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Alkaline niobate based lead-free ceramic fiber/polymer 1-3 composites: processing and electromechanical properties

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Abstract The 1-3 type lead-free piezofiber/epoxy composites were prepared using Li, Ta and Sb modified (Na, K)NbO_3 compositions as the ceramic phase by means of fiber arrangement and epoxy cast. The dense and smooth piezoelectric ceramic fibers with a diameter of 250 μm or less were fabricated by extruding plastic mud pie through micro-holes drilled in a hard mould by means of a laser-cutter. The dielectric, piezoelectric, electromechanical coupling properties and acoustic impedance characteristic of the as-prepared 1-3 composites with different ceramic volume fractions were characterized and compared with the theoretical values as well as those of monolithic ceramics. A nearly pure thickness vibration mode with a resonance frequency over 2 MHz (sample thickness ~1 mm) was formed, together with a high electromechanical coupling coefficient ($k_t \sim 0.55$–0.6), low acoustic impedances (Z ~ 9–14 MRayl) and relatively high piezoelectric voltage coefficient ($g_{33} \sim 30 \times 10^{-3}$ m^2/C). The results indicate that those composites have potential to be transducer elements in various applications.

1 Introduction

The 1-3 type piezoelectric ceramic/polymer composites have been used as transducers for medical ultrasonic imaging, whose properties can be tailored to combine high thickness electromechanical coupling coefficients and low acoustic impedances required for good matching with human tissues. Additionally, the elastic and piezoelectric properties of these composites can be also tuned by varying the ceramic volume fraction and periodicity to optimize the transducer performance. Their structures are usually involved in parallel arranged piezoceramic rods or fibers embedded in a polymer matrix. Pb(Zr, Ti)O_3 (PZT) based piezoelectric compositions have been widely used in the manufacture of 1-3 piezoelectric composites in the past decades owing to their excellent piezoelectric and electromechanical properties [1–3]. However, the toxicity of Pb has brought about concerns of environmental pollution such that the development of non-Pb piezoelectric materials has attracted much attention in recent years. Relevant research results indicate that the Li, Ta and Sb modified (Na, K)NbO_3 (NKN-LT-LS) compositions have great potential to substitute for PZT based materials for possible device application [4–6]. High piezoelectric properties, low density, low mechanical quality factor and comparable dielectric constant to that of PZT for NKN based piezoelectric ceramics demonstrate the applicability of NKN-based lead-free ceramics to 1-3 type composites for transducer applications.

Moreover, the periodicity of the composite determines the resolution of medical ultrasonic transducers, which requires the miniaturization of piezoelectric active elements in a 1-3 type piezocomposite. The methods for fabricating 1-3 piezocomposites mainly include dice-filling and arrange-casting [7–12]. Owing to the low mechanical strength and big brittleness, particularly for lead-free NKN based ceramics, high-quality flawless micro-scaled ceramic rods are difficult to process by a dice-fill method, for which high processing cost, big waste of materials and resultant

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pollution problems can not be ignored as well. By comparison, the fiber arrange-cast method is relatively simple and flexible in controlling the ceramic volume fraction, and easier for designing 1-3 composites satisfying different requirements. Chemical routes such as sol–gel processing were used to prepare ultra-fine ceramic fibers, however, their relatively low density and inhomogeneous diameter size tend to degrade the electrical properties of the composites to a certain degree [2, 13]. The mould-extrusion method is a conventional way to make fibers, while the size of fibers is usually large. Therefore, how to prepare dense, smooth and homogeneous ceramic fibers with micro-scaled diameters has become a key issue for the arrange-cast method.

A modified mould-extrusion method was used in this study to prepare NKN-LT-LS ceramic fibers by combining the optimization of the mud pie composition and the miniaturization of mould holes by means of a laser cutter. Subsequently, micro-scaled 1-3 NKN-LT-LS fiber/epoxy composites were fabricated. Their quasi-static and dynamic piezoelectric properties were characterized and compared with the theoretical models.

