論 文
36~5~5

공침법을 이용한 $PbTiO_3$–Polymer 0–3 압전 Composites.

Co – Precipitation Derived $PbTiO_3$ – Polymer 0 – 3 Piezoelectric Composites.

李 永 熙*
(Young–Hie Lee)

요 약

공침법으로 만든 $PbTio_3$분말을 이용하여 0 – 3Composite변환소자를 제작하였다. $Pb(NO_3)_2$와 $TiCl_4$를 원료로 사용하여 공침법으로 만든 $PbTiO_3$ 시료는 입자의 크기가 비교적 균일하였으며 동질성을 나타내었다.

이 시료를 Polymer와 합성하여 0 – 3Composite를 제작하였으며 이 $PbTio_3$ – Polymer Composite는 X선 회절 시험결과 충분히 분극된 것을 볼 수 있었다.

수중압전전압계수와 응력계수 $\bar{g}_h$, $\bar{d}_h$는 약 97(10^{-3}V – m / N), 43(pC / N) 이었다. 수중청음기의 성능지수 $\overline{d_h g_h}$ 는 4000(10^{-15}m² / N) 이상이였으며 압력 및 시간에 따른 변화는 거의 없었다.

Abstract

Lead titanate($PbTiO_3$) powder prepared by the co–precipitation method was synthesized as filler for 0–3

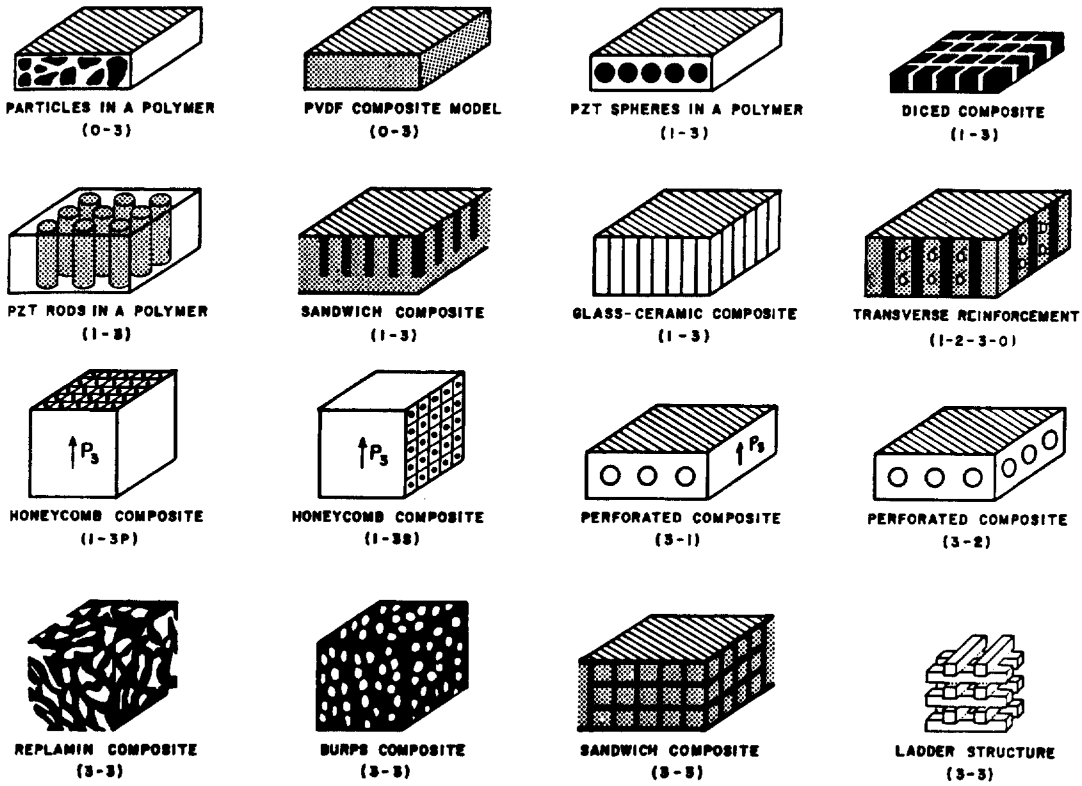

Fig. 1. The connectivity patterns of the constituent phases.

ezoelectrically active ceramic component converts underwater sound pressure waves to electrical signals, which are then amplified and displayed.

The sensitivity of a sound receiver material is characterized by a hydrophone Figure-Of-Merit(FOM), which is commonly derived as the product of the hydrostatic piezoelectric charge ($\bar{d}_h$) and voltage ($\bar{g}_h$) coefficients.

During the past few years, a number of investigators have examined piezoelectric ceramic polymer composites with different connectivity patterns. The piezoelectric properties of the composites depend, to a large extent, on the connectivity pattern of the constituent phases.

