High piezoelectric performance of novel 1–3-type lead-free composites

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The present report is devoted to the piezoelectric response of the 1–3 single crystal (SC) / polymer composite. As is known, the most commonly chosen as a piezoelectric component are the perovskite-type ferroelectric ceramics or relaxor-ferroelectric SCs [1], and the overwhelming majority of these components are lead-based materials. A new way of improving the effective electromechanical properties and applicability of piezoelectric composites may be concerned with use of a lead-free component with considerable piezoelectric activity. Recent studies [2] suggest that good candidates for composite components are SCs of ferroelectric niobate solid solutions, e.g. $[Li_x(K_{0.501}Na_{0.499})_{1-x}](Nb_{0.660}Ta_{0.340})O_3$ (KNN-TL) and $(K_{0.562}Na_{0.438})(Nb_{0.768}Ta_{0.232})O_3$ (KNN-T) with a large piezoelectric coefficient g_{33} that describes a piezoelectric sensitivity. The aim of our study is to show a performance of novel composites based on either KNN-TL or KNN-T SCs.

A prediction of effective electromechanical properties of the 1–3 SC / polymer composite with parallelepiped-shaped long SC rods (Fig. 1) enables us to analyse the piezoelectric coefficients and related parameters at volume fractions of the SC component $0< m< 1$. In connection with the large g_{33} value of the SC [2] we emphasise the piezoelectric coefficient g^*_{33} and its hydrostatic analogue $g^*_h = g^*_{33} + g^*_{32} + g^*_{31}$, squared figures of merit $(Q^*_{33})^2 = d^*_{33}\, g^*_{33}$ and $(Q^*_h)^2 = d^*_h\, g^*_h$, and hydrostatic electromechanical coupling factor k^*_h (Table 1), where d^*_{33} is the piezoelectric coefficient, and $d^*_h = d^*_{33} + d^*_{32} + d^*_{31}$ is its hydrostatic analogue. The polymer is piezo-passive with either a positive Poisson's ratio (polyurethane) or a negative one (auxetic polyethylene). While max g^*_{33} and max g^*_h are located at small volume fractions ($0< m < 0.025$) irrespective of polymer, we show data at

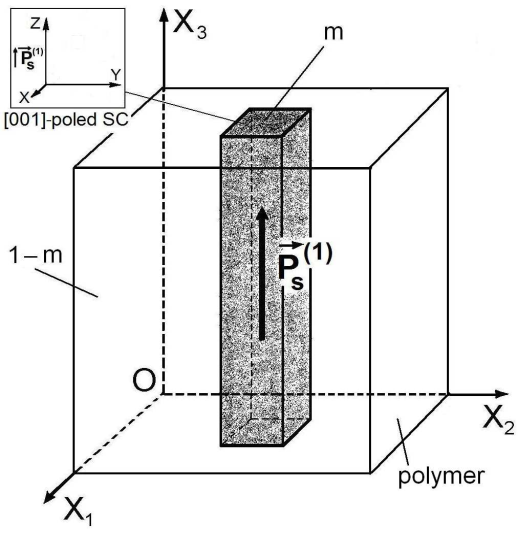

Fig. 1. Schematic of the 1–3 SC / polymer composite. $(X_1X_2X_3)$ is the rectangular co-ordinate system. m and $1 - m$ are volume fractions of SC and polymer, respectively, x, y and z are main crystallographic axes of SC. The spontaneous polarisation vector of the SC rod $\boldsymbol{P}_s^{(1)}$ is shown with the arrow. The SC rods with square bases are regularly distributed in the polymer matrix, and centres of symmetry of the bases form a simple square lattice in the (X_1OX_2) plane. Electrodes are to be applied parallel to the (X_1OX_2) plane.

Table 1. Effective parameters of the 1–3 SC / polymer composite ($0.05 \le m \le 0.15$) and SCs ($m = 1$)

SC	Polymer	m	g_{33}^*, mV·m/N	g_h^*, mV·m/N	$(Q_{33}^*)^2$, 10^{-12} Pa^{-1}	$(Q_h^*)^2$, 10^{-12} Pa^{-1}	k_h^*
KNN-TL	Polyurethane	0.05	627	142	97.9	5.03	0.135
		0.10	400	87.7	88.5	4.25	0.129
		0.15	291	61.3	74.7	3.32	0.118
	Auxetic polyethylene	0.05	888	1830	256	1080	0.439
		0.10	473	835	148	461	0.342
		0.15	322	496	104	247	0.280
	---	1	50.6	4.01	17.9	112	0.116
KNN-T	Polyurethane	0.05	839	188	78.7	3.93	0.120
		0.10	546	117	65.8	3.03	0.110
		0.15	397	81.3	52.9	2.22	0.0972
	Auxetic polyethylene	0.05	1130	2310	162	677	0.372
		0.10	622	1080	93.7	289	0.282
		0.15	429	656	66.0	154	0.227
	---	1	68.6	3.39	11.1	27.1	0.0571

Notes. 1. Room-temperature electromechanical constants of SCs and polymers were taken from Ref. 2 and Ref. 3, respectively. 2. The matrix method [1] was applied to calculate the full set of effective electromechanical constants of the 1–3 composite.

$m \ge 0.05$ to follow a manufacturing tolerance. Relatively small volume fractions of SC m do not lead to a significant decrease of the effective parameters (Table 1). The use of an auxetic polyethylene leads to larger values of all of the effective parameters listed in Table 1, and the hydrostatic response and electromechanical coupling become stronger because of $d_{32}^* > 0$ and $d_{31}^* > 0$: this peculiarity is due to positive elastic compliances of the polymer component. The data from Table 1 show that, in the case of the auxetic polymer, the effective parameters of the composite are much more than those related to a conventional 1–3 PZT ceramic / polymer composite [1, 3]. The lead-free 1–3 composites considered above can be suitable for piezoelectric sensor (large g_{33}^*), hydroacoustic (large g_h^*, $(Q_h^*)^2$ and k_h^*) and energy-harvesting applications (large $(Q_{33}^*)^2$ and k_h^*).

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