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Advanced composites based on relaxor-ferroelectric single crystals: From electromechanical coupling to energy-harvesting applications

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To determine the effective electromechanical properties and related parameters of the piezo-active composite with a specific microgeometry (see, for instance, Figs. 2 and 6 in the review paper), it is possible to apply averaging procedures[1-4] that allow for an electromechanical interaction in the composite sample. In a case of a regular distribution of components in the composite sample, the averaging procedure is based on one of the following methods: the effective field method (the Mori – Tanaka method[5] generalised for heterogeneous piezoelectric media[2,3]), the effective medium method,[4,6] the matrix method,[1,7] or the finite element method (FEM).[6,7] The effective field method and effective medium method are often regarded[2,3] as two self-consistent schemes of averaging. These methods are applicable to the 0–3 and 1–3 composites[1,6,7] with piezoelectric inclusions. The shape of the inclusions is either spheroidal (0–3 connectivity) or cylindrical (1–3 connectivity). The matrix method is applied to the composites with planar interfaces. The matrix method is often used to evaluate the effective properties of the composites with elements of 2–2 or 1–3 connectivity.[1,7] In addition, the dilute approach[2,6,7] is sometimes applied to predict the effective properties of porous piezo-active media (porous ferroelectric ceramics or composites) with a system of regularly distributed air inclusions in the form of a spheroid. In this case no electromechanical interaction between the isolated air inclusions takes place, and the porous composite is described by 3–0 connectivity.

The effective electromechanical properties of a matrix composite (such as the 1–3 composite in Fig. 6) are represented in the general form[4,6,7] as

$$|| C^* || = || C^{(2)} || + m\,(|| C^{(1)} || - || C^{(2)} ||)\,|| A ||,$$

where $|| C^{(n)} ||$ is the 9 × 9 matrix of the electromechanical properties of the RFSC (n = 1) and the surrounding polymer medium (n = 2), m is the volume fraction of the RFSC, and $|| A ||$ is the mechanical strain – electric field concentration matrix that strongly depends on the properties of the components and boundary conditions for mechanical and electric fields in the composite.

The process of FEM is used[6,7] to carry out an independent evaluation of the effective properties and related parameters of the RFSC-based composites and to compare the FEM data with those related to other methods. Below we show our results on the effective piezoelectric properties and related parameters of the studied RFSC-based composites (Tables S1–S3).

Table S1 comprises data on the 1–3-type composites (Fig. 6) with auxetic polymer matrices. The presence of the polymer component with the negative Poisson's ratio strongly influences the piezoelectric properties of the composite at $m < 0.4$, i.e., where the volume fraction of the polymer matrix is relatively large. This influence leads, for instance, to a non-monotonic volume-fraction dependence of the piezoelectric coefficient $d_{31}^*(m)$ (see the 2nd column of Table S1) and to a fairly wide volume-fraction range where $d_{31}^*(m) > 0$. The positive sign of d_{31}^* promotes large values of such hydrostatic parameters as d_h^*, g_h^* and $(Q_h^*)^2$. This is the obvious advantage of the 1–3-type RFSC / auxetic polyethylene composites over the 1–3 RFSC / polymer composites wherein the polymer matrix is characterised by a positive Poisson's ratio. It should be noted that the volume fraction m^*, at which the condition $d_{31}^*(m^*) = 0$ holds, depends on ratios of elastic constants of the components. For the composites listed in Table S1, one can state that $0.25 < m^* < 0.40$. Data from Table S1 suggest that the largest hydrostatic piezoelectric coefficient d_h^* is achieved for the composite based on the PMN–0.33PT RFSC. This RFSC exhibits the larger piezoelectric coefficient $d_h^{(1)}$ among the components poled along [001] (see Table 1). The inequality $[Q_h^*(m)]^2 > [Q_{33}^*(m)]^2$ holds in volume-fraction ranges (see Table S1) wherein the role of the auxetic polymer component is dominating.

In Table S2 we show examples of volume-fraction dependences of some effective parameters of the 1–2–2 composites. The schematic of the 1–2–2 RFSC / polymer-1 / polymer-2 composite is shown in Fig. 10. The results obtained by means of the matrix method and FEM are consistent at various volume fractions m and m_s. In contrast to the $d_{31}^*(m)$ dependences shown in Table S1, now we see the monotonic $d_{31}^*(m)$ dependences and $d_{31}^*(m) < 0$ (see the 3rd and 7th columns in Table S2). This behaviour is accounted for by the presence of the polymer components with positive Poisson's ratios. As a consequence, the hydrostatic parameters d_h^*, g_h^* and $(Q_h^*)^2$ decrease in comparison to those from Table S1. It is also seen that the electromechanical coupling factor k_{33}^* related to the longitudinal oscillation mode undergoes minor changes when replacing the polymer components at the fixed values of m and m_s (see Table S2). This is due to the important role of the anisotropic elastic properties of the laminar matrix of the 1–2–2 composite in forming its electromechanical coupling. It should be added that the k_{33}^* values of the composite (Table S2) are about (0.8–0.9) $k_{33}^{(1)}$ of the PMN–0.33PT RFSC.

