Ceramics International 30 (2004) 69–74

CERAMICS
INTERNATIONAL

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Piezoelectric composites with 3-3 connectivity by injecting polymer for hydrostatic sensors

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Received 5 July 2002; received in revised form 24 December 2002; accepted 24 February 2003

Abstract

Three kinds of polymer materials, with varying hardness, were injected into porous PZT fabricated by the conventional sintering process to form a PZT/polymer composite with the majority of 3-3 connectivity. Such properties as the dielectric constant, the coupling factor, and the hydrostatic piezoelectric constants were studied. The effect of the polymer hardness on the properties of the composites also was investigated. Although the porous PZT exhibited much higher hydrostatic piezoelectric coefficient than conventional PZT and PZT/polymer composite, it is fragile for the processes such as silver pasting, electrical poling, and so on. The PZT/Polymer composite demonstrated a more promising mechanical strength than porous PZT. The mechanically soft polymer showed less degraded effects on the hydrostatic piezoelectric coefficient than the hard polymer.

Keywords: B. Porosity; D. PZT; PZT/polymer composite

1. Introduction

One of the most impressive applications of piezoelectric ceramics was lead–zirconate–titanate (PZT) sonar transducers. PZT ceramics are suitable for high-powered underwater acoustical transmitter because of their high electromechanical coupling factor and superior piezoelectric properties, as well as their excellent dielectric properties. However, they are not suitable for hydrophone devices, the hydrostatic coefficient ($d_h = d_{33} + 2d_{31}$) of most PZT ceramics is small because the d_{31} coefficient is opposite in sign to the d_{33} coefficient.

In recent years, investigators have dedicated much effort to the development of PZT composite materials. Newnham et al. [1] found that 3-3 connectivity of a diphasic composite PZT demonstrated particular promise for piezoelectric transducer applications. Subsequently, Skinner et al. [2] developed a 3-3 connectivity transducer of $Pb(Zr_{0.52},Ti_{0.48})O_3$ associate with a silicone rubber that possessed a high voltage output coefficient (g_h-constant). The replamine form process [3] is a promising method for fabricating the 3-3 coral type of PZT/polymer composite. But Nagata et al. [4] proposed a more readily producible type of PZT composite transducer with a regularly controlled structure consisting of a ladder matrix. Specimens with porosities ranging from 40 to 60% also possessed an improved g_h constant of 90×10^{-3} V, m/N.

Theoretically, reduction of the lateral bonding in PZT ceramics should reduce the contributions of d_{31}, the so-called anisotropic piezoelectric phenomenon, for improving the hydrostatic sensitivity of the materials.

In the present study, porous PZT ceramics and PZT/polymer composites were prepared by a modified conventional powder sintering method. The properties of the specimens were investigated, and those results are discussed here. The effects of polymer hardness on the properties required for underwater hydrostatic transduction applications also were evaluated experimentally.

2. Experimental

The procedure for preparing piezoelectric composites was shown in Fig. 1. PbO, TiO_2, ZrO_2, and Nb_2O_5 raw materials with purity grade above 99.5% were weighted

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doi:10.1016/S0272-8842(03)00064-6