One of the simplest types of piezoelectric composites consists of a polymer matrix loaded with ceramic powder as shown in figure 1.[1] In such a composite the ceramic particles are not in contact with each other while the polymer phase is self-connected in three dimensions(0–3 connectivity). Early attempts to fabricate flexible composites with piezoelectric ceramic particles were made by Kitayama,[2] Pauer[3] and Harrison.[4]

An improved version of the 0–3 composite was fabricated by Banno.[5] Rather than using PZT as the ceramic filler, pure or modified $PbTiO_3$ was employed, because of its greater piezoelectric anisotropy. The $PbTiO_3$ filler was prepared by water quenching the ceramic, thereby exploiting the high strain present in the material in order to produce fine powders. The average particle size was about 5 μm. The hydrostatic voltage coefficient, $\bar{g}_h$, of these pure $PbTiO_3$ composites was found to be comparable to that of PVF_2 polymer (100×10^{-3}Vm / N) and the $\bar{d}_h$ value was 35pC / N.

Recently the sol-gel process has been used to prepare $PbTiO_3$ power for use in 0-3 composites.[6,7] The merits of sol-gel processing such as high purity, molecular homogeneity and lower processing temperatures offered advantages over the conventional mixed-oxide processing method.[8]

In this study, $PbTiO_3$ powder was prepared by the co-precipitation method. 0-3 composites were prepared using this powder. Dielectric and piezoelectric properties of these composites are reported in this paper.

2. POWDER PREPARATION

Figure 2 shows a flow chart of the procedure used to prepare co-precipitated $PbTiO_3$ powder. The $PbTiO_3$ was formed by precipitation from an aqueous solution in which the reactants were present in 1 molar stoichiometric quantities. Components were combined in the order : 1) $TiCl_4$ solution added to $Pb(NO_3)_2$ solution, 2) H_2O_2 solution added to this solution. The pH of the resulting solution was adjusted to approximately 8.95 to 9.25 by additions of deionized water and NH_4OH. Then the yellow precipitated aqueous solution was washed with deionized water and dried at 100℃. The dried materials was ground using a mortar and calcined at 800–900℃ in air for 1 hour to yield highly crystalline particles.

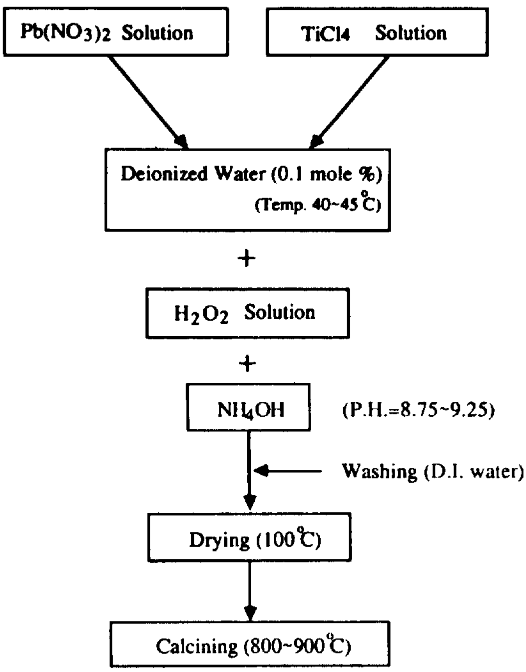

Fig. 2. $PbTiO_3$ powder preparation by coprecipitation method.

Photo. 1. SEM micrograph of the $PbTiO_3$ powder prepared by the coprecipitation method.

The SEM micrograph of the powder is shown in photo. 1. The particle shape of the powder obtained by the co-precipitation method was more round and unifrom than the powder prepared by the sol-gel method.[9]

3. 0–3 COMPOSITE FABRICATION

The $PbTiO_3$ powder was dispersed in Eccogel polymer 1365–0(Emerson and Cuming, W.R.Grace and Co., MA.) to make a 0–3 type composite, as shown in figure 3. The volume percent of $PbTiO_3$ powder in the composites

