J. Environ. Nanotechnol.
Volume 3, No.3 pp. 27-31
ISSN (Print): 2279-0748
ISSN (Online): 2319-5541
doi: 10.13074/jent.2014.09.1412088

Dielectric and Piezoelectric Properties of Various Ferroelectric Ceramic-Polymer Composites

S. Sundaram[1], P. Sampathkumar[1], P. Gowdhaman[1], V. Annamalai[1]*

[1]Department of Physics, Chikkanna Government Arts College, Tiruppur, TN, India

Received: 05.06.2014 Accepted:03.08.2014

Abstract

A study has been carried out to understand the different ceramics and different polymers to prepare composite with 0-3 connectivity. This is purely a review study on ferroelectric materials. Dielectric and piezoelectric properties for various composites have been discussed. It is clear that there is always an increase in dielectric constant (ε_r) for an increase in volume fraction. The piezoelectric strain coefficient (d_{33}) showed an increase in values to the increase in volume fraction of the various ceramic-polymer composites. There is no existence of steady pattern found in the voltage coefficient (g_{33}) values. The values obtained for the above confirms the usage of composites in various applications discussed in the introduction.

***Keywords*:** *Ceramic, polymer, ferroelectric, dielectric constant, piezoelectric strain coefficient, piezoelectric voltage coefficient.*

1. INTRODUCTION

Composite made up of ferroelectric ceramic and ferroelectric polymer are recently becoming more attractive for various applications. In accelerometer, pressure sensors, hydrophone and pyroelectric sensors, composites are highly used. The simplest ceramic-polymer composite consist of ceramic phase dispersed in a polymer matrix which is a 0-3 connectivity introduced by Newnhamn et al (1978). In this connectivity, the particulates reinforce into the polymer matrix. In this study, it is focused on various ferroelectric composites.

The lead zirconate titanate (PZT), lead titanate (PT), lead manganese niobate-lead titanate/barium titanate (PMN-PT/BaTiO3), calcium doped lead titanate(PTCa) ceramic are important ferroelectric material because of their excellent electrical properties. Among ferroelectric polymers semicrystalline polyvinylidene fluoride (PVDF), epoxy, rubber, polyvinylidene-trifluroethylene(PVDF-TrFE), polyamide, polyester resin, polyurethane, and polyvinylidene chloride are popular piezoelectric and ferroelectric material because of its flexibility, compliance and ease of fabrication (Newnham et al. 1984). This can be used in under water ultrasonic transducer such as earphones because of its recognized good ferroelectric properties. Combination of piezoelectric ceramic and polymer would form both softness of a polymer and advantages in electrical properties. In this study, a 0-3 connectivity have been analyzed for all composites. All these composites have been analyzed for various volume fractions. A comparative studies on piezo and dielectric properties have been discussed.

A corona discharge to the thin films obtained from hot roller, solvent cast, spin coating, screen printing, flow extension method have been employed. A poling apparatus have been used to pole the pellets prepared by hot press method using a high voltage DC power supply. In this work, analysis of dielectric and piezoelectric properties were studied only for samples prepared by corona discharge and direct poling method using high voltage power supply.

2. EXPERIMENTAL METHOD

It is decided to select only those ceramics and polymers which possess ferroelectric nature. The ferroelectric natured ceramics and polymers (matrix) are selected here are shown in table 1. In this study, the research papers selected are having different polymer and ceramic materials which possess ferroelectric properties. The various authors discussed the different methods of preparations in their respective papers. They discussed the 0-3 connectivity