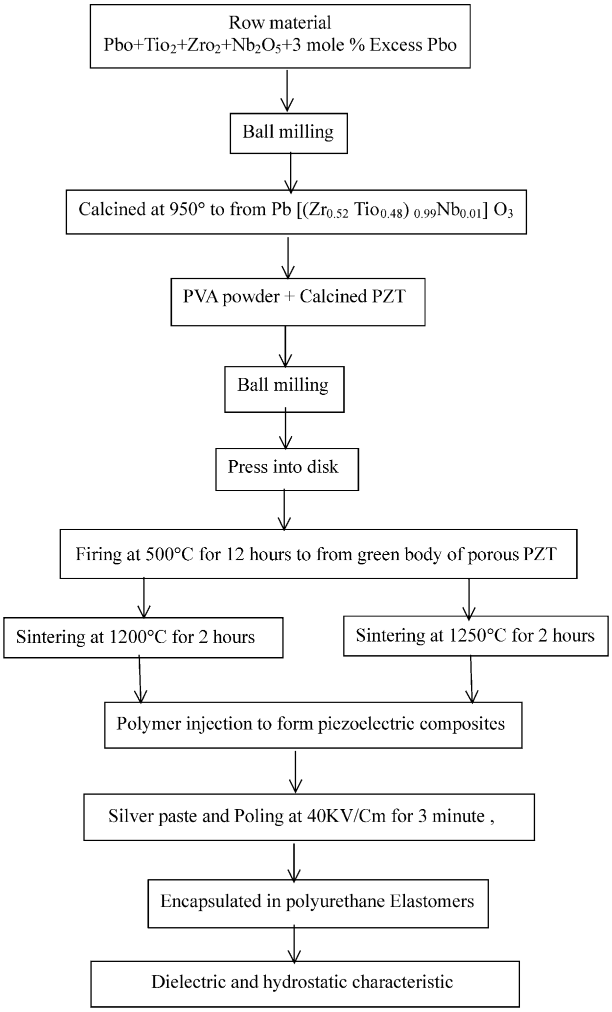


Fig. 1. Procedure for preparing piezoelectric composites.

and mixed by ball milling. A 3 mol% excess of PbO was added to the mixed powder to aid the calcining and help compensate the PbO deficiency. The powder was encapsulated in an alumina crucible and calcined at 950 °C for 2 h to form the composition $Pb[(Zr_{0.52}Ti_{0.48})_{0.99}Nb_{0.01}]O_3$. The calcined ceramic powder then was mixed with polyvinyl alcohol (PVA) powder and pressed into disk-shaped specimens. Next, the specimens were heated at a very slow rate (50 °C/h) to 500 °C and maintained at this temperature for 12 h to burn out the PVA phase and produce a green body with porous structure.

The green bodies of the specimens were brittle and easily broken. To become ceramics and increase the mechanical strength of those specimens, the samples were stacked in a hermetically sealed alumina crucible and sintered at a temperature, normally higher than 1100 °C, for more than 2 h in a PbO atmosphere. By comparison, 1200 and 1250 °C were chosen as the sintering temperature, individually. The pore size and density of the porous ceramics could be controlled by adjusting the amount of PVA powder in the burn out process at 500 °C and the sintering temperature in the sintering process at either 1200 or 1250 °C. The density and porosity of the samples were measured by the Archimedes method using a balance density measurement kit (type AEU-210, Shimadzu Co., Kyoto) with carbon tetrachloride as a dipping fluid.

The PZT/polymer composite was obtained by injecting three different liquid polymers into the opened pores of the porous specimens in a vacuum chamber and curing at 80 °C for 12 h. The properties of the injected polymers are list in Table 1. Polymers A and B are made of PU Elastomer (TU-4010, Conap, USA). The TU-4010 is composed of four chemical compounds. The hardness of the polymers is designed by modifying the compositions of the hardener compound, respectively. Polymer C is harder than polymer B, and polymer B is harder than polymer A. The hardness is measured by shore A durometer and shown in Table 1. After the PZT/polymer samples had been polished, silver paste was applied onto their surfaces and dried in air for more than 2 h. The porous PZT ceramics and the PZT/polymer composite specimens were poled in silicone oil at 100 °C by applying a dc field of 40 kV/cm for 30 min. The dielectric constant (ε_r), the coupling factor of the thickness vibration mode (k_t), and the coupling factor of the radial vibration mode (k_p) then were evaluated using a computer-controlled impedance analyzer (model HP4192, Hewlett-Packard Co.). The k_t and is expressed as [5]

$$K_t^2 = 1 - \left(\frac{f_{st}}{f_{pt}}\right)^2, \tag{1}$$

where f_{st} is the resonance frequency and f_{pt} is the anti-resonance frequency of the samples vibrating at thickness-vibration mode. The k_p is calculated by

$$K_p^2 = 1 - \left(\frac{f_{sr}}{f_{pr}}\right)^2, \tag{2}$$

Table 1
Mechanical and dielectric properties of injected polymers

Material	Polymer	Density (g/cm^3)	Hardness of polymer	Dielectric constant (at 1 kHz)
TU-4010 (Conap Inc. USA)	A	1.4	Shore A 20	4.7
TU-4010 (Conap Inc. USA)	B	1.4	Shore A 30	4.7
Araldite 1300/Series (Nan-Pao Chemistry Inc. Taiwan)	C	1.2	Shore A 60	8.2

where f_{sr} is the resonance frequency and f_{pr} is the anti-resonance frequency of the samples vibrating at radial-vibration mode. The piezoelectric strain coefficient (d_{33}) were measured with a piezo d_{33} meter (Berlincourt piezo meter, model CADT-3300, Channel Products Inc.) at 100 Hz. The porous PZT ceramics and the PZT/polymer composite specimens were encapsulated in polyurethane Elastomers (Adiprene L-100, Uniroyal Inc.) to form water-resistance hydrophone devices.