Table S1. Volume-fraction dependences of piezoelectric coefficients d_{31}^*, d_{33}^* and d_h^* (in pC /N), g_{31}^*, g_{33}^* and g_h^* (in mV·m / N), and squared figures of merit $(Q_{33}^*)^2$ and $(Q_h^*)^2$ (in 10^{-12} Pa^{-1}) of 1–3-type composites based on [001]-poled RFSCs, FEM calculations

m	d_{31}^*	d_{33}^*	d_h^*	g_{31}^*	g_{33}^*	g_h^*	$(Q_{33}^*)^2$	$(Q_h^*)^2$
PMN–0.28PT / auxetic polyethylene								
0.01	517	664	1700	1590	2040	5220	1350	8870
0.03	608	887	2100	523	763	1810	677	3800
0.05	576	955	2110	282	468	1030	447	2170
0.07	523	992	2040	178	338	694	335	1420
0.10	438	1030	1910	102	239	443	246	846
0.15	305	1060	1670	46.0	160	252	170	421
0.20	190	1080	1460	21.2	120	162	130	237
0.30	5.11	1110	1120	0.371	80.5	81.2	89.4	90.9
0.50	–244	1150	662	–10.3	48.8	28.2	56.1	18.7
0.70	–406	1170	358	–12.1	34.9	10.7	40.8	3.83
0.90	–523	1180	134	–12.0	27.1	3.1	32.0	0.415
PMN–0.33PT / auxetic polyethylene								
0.01	592	758	1940	2280	2920	7480	2210	14500
0.03	894	1300	3090	800	1160	2760	1510	8530
0.05	929	1530	3390	437	720	1590	1100	5390
0.07	892	1670	3450	278	521	1080	870	3730
0.10	789	1820	3400	161	371	693	675	2360
0.15	587	1980	3150	74.0	250	398	495	1250
0.20	387	2100	2870	34.7	189	258	397	740
0.30	31.1	2280	2340	1.73	127	130	290	304
0.50	–51.2	2520	2420	–1.57	77.1	74.0	194	179
0.70	–904	2670	862	–18.7	55.3	17.9	148	15.4
0.90	–1210	2780	360	–18.8	43.1	5.5	120	1.98
PZN–0.08PT / auxetic polyethylene								
0.01	531	681	1740	2140	2740	7020	1870	12200
0.03	820	1200	2840	803	1180	2790	1420	7920
0.05	859	1430	3150	446	742	1630	1060	5130
0.07	827	1580	3230	285	545	1120	861	3620
0.10	731	1730	3190	164	389	720	673	2300
0.15	537	1900	2970	74.6	264	413	502	1230
0.20	340	2040	2720	33.6	201	268	410	729
0.30	–16.4	2240	2210	–0.999	136	134	305	296
0.50	–576	2510	1360	–19.1	83.2	45.0	209	61.2
0.70	–992	2700	716	–22.1	60.1	15.9	162	11.4
0.90	–1320	2830	190	–21.9	46.9	3.1	133	0.589

Data from Table S3 allow a comparison of the piezoelectric performance of the 1–2–2 composites wherein the RFSC rods are in the form of either a rectangular parallelepiped or circular cylinder. We observe small differences between the values of d_{31}^* evaluated for the related 1–2–2 composites with the regular rod arrangement, however these differences do not lead to considerable changes in the hydrostatic parameters, especially at volume fractions of the RFSC at $m < 0.30$.

Finally, the results shown in Tables S1–S3 can promote the manufacturing of novel advanced piezo-active composites with effective parameters from specific ranges of volume fractions.

