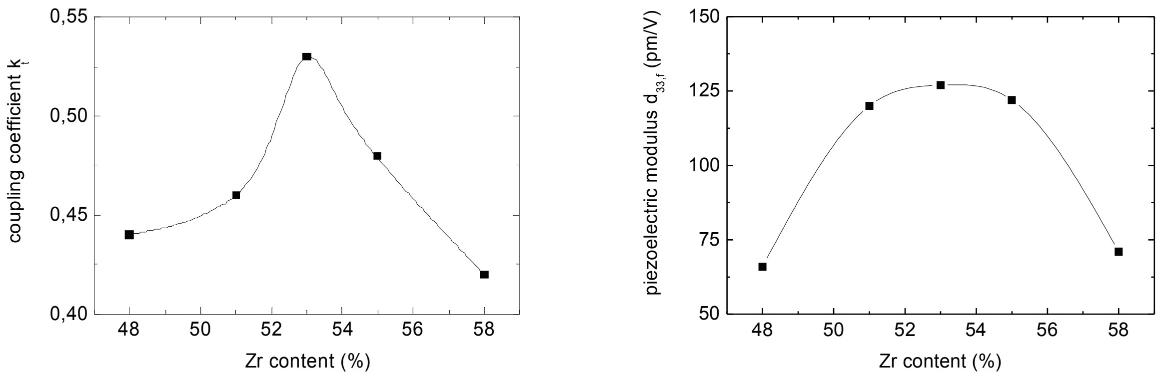

Figure 5: Coupling coefficient k_t of 1-3 composites with embedded undoped PZT fibres (left); recalculated piezoelectric coefficient d_{33} of these fibres (right)

To avoid all this problems a measurement method for single piezoelectric ceramic fibres was developed [Steinhausen-10]. It based on a capacitive displacement sensor. In Fig. 6 (left) a photograph of the equipment is shown. The fibre (1) with a length of about 5 mm is fixed at the top into a sample holder. On the bottom end of the fibre a disc (3) is glued. This disc is one plate of the measurement capacitance. The other plate (4) is on the top of a ceramic pin which is free movable. If an electric AC-voltage is applied to the fibre the distance between the capacitor plates changes due to the piezoelectric displacement of the fibre. The capacitor is a part of a high-frequency serial resonant circuit. The change of the capacitance causes a shift of the resonance frequency which can be detected very sensitively. Below the pin a quartz disc (2) for measurement calibration is fixed. For very sensitive measurements a compensation technique is used. In this case the quartz is driven with the same frequency as the fibre but with a 180° phase shift to compensate the fibre displacement. In this way, it is possible to measure the low-voltage piezoelectric coefficient applying a voltage of only 10 V.

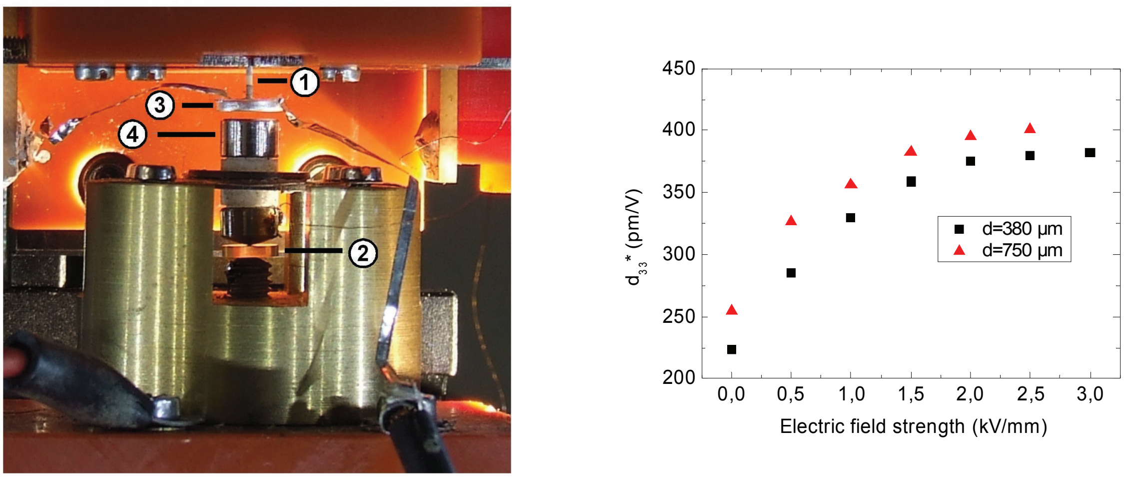

Figure 6: Measurement equipment for single fibre characterization (left); measured piezoelectric coefficient d_{33} of single PZT fibres with different diameters in dependence on the applied electric field strength (right)