The hydrophone device was placed in a water chamber and hydrostatic piezoelectric coefficients (d_h, g_h) were measured by the reciprocity method at 1 kHz. The d_h coefficient was measured by changing hydraulic pressure in the water chamber at a rate of 50 psi/s and collecting the charge with a Digital Electrometer (model TR8652, Advantest Co.). The electrometer was in a feedback mode which maintains nearly zero sample potential. The charges produced from the sample were buffered with an impedance converter, and the voltages produced were measured on a Hewlett-Packard 3585A spectrum analyzer. The ratio of the voltages produced is proportional to the g_h coefficients. By accounting for the sample geometries and the stray capacitance of the holder, the d_h and g_h coefficient of the sample was calculated. The d_h is expressed as

$$V\times\left(1/C_{\text{sample}} + 1/C_{\text{stray}}\right)^{-1}/F, \tag{3}$$

where V is voltage reading from Hewlett-Packard 3585A, C_{sample} is capacitance of specimen, C_{stray} is stray capacitance of the holder and F is hydrostatic pressure applied on the specimen.

The g_h is expressed as

$$\left(V\times\left(1/C_{\text{sample}} + 1/C_{\text{stray}}\right)^{-1}/C_{\text{sample}}\right)/F \tag{4}$$

The piezoelectric strain coefficient (d_{31}) were evaluated by the expression

$$d_h = d_{33} + 2d_{31}. \tag{5}$$

The sensitivity of the devices were evaluated in a water tank lined with an automatic testing system which is composed of a couple of Hewlett-Packard instruments and a personal computer.

3. Results and discussion

Fig. 2 shows the porosity and the density in relation to the percentage of PVA, after the specimens had been burned at 500 °C for 12 h and sintered at 1200 or 1250 °C, separately. As the PVA content in the calcining powder increased, the porosity of the green body increased, but the density decreased. For the fixed PVA content, the porosity of the green body is larger than those of sintered specimen, and that of the 1200 °C sintered specimen is larger than that of the 1250 °C sintered specimen, but the relations of density is inverse. The porosity of the 1250 °C sintered samples also increases as the PVA content increases, but decreases when the PVA content is more than 26%, which phenomena is due to the collapse of the interior structure in the specimens. The 1250 °C sintering show stronger densification reaction between grains than the 1200 °C does. However, the structure of the sintered specimens became less brittle and easier to handle as the sintering temperature increased. Since the structure of the specimens do not collapses at 1200 °C sintering process, the 1200 °C sintering process was chosen for fabricating porous PZT ceramics for hydrophone devices.