2 Experimental

NKN-LT-LS ceramic powder was prepared by a conventional solid state reaction method. Na_2CO_3 (99.8%), K_2CO_3 (99.0%), Li_2CO_3 (99.9%), Nb_2O_5 (99.5%), Ta_2O_5 (99.9%) and Sb_2O_3 (99.9%) were used as raw materials. After mixing in ethanol, the powder mixture was calcined twice at 850 °C for 5 h, followed by a ball milling for 24 h. Their compositions and detailed processing procedures can be referred to elsewhere [6]. NKN-LT-LS ceramic fibers were fabricated by extruding plastic mud pie composed of ball-milled ceramic powder, PVB binder and dibutyl ester phthalate in a certain mass ratio of 28–32:4:1. The diameter of green fibers was controlled by small holes on bottom of the stainless-steel extrusion mould. Those holes were made by a laser cutter such that the fibers with a diameter of 100–300 μm can be made depending on the mould material (for example, nylon mould for smaller holes) and the mud recipe. The surface quality of fibers was modified by adjusting the ratio of ceramic to PVB and the extrusion speed. After an appropriate burnout treatment, the as-prepared green fibers underwent a sintering process at 1,100 °C for 3 h to obtain dense and crack-free ceramic fibers. The NKN-LT-LS/epoxy 1-3 type piezocomposites were fabricated by inserting as-sintered ceramic fibers into a polymer tube, then filling it with epoxy E51, together with maleic anhydride as hardener and DOP as thinner, and finally solidifying at 180 °C for 4 h after degassing. The composite sheet was sliced using a diamond saw perpendicular to the direction of fibers, polished on both sides to the end of the fibers and then electroded with air-dried silver paste for electrical characterization. The composite samples were poled at 80 °C for 15 min under an electric field of 2.5 kV/mm in silicone oil.

Density of the samples was measured based on the Archimedes method. The morphology on the surface of the piezoelectric ceramic fibers and the cross section of the composite samples was observed by scanning electron microscopy (SEM, JEOL JSM-6490LV, Tokyo, Japan). The volume fraction υ of the ceramic phase in the composite was adjusted by changing the number of ceramic fiber in a certain cross-section area. The piezoelectric constant d_{33} was measured by a quasi-static Belincourt-meter (YE2730A, Sinocera, Yangzhou, China). The impedance and phase angle of the samples were measured by an impedance/grain phase analyzer (HP4194A). The mechanical quality factor, planar and thickness electromechanical coupling coefficient (k_p and k_t, respectively) and acoustic impedance Z were determined by a resonance and anti-resonance method on the basis of IEEE standards using the following formula:

$$Q_m = \frac{1}{2\pi f_s R_1 C^T \left(1 - \frac{f_s^2}{f_p^2}\right)} \tag{1}$$

$$k_t^2 = \frac{\pi f_s}{2f_p} \tan \frac{\pi \left(f_p - f_s\right)}{2f_p} \tag{2}$$

$$Z = \rho V^D \tag{3}$$

and

$$V^D = 2f_p t \tag{4}$$

where C^T is the free capacitance at 1 kHz, R_1 the real part of the resonance impedance, f_s the series resonance impedance, f_p is the parallel resonance impedance, t, ρ and V^D are the thickness and density of the composite sample and the spread speed of sound, respectively. The longitudinal coupling coefficient k_{33} was estimated from the thickness and planar coupling coefficients [14]:

$$k_{33}^2 = k_p^2 + k_t^2 - k_p^2 k_t^2 \tag{5}$$

3 Results and discussion

The SEM micrographs of the as-prepared ceramic fibers and 1-3 composites are shown in Fig. 1. The as-extruded green fibers look smooth with an identical size in diameter and do not have evident surface flaw, although the holes on the mould bottom are rather small (Fig. 1a). This can be achieved by adjusting the pushing load and speed, and the content of PVB binder. The post-sintered fibers exhibit