*** V. Annamalai** *Tel.: +919791493045*
E-mail: annamalai_140795@yahoo.co.in

for all the composites. In this review, the papers have been selected for those who worked in preparing films and pellet samples. The method followed are solvent casting, spin coating techniques (Banerjee et al. 2013; Olszowy. 2003; Dietze et al. 2007; Arlt et al. 2010), screen printing (Matthias Dietze et al. 2008), hot roller for thin films and hot press apparatus for preparing pellets (Satish et al. 2002; Senthilkumar et al. 2005; Zhang De-Qing et al. 2008; Pailyn Thongsanitgarn et al. 2010; Young Jun Choi et al. 2013; Kwok et al. 2007). By measuring the capacitance value using capacitance meter, LCR meter…etc. the dielectric constant (ε_r) were calculated using [$Cd/\varepsilon_0 A$], where'd' is thickness of film or pellet, 'A' is the area of the prepared sample. The piezoelectric strain coefficient (d_{33}) value were measured using piezometer or d_{33} meter. The values were shown in table (2). The piezoelectric voltage coefficient (g_{33}) was calculated using the relation $g_{33}=d_{33}/\varepsilon_0\varepsilon_r$, where ε_0 is the permittivity of free space.

The various range of leakage current generated by corona discharge were applied to the thin film composites prepared by the methods quoted above (Banerjee et al. 2013; Olszowy. 2003; Dietze et al. 2007; Arlt et al. 2010; Matthias Dietze et al. 2008). Direct contact poling method were used for polymer-ceramic composites prepared in the form of pellets and the applied voltage for poling ranges from 5 kV to 30 kV. The capacitance value, d_{33} and g_{33} were tabulated for both films and pellets.

3. RESULT AND DISCUSSION:

3.1 Dielectric properties

The dielectric properties of composites depend on three factors (i) the properties of the constituent phase (ii) their intervening volume fraction and (iii) the way in which they are connected. A fourth factor emulating the micro geometry of the inclusions can be also of considerable important in 0-3 composites (Dias et al. 1996).

In this review paper various ceramic with different polymers and co-polymers have been selected for the study showed in table (1).The table illustrates an increases of dielectric constant value with an increase in volume fraction while tan δ decreases. This result is due to the increase contribution in reinforcement of ceramic particles into the polymer matrix which has higher dielectric constant. The continuous increase of dielectric constant with ceramic volume fraction in polymer composite reported by other worker is due to the absence of porosity. Because the composites were prepared by pressing at high temperature. There is a dielectric constant value difference between the polymers and it is due to relaxation of polymers with ceramic.

Table 1. Dielectric properties of Different Ferroelectric Ceramic polymer composites

Ceramic	Matrix	V_f	ε_r	tan δ	Reference
PZT	PVDF	0	8.86	0.018	Pailyn Thongsanitgarn et al. 2010
PZT	PVDF	0.1	9.84	0.025	
PZT	PVDF	0.3	12.57	0.040	
PZT	PVDF	0.5	18.09	0.042	
PZT	PVDF	0.7	35.96	0.040	
PZT	PVDF	0.9	126.50	0.045	
PZT	PVDF	1.0	957.75	0.005	
PZ21	PVDF-TrFE	0.1	22	0.041	Dietze et al. 2007
PZ21	PVDF-TrFE	0.2	29	0.034	
PZ21	PVDF-TrFE	0.3	34	0.036	
$BaTiO_3$	Epoxy	0.5	24		Sangyong Lee et al. 2007
$BaTiO_3$	EPOXY	0.6	45	0.035	Ramajo et al. 2008; Das et al. 2008
PZT	PVDF	0.5	90		Abdullah 1990
PZT	PVDF	0.7	140	0.3	Junlong Yao et al. 2009
$BaTiO_3$	PVDF	0.2	20		Tripathi et al. 1991
$BaTiO_3$	polyimide	0.1	35	0.0082	Amin et al. 1988
$BaTiO_3$	polyimide	0.9	117		
PZ21	PVDF-TrFE	0.2	35	0.033	Matthias Dietze et al. 2008
PZ21	PVDF-TrFE	0.3	45	0.032	
PZ21	PVDF-TrFE	0.4	65	0.026	
PZ21	PVDF-TrFE	0.5	72	0.023	
$BaTiO_3$	Rubber	0.3	17		Yang Rao et al. 2002
PMN-PT-BT	Epoxy	0.7	110	0.016	Naga Gopi Devaraju et al. 2005

3.2 Piezoelectric properties

In this paper, the piezoelectric strain coefficient (d_{33}) and voltage coefficient (g_{33}) have been analyzed for the different ceramic and polymer composites. In table 2, the values of d_{33} and g_{33} along with volume fraction have been illustrated. There is always an increase in d_{33} and g_{33} values with increase in volume fraction. This is due to the increase in ceramic content in polymer matrix. Whereas in the case of polymers like PVDF-TrFE and PVC with PZT, the d_{33} and g_{33} values are nonlinear. This is due to the ceramic and polymer phases polarized in opposite direction (Kar Lai Ng et al. 2000).