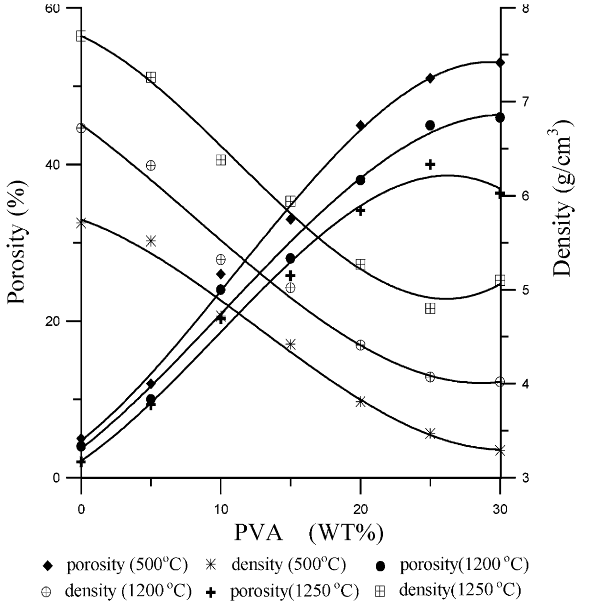
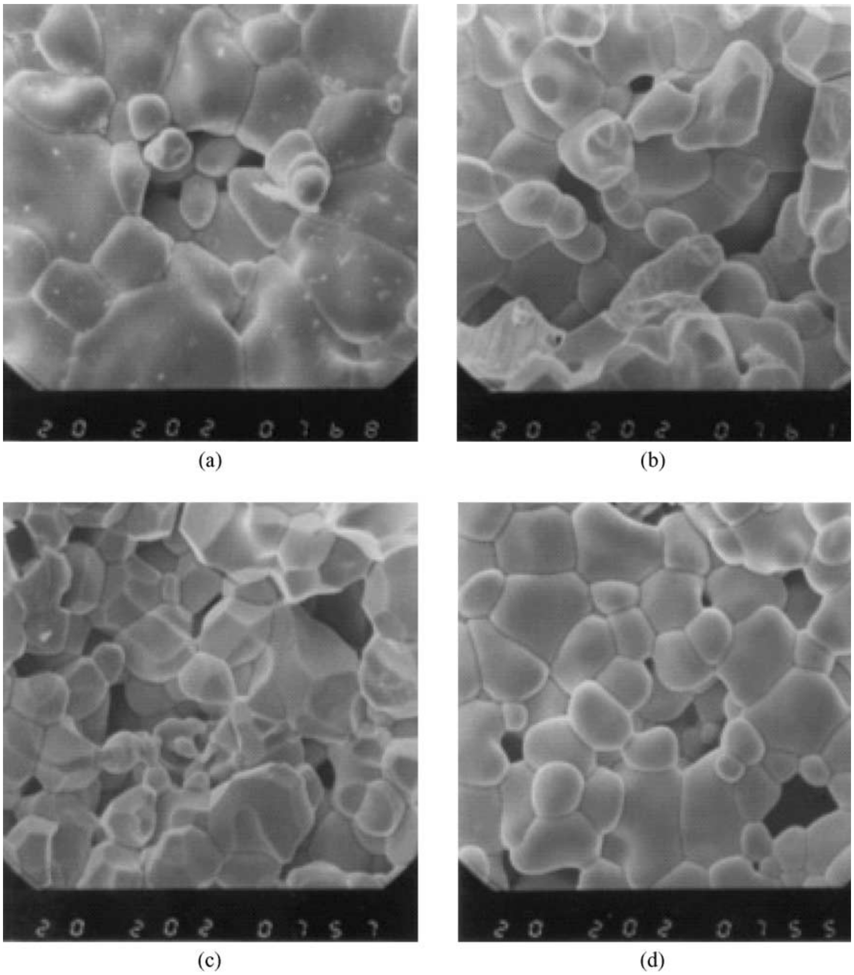


Fig. 2. Porosity and density related to PVA (wt.%) of porous PZT ceramics.

The ceramic grains with 10 and 20% PVA sintered at both 1200 and 1250 °C to form porous PZT are shown in Fig. 3. Fig. 3 shows that high PVA content will result in high porosity. There are still closed pores (3-0 connectivity) in the composite, especially for the low-porosity composites. As the porosity increasing, the 3-3 connectivity will become dominate. The dielectric and piezoelectric properties of the porous PZT ceramics are shown in Figs. 4 and 5. In Fig. 4, the relative dielectric constant (ε_r) decreases dramatically in accordance with the increase in porosity. Although the piezoelectric coefficient d_{33} decreases in relation to the increasing porosity, g_{33} is inclined to increase owing to the lower dielectric constant.

The hydrostatic piezoelectric coefficient d_h, shown in Fig. 5, increases depended on the increase in porosity. The improved hydrostatic coefficient d_h can be interpreted as the increasing anisotropic piezoelectric effect and the decreasing dielectric constant on the specimens,



(a) (b)

(c) (d)

Fig. 3. The grain structure of the porous ceramics related to percentage of PVA added and sintering temperature. (a) 10% PVA added and sintered at 1200 °C; (b) 20% PVA added and sintered at 1200 °C; (c) 10% PVA added and sintered at 1250 °C; (d) 20% PVA added and sintered at 1250 °C.