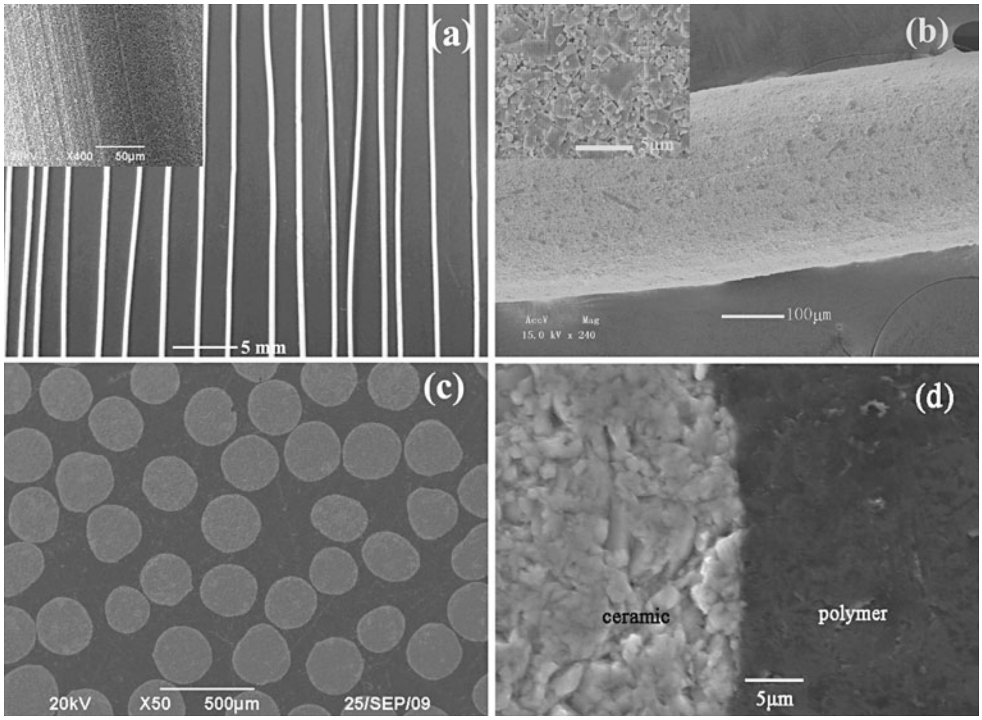

Fig. 1 The SEM images of **a** green fibers, **b** single sintered fiber, **c** the cross-section of as-prepared 1-3 composite and **d** the interface between NKN-LT-LS fiber and polymer. *Inserts* are locally magnified photos on the surface of single fiber

dense microstructure with an average grain size of 3–4 µm and good surface quality without detectable micro-cracks (Fig. 1b). Compared to ceramic rods made by cross-dicing, the fibers prepared by extruding plastic mud show advantages in terms of the surface quality. Figure 1c indicates the cross section of 1-3 NKN-LT-LS/epoxy composite where ceramic fibers are randomly distributed in a continuous polymer matrix. The ceramic fibers form good contacts with epoxy (Fig. 1d). No cracks or pores can be found at the interface. The adjustment of the epoxy resin content and the degassing procedure prove definitely necessary. The aspect ratio of 2–5 of ceramic fibers can be obtained by changing the thickness of 1-3 composite sheets. The 1-3 NKN-LT-LS/epoxy composites with a thickness of 1 mm were used in this study for further electrical characterization although it can be easily scaled down for various purposes. Furthermore, the diameter of fibers can be further reduced to ~ 100 µm by using different moulds in combination with a laser-assisted drilling technique. The relevant work is in progress.