Table 2. Comparison of Piezoelectric properties with Volume fraction of different ceramic polymer composites

Polymer ceramic composite	Volume fraction%	ε_r	d_{33} (pCN^{-1})	g_{33} 10^{-3} (V-mN−1)	Reference
PZT-PVDF	50	93.09	17.87	21.68	Senthilkumar et al. 2005
	65	45	33	82.82	Wim Nhuapeng et al. 2004
PZT-P(VDF-TrFE)	0	9.5	37	439.88	Kar Lai Ng et al. 2000
	0.1	12.3	32	293.83	
	0.2	18	28	175.68	
	0.3	27.6	20	81.84	
	0.4	42.8	27	71.24	
	0.5	70.2	21	33.78	
	0.6	124.2	42	38.19	
	1.0	1116	410	41.49	
PZT-PVC	30	8.61	4	52.47	Liu et al. 2009
	40	25.06	6	27.04	
	50	39.30	15	43.10	
	60	73.11	22	33.98	
	70	97.78	31	35.80	
PZT/C/PVC	50/0.5/49.5	47.8	20	47.25	Liu Xiaofang et al. 2005
PZT/PU	33	24	23.7	111.53	Malmonge et al. 2008
	60	51+_5	25+_5		Wim Nhuapeng et al. 2004
	70	45+_5	28+_5		
PZT/PVC Thin film	60	134	29	24.44	
PZT-Epoxy	57		140		Dias et al. 1996
PZT-polyester resin	40		45		Wim Nhuapeng et al. 2004
	50		52		
	60		84		
	65		88		
$BaTiO_3$-PVDF		23.89	7.8	36.87	Xuetao Luo et al. 2004
PT/P(VDF-TrFE)	0	9.5	-		Chan, H.L.W et al. 1998
	0.09	14.3	5.1	40.28	
	0.19	18.4	8.3	50.94	
	0.28	24.2	11.7	54.60	
	0.39	30.3	13.5	50.32	
	0.48	42.4	20.8	55.40	
	0.54	57.3	22.8	44.94	
	1	245	72.8	33.56	
PTCa/P(VDF-TrFE)	65	67	28	47.20	Malmonge et al. 2008
PT-Epoxy	70		25		Dias et al. 1996
PTCa-Epoxy	50		22		
	55		45		

4. CONCLUSION

The different ferroelectric ceramic polymer composites with 0-3 connectivity were considered for this study. The dielectric and piezoelectric properties of all the above composites were analyzed. From this study it has been revealed that there is a relative variation in the values of dielectric constant and piezoelectric strain coefficient with respect to volume fraction. The piezoelectric voltage coefficient g_{33} is directly proportional to the piezoelectric strain coefficient and inversely proportional to the permittivity. These materials are suited for radiating/receiving ultrasonic devices, technological power ultrasonic devices since, they have different dielectric constant.

REFERENCES

Abdullah, M. J., A Study of Electroactive Properties of Polymer/Ceramic Composites, Ph.D. Thesis, University of Wales, SEECS, Bangor, (1990).

Amin, M., Balloomal, L. S., Darwish, K. A., Osman, H. and Kamal, B., Pyroelectricity in rubber composite films, *Ferroelectrics*, 81(1),381-386 (1988). doi:10.1080/00150198808008887.

Arlt, K. and Wegener, M., Piezoelectric PZT / PVDF-copolymer 0-3 Composites: Aspects on Film Preparation and Electrical Poling, *IEEE Transactions on Dielectrics and Electrical Insulation*, 17(4), 1178-1184(2010). doi:10.1109/TDEI.2010.5539688.