References

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Table S2. Effective piezoelectric coefficients d^*_{31}, d^*_{33} (in pC /N), g^*_{31}, g^*_{33} (in mV·m / N) and electromechanical coupling factor k^*_{33} of 1–2–2 composites based on the [001]-poled PMN–0.33PT RFSC

m_s	m	d^*_{31} [a]	d^*_{33} [a]	g^*_{33} [a]	k^*_{33} [a]	d^*_{31} [b]	d^*_{33} [b]	g^*_{33} [b]	k^*_{33} [b]
PMN–0.33PT / araldite / polyethylene (m_s is the volume fraction of araldite in the laminar matrix)									
0.10	0.15	–394	1820	247	0.935	–397	1820	247	0.935
	0.20	–484	2030	188	0.941	–486	2030	188	0.941
	0.25	–562	2180	152	0.945	–565	2180	152	0.945
0.15	0.15	–369	1780	246	0.934	–371	1780	246	0.934
	0.20	–454	1990	188	0.940	–458	1990	187	0.940
	0.25	–536	2150	151	0.944	–538	2140	151	0.944
0.20	0.15	–349	1750	246	0.932	–352	1740	246	0.932
	0.20	–436	1960	187	0.939	–438	1950	187	0.939
	0.25	–517	2120	151	0.943	–518	2120	151	0.943
0.25	0.15	–334	1710	245	0.931	–337	1710	245	0.931
	0.20	–420	1920	186	0.938	–423	1920	186	0.938
	0.25	–499	2080	151	0.943	–502	2080	151	0.943
PMN–0.33PT / polyurethane / polyethylene (m_s is the volume fraction of polyurethane in the laminar matrix)									
0.10	0.15	–453	1850	248	0.936	–456	1850	248	0.936
	0.20	–543	2060	188	0.942	–546	2050	188	0.942
	0.25	–623	2200	152	0.946	–625	2200	152	0.946
0.15	0.15	–439	1820	247	0.935	–442	1820	247	0.935
	0.20	–528	2030	188	0.941	–531	2030	188	0.941
	0.25	–607	2180	151	0.945	–610	2180	152	0.945
0.20	0.15	–428	1790	247	0.934	–431	1790	247	0.934
	0.20	–517	2000	188	0.941	–520	2000	188	0.940
	0.25	–597	2160	151	0.945	–599	2160	151	0.945
0.30	0.15	–412	1730	245	0.932	–415	1730	245	0.932
	0.20	–501	1950	187	0.939	–504	1950	187	0.939
	0.25	–580	2110	151	0.943	–583	2110	151	0.943

[a] Calculated by means of the matrix method for the 1–3-type composite structure

[b] Calculated by means of FEM for the 1–3-type composite structure

Table S3. Effective piezoelectric coefficients d_{31}^*, d_{33}^*, d_h^* (in pC / N), g_{33}^* and g_h^* (in mV·m / N)[a] of the 1–2–2 PMN–0.33PT / araldite / polyethylene composite

m	0.03	0.05	0.10	0.15	0.20	0.30	0.50	0.70
SC rods in the form of the rectangular parallelepiped with the square base, volume fraction of araldite in the laminar matrix m_s = 0.15								
d_{31}^*	–101	–156	–273	–371	–458	–612	–865	–1070
d_{33}^*	667	970	1470	1780	1990	2260	2540	2690
g_{33}^*	988	661	359	246	187	127	77.0	55.3
d_h^*	465	658	924	1040	1070	1040	810	550
g_h^*	689	448	226	144	101	58.4	24.6	11.3
SC rods in the form of the circular cylinder, volume fraction of araldite in the laminar matrix m_s = 0.15								
d_{31}^*	–100	–155	–271	–367	–453	–604	–862	–1100
d_{33}^*	667	971	1470	1790	1990	2260	2540	2690
g_{33}^*	988	661	359	246	188	127	77.0	55.3
d_h^*	467	661	928	1050	1080	1050	816	490
g_h^*	692	450	227	145	102	59.0	24.7	10.1
SC rods in the form of the rectangular parallelepiped with the square base, volume fraction of araldite in the laminar matrix m_s = 0.20								
d_{31}^*	–92.1	–144	–256	–352	–438	–592	–849	–1060
d_{33}^*	639	935	1430	1740	1950	2230	2520	2680
g_{33}^*	975	655	358	246	187	127	77.0	55.3
d_h^*	455	647	918	1040	1070	1050	822	560
g_h^*	694	453	230	147	103	59.8	25.1	11.6
SC rods in the form of the circular cylinder, volume fraction of araldite in the laminar matrix m_s = 0.20								
d_{31}^*	–91.7	–143	–254	–348	–433	–585	–847	–1090
d_{33}^*	640	936	1430	1750	1960	2230	2530	2670
g_{33}^*	975	655	358	246	187	127	77.0	55.3
d_h^*	457	650	922	1050	1090	1060	836	490
g_h^*	696	455	231	148	104	60.4	25.4	10.1

[a] Calculated by means of the matrix method (2–2 laminar matrix) and by means of FEM (1–3-type composite structure)