In respect to the modified series and parallel model [15, 16], the theoretical properties of the composite can be expressed as a function of υ. Figure 2 shows the density ρ of 1-3 type piezoelectric composites as a function of the ceramic fiber fraction υ. It can be seen that the density of piezoelectric composites linearly increases with υ due to the increased contribution of the active ceramic phase. The experimental result is in good agreement with the theoretical prediction for an ideal biphasic composite using the formula: $\rho = \upsilon\rho_{\mathrm{NKN-LT-LS}} + (1-\upsilon)\rho_{\mathrm{epoxy}}$. In addition, the dielectric constant ($\varepsilon_r = \varepsilon_{33}^T/\varepsilon_0$), piezoelectric charge coefficient d_{33}, piezoelectric voltage coefficient g_{33}, electromechanical coupling coefficient k_t and acoustic impedance Z can be calculated using the following equations:

$$\varepsilon_{33}^T = \upsilon\varepsilon_{33,\mathrm{NKN-LT-LS}}^T - \upsilon(1-\upsilon)(d_{33,\mathrm{NKN-LT-LS}})^2/s(\upsilon) + (1-\upsilon)\varepsilon_{11,\mathrm{epoxy}} \quad (6)$$

$$d_{33} = \upsilon s_{11,\mathrm{epoxy}} d_{33,\mathrm{NKN-LT-LS}}/s(\upsilon) \quad (7)$$

$$g_{33} = d_{33}/\varepsilon_{33}^T \quad (8)$$

$$k_t = \sqrt{1 - c_{33}^E / c_{33}^D} \quad (9)$$

$$Z = \sqrt{\rho c_{33}^D} \quad (10)$$

where s is the elastic compliance of the composite ($s(\upsilon) = \upsilon s_{11,\mathrm{epoxy}} + (1-\upsilon)s_{33,\mathrm{NKN-LT-LS}}$), c is the elastic stiffness and ε_0 is the permittivity of vacuum (8.858×10^{-12} F/m).

The dielectric and piezoelectric constants of the NKN-LT-LS/epoxy 1-3 composites as a function of υ are shown in Fig. 3. Because the dielectric constant of bulk piezoelectric ceramics is far more than that of polymer, the dielectric constant of the composite can be evaluated as

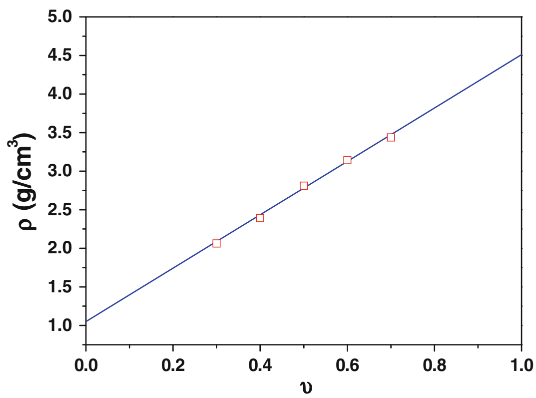

Fig. 2 Density of 1-3 piezoelectric composites as a function of ceramic fiber fraction (*Symbols* experimental data; *Line* theoretical calculation)

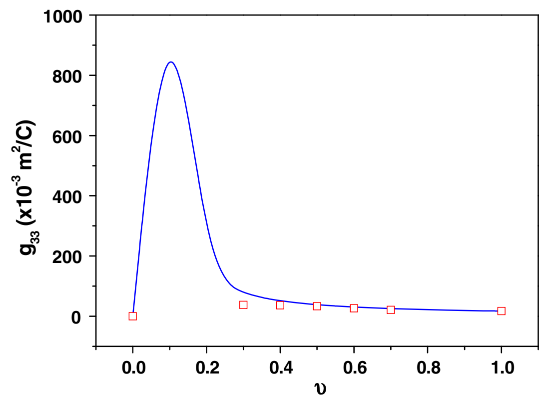

Fig. 4 Piezoelectric voltage constant g_{33} of the NKN-LT-LS fiber/epoxy 1-3 composites as a function of ceramic fiber fraction (*Symbol* experimental data; *Line* theoretical calculation)