and this anisotropic piezoelectric phenomenon is evident in the great difference between thickness coupling factor (k_t) and radial coupling factor (k_p). The dielectric and piezoelectric properties of the 45% porous PZT ceramics and the PZT/polymer composites prepared from that porous PZT ceramics are shown in Table 2. In the same time, the data for conventional PZT ceramics also are included in this table, for references. For comparison, each measured data of piezoelectric composite in Table 2 is normalized by the data of dense PZT(S1) individually, and is shown in Fig. 6. As expected, the dielectric constants of the porous PZT ceramics and the

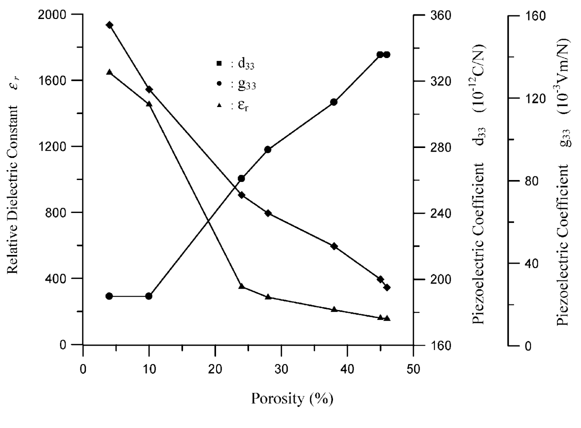


Fig. 4. Dielectric and piezoelectric properties of porous PZT.

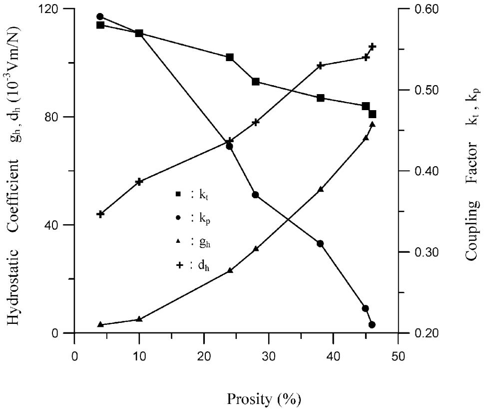


Fig. 5. Hydrostatic and coupling factors of porous PZT.

Table 2
Mechanical and ferroelectric properties of the 45% porosity porous PZT ceramics and PZT/polymer composite

	Properties							
	1	2	3	4	5	6	7	8
Type	Density (g/cm^3)	ε_r	d_{33} (10^{-12} C/N)	g_{33} (10^{-3} Vm/N)	d_h (10^{-12} C/N)	g_h (10^{-3} Vm/N)	k_t	k_p
dense PZT (S1)	6.72	1647	354	24	44	3	0.58	0.59
porous PZT (S2)	4.07	160	200	141	102	72	0.48	0.23
PZT/polymer A (S3)	4.57	101	165	184	60	67	0.26	0.11
PZT/polymer B (S4)	4.60	98	164	188	49	57	0.25	0.12
PZT/polymer C (S5)	4.47	83	160	217	10	13	0.24	0.17

PZT/polymer composites were considerably lower than those of the conventional PZT ceramics. The d_{33} values of the PZT/polymer composites were lower than those of the porous PZT ceramics and the conventional PZT ceramics because the existence of the non-piezoelectric polymeric phase.

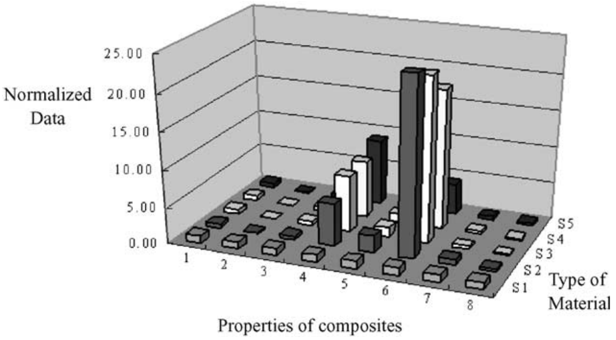
The porous PZT ceramics possessed a predictable higher hydrostatic coefficient (d_h, g_h) than the conventional PZT ceramics, because the porous specimens were more compliant that contribute to decrease the d_{31} and the dielectric constant. The PZT/polymer composite with polymers A and B exhibited higher g_h constants than did that with polymer C, since polymers A and B were polymeric phase possessing damping characteristics, whereas polymer C was a stiffener. The coupling factors of both the thickness vibration mode (k_t) and the radial vibration mode (k_p) in the PZT/polymer composite were lower than those of the porous PZT ceramics and the conventional PZT ceramics.