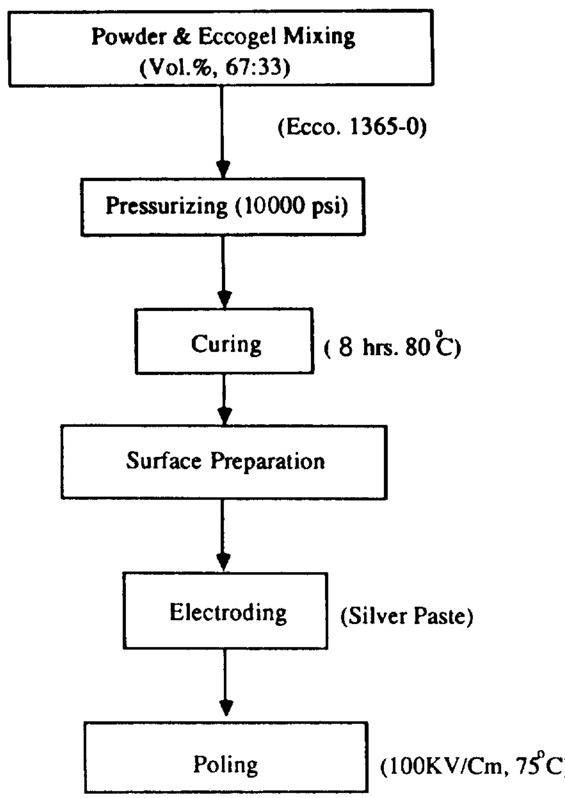

Fig. 3. $PbTiO_3$-polymer 0–3 composite preparation.

was about 67. The filler material was mixed with the Eccogel polymer and placed between two sheets of teflon in a 1.25 inch diameter die. The mixture was then pressed with a pressure of 10,000 psi and cured at 80℃ for about 8 hours. Electrodes of an air-dried silver paste were applied on both surfaces of the composites. The composites were poled at 75℃ with a field of 100KV/cm for 30 minutes.

4. EVALUTION OF DIELECTRIC AND PIEZOELECTRIC PROPERTIES.

The capacitance and dissipation factor were measured at 1 KHz using a Hewlett-Packard 4270A Multi-Frequency LCR Meter. The $\bar{d}_{33}$ coefficients were measured dynamically using a Berlincourt Piezo d_{33}-Meter with the electromagnetic driver operating at a frequency of 100Hz.

The $\bar{g}_h$ coefficients were determined by the dynamic A.C technique at a pressure of 100-1000 psi and a frequency of 75 Hz. An electromagnetic driver was used as an A.C. stress generator to apply pressure waves to the sample and a PZT standard, which was also under a static pressure from the hydraulic press. The charges produced from the sample and from the standard were buffered with an impedance converter and the voltages produced were measured on a Hewlett-Packard 3538A Spectrum Analyzer. The ratio of the voltages produced is proportional to the $\bar{d}_h$ coefficients. By accounting for the sample geometries, the $\bar{d}_h$ coefficients of the samples were calculated. The $\bar{d}_{31}$ and $\bar{g}_h$ coefficients and $\overline{d_h g_h}$ figure of merit were then calculated from the measured coefficients.

5. RESULTS AND DISCUSSION.

The 001-100 and 002-200 x-ray diffraction peaks from the surface of the composites, before and after poling, were observed to determine the degree of poling. The reversal of the peak intensities indicated that the co-precipitation method composites were completely poled Figure 4 and 5 show the reversal of peak intensities for a co-precipitation method composite before and after poling.

Also the 001-100 x-ray diffraction peaks as a function of applied poling voltage were shown in the figure 6.

In the table 1, the dielectric and piezoelectric properties of the co-precipitation method 0-3 composites are compared with the previous work.[9]

Also shown in this table are the maximum poling fields that could be applied without electric breakdown.The

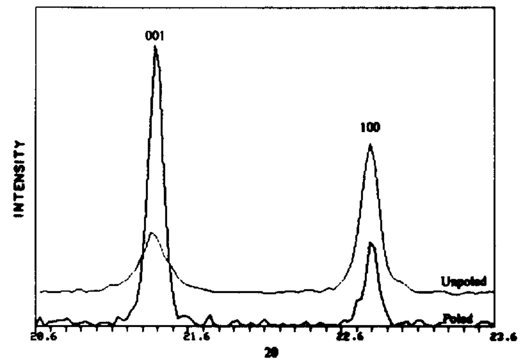

Fig. 4. Variation of 001, 100 x-ray diffraction peaks.

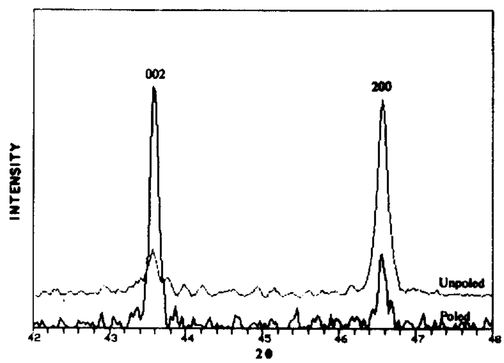

Fig. 5. Variation of 002, 200 x-ray diffraction peaks.

Table. 1. Comparision of the dielectric and piezoelectric properties.