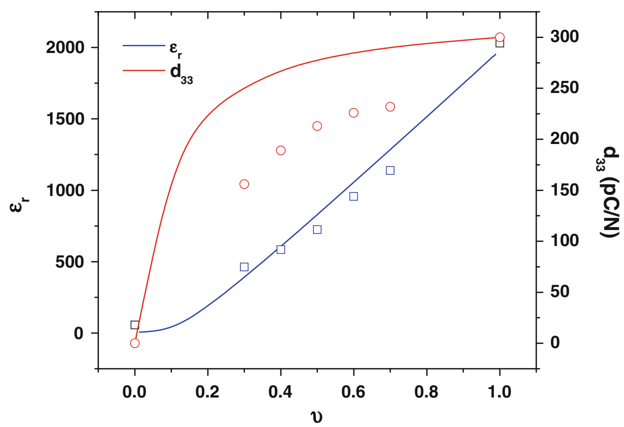

Fig. 3 Dielectric and piezoelectric constants of the NKN-LT-LS fiber/epoxy 1-3 composites as a function of ceramic fiber fraction (*Symbols* experimental data; *Line* theoretical calculation)

$\varepsilon_{33}^T = \upsilon\varepsilon_{33,\mathrm{NKN-LT-LS}}^T + (1-\upsilon)\varepsilon_{33,\mathrm{Epoxy}}^T \approx \upsilon\varepsilon_{33,\mathrm{NKN-LT-LS}}^T$, supposed that ceramic fibers have the same properties as the bulk ceramics. The dielectric and piezoelectric constant values of NKN-LT-LS bulk ceramics, rather than NKN-LT-LS fibers, were used in the theoretical calculation because the electrical properties are difficult to measure for slim ceramic fibers. It can be seen that the dielectric constant of the composite exhibits a linear relationship with υ. In contrast, the d_{33} value of the composite seems to have a quadratic function of υ. When $\upsilon < 0.2$, the d_{33} value of the composite rapidly increases with the increase of υ; however, almost constant values of d_{33} can be retained for $0.4 < \upsilon < 0.8$. Although they behavior differently with υ, it is still clear that the experimental values of both parameters have similar trends with υ to their theoretical values. Nevertheless, the measured values are slightly lower than the predicted ones, particularly for the d_{33} value of the composite. This could be ascribed to the following aspects: firstly, the density of piezoelectric ceramic fibers would not be as high as that of bulk ceramics, owing to that the fibers are involved in much more organic matters and less molding pressure than bulk ceramics during processing; secondly, the electric poling effect would be another reason. The NKN-LT-LS/epoxy 1-3 composites have larger loss values than those of monolithic ceramics, which makes the ceramic fibers relatively difficult to be poled owing to the formation of larger leakage current; thirdly, considering that ceramic fiber is slim and fragile, it would be possible to break during the preparation of the composite such that ceramic fibers are not completely connected through the whole thickness of the composite samples.

Figure 4 shows the piezoelectric voltage coefficient of the NKN-LT-LS/epoxy composite as a function of υ. It was known that the piezoelectric constant d_{33} characterizes the ultrasonic beam transmission capability of a transducer, while its echo receiving sensitivity is directly related to its longitudinal piezoelectric voltage coefficient g_{33}. The NKN-LT-LS lead-free ceramics used in this study have similar dielectric and piezoelectric constant values ($\varepsilon_r = 1{,}850$, $d_{33} = 300$ pC/N) as one of commercial PZT ceramics ($\varepsilon_r = 1{,}800$, $d_{33} = 400$ pC/N for APC 850 Ceramics). For the NKN-LT-LS/epoxy 1-3 composite with $0.4 < \upsilon < 0.8$, its d_{33} can be almost retained while ε_r linearly decreases with the decrease of υ, g_{33} of 1-3 composite samples is thus higher than that of monolithic ceramics. For the composite with $\upsilon = 0.6$, its $g_{33} = 30 \times 10^{-3}$ m^2/C, slightly better than that of commercial PZT ceramics. Higher g_{33} values imply an ability to detect low intensity ultrasound, leading to improved detecting sensitivity of the transducers. As expected, the thickness electromechanical coupling factor k_t of the NKN-LT-LS fiber/epoxy 1-3 composites can be effectively enhanced using the 1-3 connectivity mode as shown in Fig. 5. The k_t values of the composite can almost reach 0.6, which is much better than