Banerjee, S., Du, W. and Wang, L., Cook Chennault, K.A., Fabrication of dome-shaped PZT-epoxy actuator using modified solvent and spin coating technique, *J Electroceram.*, 31(1), 148-158(2013). doi:10.1007/s10832-013-9834-8.

Chan, H. L. W., Chan, W. K., Zhang, Y. and Choy, C. L., Pyroelectric and piezoelectric properties of Lead Titanate/Polyvinylidene Fluoride-Trifluoroethylene 0-3 composites, *IEEE Transactions on Dielectrics and Electrical Insulation*, 5(4), 505–512(1998). doi:10.1109/94.708265.

Das, R. N., Egitto, F. D., Lauffer, J. M. and Markovich, V. R., Laser Micromachining of Barium Titanate ($BaTiO_3$) -Epoxy Nanocomposite-Based Flexible/Rollable Capacitors: New Approach for Making Library of Capacitors, Electronics IEEE Transactions on Packaging Manufacturing, 31(2), 97-103 (2008). doi:10.1109/TEPM.2008.919337.

Dias, C. J. and Das-Gupta, D. K., Inorganic ceramic/polymer ferroelectric composite electrets, *IEEE Transactions on Dielectrics and Electrical Insulation,* 3(5), 706-734(1996). doi:10.1109/94.544188.

Dietze, M., Krause, J., Solterbeck, C. H. , and Es-Souni, M., Thick film polymer-ceramic composites for pyroelectric applications, *J. Appl. Phys.*, 101(5), 54-113(2007). doi:10.1063/1.2653978.

Junlong Yao., Chuanxi Xiong., Lijie Dong.,Cheng Chen., Youan Lei., Lei Chen., Rui, Li., Qingming Zhu. and Xiaofang Liu., Enhancement of dielectric constant and piezoelectric coefficient of ceramic–polymer composites by interface chelation, *J. Mater. Chem*, 19, 2817-2821(2009). doi:10.1039/ B819910H.

Kar Lai Ng, Chan, H. L. W., Choy, and Chung Loong, Piezoelectric and pyroelectric properties of PZT/P(VDF-TrFE) composites with constituent phases poled in parallel or antiparallel directions, *IEEE Transactions on Ultrasonics, Ferroelectrics and Frequency Control*, 47(6), 1308-1315(2000). Doi:10.1109/58.883519.

Kwok, K. W., Lau, S. T., Wong, C. K., Shin, F. G., Effects of electrical conductivity on poling of ferroelectric composites, *J. Phys. D: Appl. Phys.*, 40(21), 38-51(2007). doi:10.1088/0022-3727/40/21/049.

Liu Xiaofang, Xiong Chuanxi, Sun Huajun, Dong Lijie, Li Rui, and Liu Yang, Characterization of PZT/PVC composites added with carbon black, *Journal of Wuhan University of Technology-Mater. Sci. Ed.*, 20(4), 60-64(2005). doi:10.1007/BF02841284.

Liu, X. F., Sun, H. J., Xiong, C. X., Zhang, C. Y, Zheng, H. and Wei, M., Effect of volume fraction and molding temperature on the electric properties of PZT/PVC composites, IEEE International Symposium on the Applications of Ferroelectrics, 1-4(2009). doi:10.1109/ISAF.2009.5307545

M.Olszowy, Dielectric and Pyroelectric Properties Of The Composites Of Ferroelectric Ceramic And Poly (Vinyl Chloride), Condensed Matter Physics, 6(2), 307-313 (2003).

Malmonge, J. A., Malmonge, L. F., Fuzari, G. C., Jr., Malmonge, S. M. and Sakamoto, W. K., Piezo and dielectric properties of PHB–PZT composite, *Polymer Composites*, 30(9), 1333-1337(2008). doi:10.1002/pc.20719.

Matthias Dietze., Mohammed Es-Souni., Structural and functional properties of screen-printed PZT–PVDF-TrFE composites, *Sensors and Actuators A*, 143, 329-334(2008). doi:10.1016/j.sna.2007.11.016.