0-3 Composite	Vol. % PT	Poling Field (KV/cm)	$\bar{d}_{33}$ (pC/N)	$\bar{d}_{31}$ (pC/N)	K_{33}	$\bar{d}_h$ (pC/N)	$\bar{g}_h$ (10^{-3} Vm/N)	$\overline{d_h g_h}$ (10^{-15} m^2/N)
Mixed-Oxide Prep.	70	115	25	−6.0	45	13	33	430
Sol-Gel Prep.	70	80	35	−4.5	50	26	59	1530
Co-Precipitation	67	105	60	−8.7	50	43	97	4170

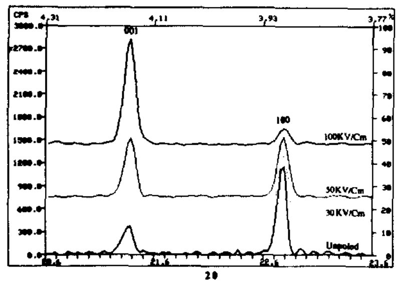

Fig. 6. 001, 100 X-ray diffraction peaks as a function of applied voltage.

sol-gel and co-precipitation method composites were poled with lower electric fields than the mixed-oxide method composites, but the degree of poling (as observed by the reversal of the x-ray diffraction peaks) and the piezoelctric coefficients were higher. This was possibly due to the greater purity and homogeneity of the sol-gel and co-precipitation powders.

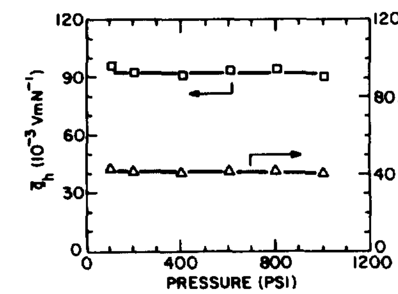

Fig. 7. The hydrostatic piezoelectric $\bar{d}_h$ and $\bar{g}_h$ coefficients plotted versus pressure at 75Hz for a co-precipitation method 0-3 composite.

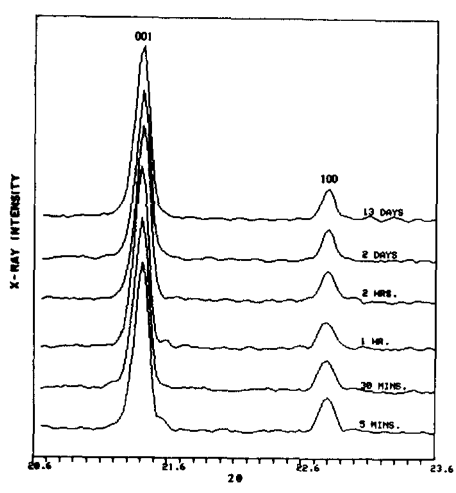

Fig. 8. The effect of aging on the 001, 100 x-ray diffraction peaks for a co-precipitation method 0-3 composite.

The lower maximum poling field of the sol-gel method composites may not have allowed these composites to be fully poled, resulting in lower piezoelectric coefficients than the more fully poled co-precipitation method composites. This was possibly due to the non-uniform particle size distribution in the sol-gel powder. The co-precipitation powder was also more reguarly shaped than the sol-gel or mixed-oxide powders.

The $\bar{g}_h$ and $\bar{d}_h$ of the 0-3 composites prepared by the co-precipitation method showed no pressure dependence up to 1000 psi, as shown in figure 7. These composites also showed no significant aging, as shown in figure 8 by no change in the x-ray diffraction peak intensities with time.

6. SUMMARY.

$PbTiO_3$ powder prepared by the co-precipitation method was used as filler materials in 0-3 composites. The $PbTiO_3$ powder prepared by the co-precipitation method had more uniformly shaped particles than the sol-gel or mixed-oxide powders.

X-ray diffraction of the composites before and after poling showed that the co-precipitation method composites were poled more completely than the sol-gel or mixed-oxide method composites, and therefore resulted in the highest piezoelectrc coefficients, with a $d_h g_h$ figure of merit of over 4000($\times 10^{-15} m^2 / N$). These composites showed no significant pressure or aging effects.

References

1) R. E. Newnham, A. Safari, J. Giniewicz and B. H. Fox; Ferroelectrics, 60, 15, (1984).
2) T. Kitayama and S. Sugawara, Rept. Proc. Gr. Inst. Elec. comm. Eng. Japan, CPM 27-17, (1972).
3) L. A. Pauer, IEEE Intl. Conv. Rea., 1, (1973).
4) W. B. Harrison, Proc. Workshop on Sonar Transducer Materials, Naval Research Lab., (1976).
5) H. Banno, Ferroelectrics, 50, 3, (1983).
6) S. R. Gurkovich and J. B. Blum, Ferroelectrics,

62, 189, (1985).

7) J. B. Blum and S. R. Gurkovich, J. Mater. Sci. 20, 4479, (1985).

8) D. L. Monroe, J. B. Blum, A. Safari, Ferroelectrics Letters, Vol. 5, pp. 39–46, (1986).

9) Y. H. Lee,M. J.Haun, A.Safari and R. E. Newnham, IEEE, ISAF, (1986).