In the PZT/polymer composites, the k_t value seemed relatively unaffected by the various polymeric phases. The k_p value, however, increased when the impregnated polymeric phase become harden experimentally. The higher the k_p, the better the lateral bonding in the specimens, so that the contributions of d_{31} decreasing become dominated and lead to the degradation of the hydrostatic piezoelectric coefficients of the hydrophone devices.

From a theoretical viewpoint, g_h is related to d_h by [6]

$$g_h = d_h/\varepsilon_{33} \qquad (6)$$

The constant g_h of the porous PZT ceramics and the PZT/polymer composite with polymers A and B could be attributed to the poisson's effect and dielectric constant attenuation [7]. On the other hand, the PZT/polymer composite with polymer C shows a degradation in the constant g_h [8] because of increased lateral bonding in the materials.



1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Density (g/cm^3)	ε_r	d_{33} **(10^{-12} C/N)**	g_{33} **(10^{-3} Vm/N)**	d_h **(10^{-12} C/N)**	g_h **(10^{-3} Vm/N)**	k_t	k_p

S1	**S2**	**S3**	**S4**	**S5**
dense PZT	**porous PZT**	**PZT/ polymer A**	**PZT/ polymer B**	**PZT/ polymer C**

Fig. 6. Normalized properties of PZT/polymer composite.

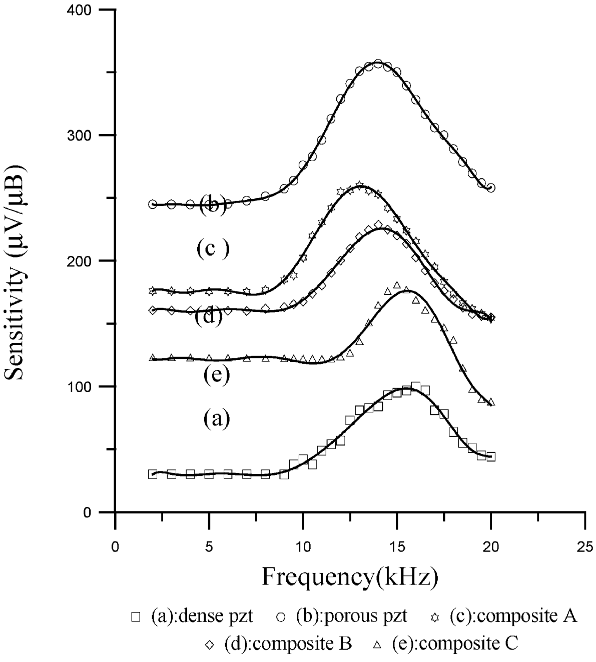


Fig. 7. Sensitivity of the hydrophone using conventional PZT ceramics, porous PZT ceramics and PZT/polymer composites.

The sensitivity profiles of the hydrophone devices in Fig. 7 show good agreement with the constant g_h obtained previously. Hydrophone devices made of porous PZT ceramics and PZT/polymer composites demonstrated larger 3 dB bandwidth than those fabricated by conventional PZT ceramics in regard to low density, thus providing good impedance matching with water. In this case, high temperature sintering did not improve the sensitivity of the hydrophone devices; however it did provide an effective method for modifying the density of the specimens, which could lead to acoustical properties suitable for medical ultrasonic transducers [9].

4. Conclusion

Procedures for fabricating porous PZT ceramics and PZT/polymer composites with the majority of 3-3 connectivity are described in the present paper. The porous structure increases the anisotropic piezoelectric coefficients, which can be confirmed by the discrepancy between the thickness (k_t) and the radial coupling factor (k_p), and contributes to improving the hydrostatic properties of underwater devices. The hydrostatic properties of the PZT/polymer composites tend to diminish as the polymer phase hardens. The PZT/polymer composites with soft polymer-phase could act as a sensitive hydrophone device.

Acknowledgements

This research was support by the National Science Council of Republic of China, under grant No. NSC91-2626-E-272-004.

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