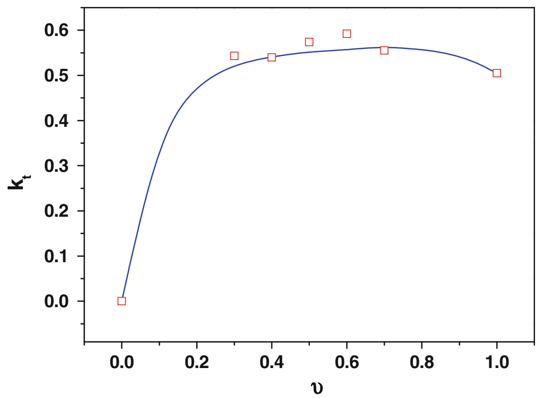

Fig. 5 Thickness electromechanical coupling factor k_t of the NKNLS fiber/epoxy 1-3 composites as a function of ceramic fiber fraction (*Symbols* experimental data; *Line* theoretical calculation)

that of bulk ceramic discs ($k_t \sim 0.5$) and comparable to its k_{33} value ($k_{33} \sim 0.62$). In the NKN-LT-LS fiber/epoxy 1-3 composites, each ceramic fiber can vibrate comparatively freely because of huge differences in the stiffness and compliance coefficients between ceramic fibers and epoxy, such that its longitudinal extension or contraction is almost not influenced by its radial distortion. Therefore, the thickness resonance of the composite samples is actually a coupling of the longitudinal vibration of each ceramic fiber. However, the bulk ceramic disc has a homogeneous polycrystalline structure and thus its thickness extension or contraction must be seriously restricted by its radial distortion. Moreover, each fiber could have slightly different length in the composite owing to the processing such that the resonance frequency of each fiber slightly differs, which tends to cause the broadening of the resonance frequency and a relatively high k_t value for a composite.

Figure 6 shows the impedance characteristic of the 1-3 NKN-LT-LS fiber/epoxy composite compared with monolithic NKN-LT-LS ceramics. It is obvious that the resonance mode is rather complicated for the monolithic NKN-LT-LS ceramics (Fig. 6a). There are many sub-resonance peaks around main resonance modes (typical radial resonance at ~370 kHz), which is prone to make the working modes being coupled and inefficient. By comparison, the harmonics of low-frequency resonance have been strongly weakened in the NKN-LT-LS/epoxy 1-3 composite (Fig. 6b). A pure thickness resonance mode with a resonance frequency of >2 MHz can be observed without significant mode coupling (for the sample thickness of 1 mm). Thereby the thickness-mode resonance becomes more evidently enhanced for the composite (Fig. 5). This is an important feature for ultrasonic transducer applications because it can improve the signal-to-noise of an ultrasonic transducer.

For ultrasonic imaging and hydrophone application, the acoustic impedance Z is another important dynamic performance parameter, which is related to the density ρ and sound velocity V^D of the composite samples. It can be seen from Fig. 7 that the Z value of the composites increases almost linearly with υ and fits well with the theoretical prediction. Bulk ceramics generally have higher acoustic impedances, particularly for commercially used PZT ceramics ($Z \sim 31$ MRayl). The acoustic impedance of NKN-LT-LS ceramics is relatively low ($Z \sim 28$ MRayl) because of their low densities, while the acoustic impedance of the human tissue and water are only 1.54 and 1.48 Mrayls, respectively. When sound wave propagates in such mediums, higher Z values usually cause much energy loss at interfaces of transducers and mediums. Therefore, the acoustic impedance of a transducer should closely match with that of mediums for strong acoustic coupling and minimization of the reflection from the transducer/medium interface. As can be seen from Fig. 7, the NKN-LT-LS fiber/epoxy 1-3 composites have much lower Z values (9–14 MRayl) than bulk ceramics due to the contribution of low acoustic impedance of epoxy, showing