Naga Gopi Devaraju, Eung Soo Kim, and Burtrand I Lee, The synthesis and dielectric study of BaTiO3/Polyimide nanocomposite films, *Microelectronic Engineering*,82(1), 71-83(2005). doi:10.1016/j.mee.2005.06.003.

Newnham, R. E. and Runt, J. P., Polymer-Piezoelectric Ceramic Composites, *Polymer News*, 10, 132-138 (1984).

Newnham, R. E., Skinner, D. P., and Cross, L.E., Connectivity and piezoelectric-pyroelectric composites, *mat. Res. Bull*. 13, 525 (1978).

Pailyn Thongsanitgarn, Anucha Watcharapasorn, and Sukanda Jiansirisomboon, Electrical and Mechanical Properties of PZT/PVDF 0–3 Composites, *Surf. Rev. Lett.*, 17(1), 1-7(2010) doi:10.1142/S0218625X10013540

Ramajo, L., Reboredo, M., Santiago, D., Castro, M. and Ramajo, D., Computational Approach of Dielectric Permitivities in $BaTiO_3$—Epoxy Composites, *J. Compos. Mater.*, 42(19), 2027 - 2037(2008). doi:10.1177/ 0021998308094543

Sangyong Lee, Jin-Gul Hyun and Hyungsoo Kim, Kyung-Wook Paik, A Study on Dielectric Constants of Epoxy/$SrTiO_3$ Composite for Embedded Capacitor Films (ECFs), *IEEE Transactions on Advanced Packaging*, 30(3), 428-433(2007). doi:10.1109/TADVP. 2007.898614.

Satish, B., Sridevi, K., and Vijaya, M. S., Study of piezoelectric and dielectricproperties of ferroelectric PZT–polymercomposites prepared by hot-press technique, *J. Phys. D: Appl. Phys.*, 35(16), 2048-2050(2002). doi:10.1088/0022-3727/35/16/321.

Senthilkumar, R., Sridevi, K., Venkatesan, J., Annamalai, V. and Vijaya, M. S., Investigations on Ferroelectric PZT-PVDF Composites of 0–3 Connectivity, *Ferroelectrics*, 325(1), 121–130(2005). doi:10.1080/ 00150190500328544.

Tripathi, A. K., Goel, T. C. and Pillai, P. K. C., Pyroelectric and Piezoelectric Properties of Sol–Gel Derived BaTiO3 Polymer Composites, *Electrets*, 7, 415–420(1991). doi:10.1109/ ISE.1991.167247.

Wim Nhuapeng and Tawee Tunkasiri, Properties of 0–3 Lead Zirconate Titanate–Polymer Composites Prepared in a Centrifuge, *Journal of the American Ceramic Society*, 85(3), 700–702(2004). doi:10.1111/j.1151-2916.2002.tb00154.x.

Xuetao Luo, Lifu Chen, Xiaojun Chen, Qianjun Huang, Preparation and Electromechanical Properties of PVDF Matrix Piezoelectric Composites Containing Highly Oriented BaTiO3 Whiskers, *J. Mater. Sci. Technol*., 20(4), (2004) .

Yang Rao., S. Ogitani., Paul Kohl., C. P. and Wong., Novel polymer–ceramic nanocomposite based on high dielectric constant epoxy formula for embedded capacitor application, *Journal of Applied Polymer Science*, 83(5), 1084–1090 (2002). doi:10.1002/app.10082.

Young Jun Choi, Myong-Jae Yoo, Hyung-Won Kang, Hyeung-Gyu Lee, Seung Ho Han, Sahn Nahm, Dielectric and piezoelectric properties of ceramic-polymer composites with 0–3 connectivity type, *Journal of Electroceramics*, 30(1-2), 30-35(2013). doi:10.1007/s10832-012-9706-7

Zhang De-Qing., Wang Da-Wei., Yuan Jie., Zhao Quan-Liang., Wang Zhi-Ying and Cao Mao-Sheng., Structural and Electrical Properties of PZT/PVDF Piezoelectric Nanocomposites prepared by Cold-Press and Hot-Press Routes, *Chin. Phys. Lett.*, 25(12), 4410-4413(2008).