In Fig. 6 (right) the piezoelectric coefficient d^*_{33} of SKN-PZT fibres is shown. The fibres were prepared by the Fraunhofer Institute (IKTS Dresden, Germany) using the polysulfone process [Scheithauer-10]. The commercial piezoceramic powder Sonox P505 from CeramTec AG was used. In comparison with the bulk value (d_{33} = 475 pm/V, CeramTec AG) the piezoelectric low-field value (at E = 0 kV/mm in Fig. 6) of the fibres decreased. For increasing electrical field strength the piezoelectric high-voltage coefficient $d^*_{33} = S_{max} / E_{appl}$ increases up to about 400 pm/V (S_{max} - maximum strain, E_{appl} – applied electrical field). But the performance of the fibres is still lower than the bulk ceramics. Additionally, a deterioration of performance connecting with increasing fibre diameter was observed. The thinner the fibres are the stronger is the influence of the surface. Very thin fibres are in principle only a surface. The control of the sintering conditions and the sintering atmosphere become very important. The single fibre measurements have shown that the quality of the fibres seems to be the more important reason for unsatisfactory ultrasonic properties of fibre composites. On the other hand, the role of the local inhomogeneous volume fraction of fibres can be clarified only by a direct comparison between single fibre measurement and composite characterization. This work will be done in the future.

References

Cass-91	Cass, R.B. 1991: Fabrication of Continuous Ceramic Fiber by the Viscous Suspension Spinning Process, American Ceramic Society Bulletin, 70(3) (1991), 424–429.
Chan-89	H. L. W. Chan, J. Unsworth: Simple model for piezoelectric ceramic/polymer 1-3 composites used in ultrasonic transducer applications, IEEE Trans. Ultrason. Ferroelec. Freq. Control, Vol. 36 (4) (1989), 434-441.
Gebhardt-00	S. Gebhardt, A. Schönecker, R. Steinhausen, T. Hauke, W. Seifert, H. Beige: Fine Scale 1-3 Composites Fabricated by the Soft Mold Process: Properties and Modeling, Ferroelectrics 241 (2000), 67-73.
Gebhardt-03	S. Gebhardt, A. Schönecker, R. Steinhausen, W. Seifert, H. Beige: Quasistatic and Dynamic Properties of 1-3 Composites Made from the Soft Mold Process, Journal of the European Ceramic Society, 23(1) (2003), 153-159.
Hauke-01	T. Hauke, R. Steinhausen, W. Seifert, H. Beige and M.Kamlah: Modeling of poling behavior of ferroelectric 1-3 composites, J. Appl. Phys. 89, 9 (2001), 5040-5047.
Heiber-09	J. Heiber, A. Belloli, P. Ermanni and F. Clemens: Ferroelectric Characterization of Single PZT Fibers, J. Int. Mat. Sys. Struc. 20 (2009), 379-385.
Meister-03	Meister, F., Vorbach, D., Niemz, F., and Schulze, T.: Functional High-tech-cellulose Materials by the ALCERU process,'' Materialwissenschaft und Werkstofftechnik, 34(3) (2003), 262–266.
Scheithauer-10	Scheithauer, U.; Schlenkrich, F.; Kretzschmann, L.; Schönecker, A.: Low-Temperature Sintering of SKN-doped PZT-Fibres, Electroceramics XII (13-16.06.2010), Trondheim, N, Poster
Smith-91	W. A. Smith, B. A. Auld: Modeling 1-3 composite piezoelectrics: thickness-mode oscillations, IEEE Trans. Son. Ultrason., Vol. 38, No. 1 (1991), 40-47.
Smith-93	W. A. Smith: Modeling 1-3 composite piezoelectrics: hydrostatic response, IEEE Trans. Ultrason. Ferroelec. Freq. Contr., Vol. 40, No. 1 (1993), 41-49.
Sonotec	Personal notice from Sonotec GmbH Halle, Germany
Steinhausen-01	R. Steinhausen, T. Hauke, H. Beige, W. Watzka, U. Lange, D. Sporn, S. Gebhardt, A. Schönecker: Properties of fine scale piezoelectric PZT fibers with different Zr-content, Journal of the European Ceramic Society 21 (2001), 1459-1462.
Steinhausen-10	R. Steinhausen, S. Kern, C. Pientschke, H. Beige, F. Clemens, J. Heiber: A new measurement method of piezoelectric properties of single ceramic fibres, J. Europ. Ceram. Soc. 30 (2010), 205 -209.
Strock-99	Strock, H.B., Pascucci, M.R., Parish, M.V., Bent, A.A., and Shrout, T.R.: Active PZT Fibers, a Commercial Production Process,'' In: Wuttig, M.R. (ed.), SPIE Smart Structures and Materials – Smart Materials Technologies, SPIE Conference Proceedings, SPIE, Vol. no. 3675, (1999), 22–31, Newport Beach, CA.
Walter-09	S. Walter, Fraunhofer-Institute IzfP Dresden, DGzfP-Jahrestagung 2009, poster.