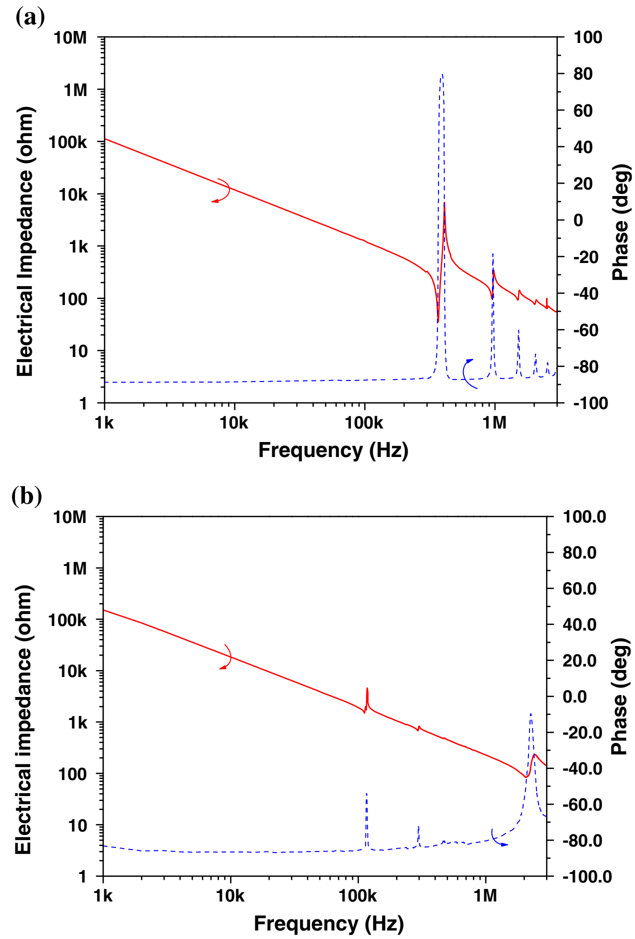

Fig. 6 Electrical impedance and phase versus frequency spectrum of **a** the monolithic NKN-LT-LS ceramics and **b** the NKN-LT-LS fiber/epoxy 1-3 composites with $\upsilon = 0.7$

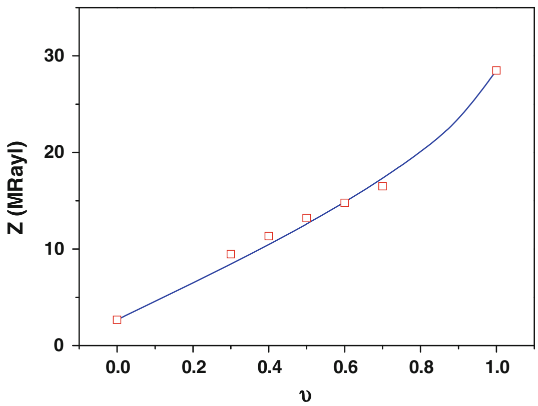

Fig. 7 Acoustic impedance *Z* of the NKN-LT-LS fiber/epoxy 1-3 composites as a function of ceramic fiber fraction (*Symbols* experimental data; *Line* theoretical calculation)

better matching with soft mediums. The 1-3 composites with suitable acoustic impedances can be obtained by changing the density of the composite (i.e., the ceramic volume fraction, see Fig. 2), when the characteristic impedance of the medium is known, which are favorable for ultrasonic biomedical imaging applications based on the enhanced acoustic impedance matching.

4 Conclusions

Lead-free NKN-LT-LS piezofiber/epoxy 1-3 composites were fabricated by arranging ceramic fibers and then casting epoxy resin. The improved processing of plastic mud pie and laser-assisted manufacture of micro-holes enable homogeneous and high-quality NKN-LT-LS ceramic fibers. The dielectric constant, piezoelectric voltage coefficient and acoustic impedance of the as-prepared 1-3 composites are measured as a function of the ceramic volume fraction and compared to the theoretical prediction. A clear thickness mode can be obtained for the composites (sample thickness $\sim$1 mm) with a resonance frequency of >2 MHz. The results indicate that the 1-3 composites reported in this study are environmentally friendly and suitable for high-frequency ultrasonic transducer applications.

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