INVESTIGATIONS ON THE PREPARATION AND CHARACTERIZATION OF BARIUM TITANATE ($BaTiO_3$)/POLYVINYLIDENE FLUORIDE (PVDF) COMPOSITES

By

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TO

F A T H E R AND M O T H E R

IN HEAVEN

CERTIFICATE

I am satisfied that the thesis entitled "Investigations on the preparation and characterization of Barium Titanate ($BaTiO_3$)/Polyvinylidene fluoride (PVDF) composites" by MURALIDHAR CHATURVEDULA is worthy of consideration for the award of the degree of DOCTOR OF PHILOSOPHY and is a record of the original bonafide research work carried out by him under my supervision. The results in it have not been submitted in part or full to any other university or institute for award of any Degree/Diploma.

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SYNOPSIS

Material science has entered a new era, an era of carefully patterned inhomogeneous solids designed to perform specific functions. Instead of concentrating on the properties of the best single phase materials, many scientists are now searching for the best combination of materials and ways to process them. Composite materials in which combinations of phases selected for the best individual properties are put together in a manner designed to show their enhanced properties. Therefore compostie materials play an important role in future applications like pyro, piezoelectric detectors, capacitors, memories etc .

In most electronic devices there are several phases involved and a number of material parameters are to be optimized. Ceramics are brittle in nature and have very high pyroelectric, piezoelectric constants and high dielectric constants. On the other hand polymers have low pyro, piezoelectric and dielectric constants but have flexibility and lightness. Therefore, a composite material comprising the above two materials would be an ideal replacement for both the classes having the desirable properties of both the materials. The main thing one has to look for is to exploit the desirable features of both components. Also the properties of the composites can be tuned to requirement by changing the proportions of the constituents.

Majority of the workers in the field so far have concentrated on different polymer/ceramic composites and none of the studdies is

systematic on any polymer/ceramic composite and very few workers have explained their results satisfactorily. Since it is an upcoming field, there is a definite need to understand them thoroughly and brought into limelight for using them effectively. Therefore in the present work it has been found desirable to make a detailed study on $BaTiO_3$/PVDF composite to understand the different mechanisms involved before using it on the application side.

Chapter I contains, a literature review of the polymer/ceramic composites and also a brief discussion of some of the basic properties of the polymers, ceramics and polymer/ceramic composites. The aim and objectives of the present work has also been given briefly.

In Chapter II the details of various chemicals used, preparation of the $BaTiO_3$/PVDF composites and methods used for measuring the properties of the composites are given.

Chapter III deals with the pyroelectric behaviour of $BaTiO_3$/PVDF composites as pyroelectricity is a necessary attribute for a ferroelectric material. Pyroelectricity is defined as change of polarization of a dielectric with temperature after eliminating polarization effects produced by thermal strains which accompany the temperature change. The wt.fraction of $BaTiO_3$ in the composite has been varied to identify the critical composite which gives the desirable properties. The enhancement in pyroelectric behaviour was explained on the basis of domains and

the dipolar contribution from PVDF.

Chapter IV deals with the dielectric behaviour of all the composites from 10 Hz to 10 MHz at 30°C. The composite with 70% wt.fraction of $BaTiO_3$ has a high dielectric constant (ϵ' = 133 at 10 Hz & 30°C) among others and proved to be the critical composition. The dielectric behaviour of this composition has been discussed in detail at different temperatures and frequencies. It has been shown that due to the ultra fine particle size of $BaTiO_3$ (about 1 μm), the usual curie peak has been shifted from 120° to 150°C in $BaTiO_3$. Due to the combined effects of ultra fine particle size of $BaTiO_3$ and off-valency additive effects, which is the substitution of O^{-2} by F^{-1}, the curie peak is washed out in the above composite. No abrupt change has been observed in the dielectric behaviour of the composite due to the absence of curie peak. ϵ' decreases with increase in frequency upto 1 MHz. The results were explained on the basis of domain motion, inhomogeneous conductivity which arises due to interfacial polarization and also domain wall motion.

Chapter V deals with the resistivity behaviour of the composites. The composite with 70% wt.fraction of $BaTiO_3$ has a considerably high resistivity. The temperature dependence of resistivity behaviour of this composition has been studied in detail at field and zero bias. Since the curie peak is absent due to the combined effects of above said efects, there is no abrupt change in the behaviour of the composite either at field or zero bias. No positive temperature coefficient of resistivity (PTCR)

behaviour has been observed in the composite. The resistivity is found to decrease one order in the composite with increase in temperature. Current vs Voltage variations of this composite at different temperatures have also been studied. The results were explained on the basis of liberation of electrons or ions from traps or the greater ease of charge carriers through the amorphous region of PVDF, and also the relatively important roles played by the effects of internal stresses and surface effect.

Chapter VI deals with the hysteresis behaviour of $BaTiO_3$/PVDF composites. The composite with 70% wt.fraction of $BaTiO_3$ has high values of saturation polarization (P_{sat}), remanent polarization (P_r) and low value of coercive field (E_c) among other compositions and proved to be the critical composition. The temperature dependence of P_{sat}, P_r & E_c has also been studied for this composition.Since the curie peak is absent due to the combined effects of above said effects, there is no abrupt change in the behaviour of the comosite. Hysteresis curve has very little open area with low values of P_{sat}, P_r & E_c have been observed in the composite. The results were explained on the basis of domains overcoming the internal stresses in the composite with temperature.

Chapter VII deals with the structural studies of the composites by using scanning Electron microscope (SEM), X-ray diffractometer and Infrared spectrophotometer etc. These studies were carried out on $BaTiO_3$/PVDF composites to see what type of structural

variations have taken place by changing the wt.fraction of $BaTiO_3$. Also attempts have been made to correlate the structure-property relationship of the composites.

The details on the use of the composite as a thermocompensated capacitor and dielectric memory cell have been presented in Chapter VIII.

Chapter IX is a brief summary of the results and salient conclusions of the entire work along with the scope for further work in the field.

The above mentioned work has also been resulted in the following publications :

(1) Pyroelectric behaviour in Barium Titanate ($BaTiO_3$)/Polyvinylidene fluoride (PVDF) composite.
Paper presented at International symposium on Electrets (ISE-5), Heidelberg, West Germany, 4-6 Sep'85, p.865-870.

(2) Pyroelectric behaviour in Barium Titanate ($BaTiO_3$)/Polyvinylidene fluoride (PVDF) composites (in extended form).
IEEE transactions on Electrical Insulation, EI-21, 501-504, 1986.

(3) Thermocompensated capacitor with Barium Titanate ($BaTiO_3$)/Polyvinylidene fluoride (PVDF) composite.
J.of Material Science letters (in press).

(4) Dielectric behaviour of Barium Titanate ($BaTiO_3$)/Polyvinylidene fluoride (PVDF) composite.

J.of Material Science letters (in press).

(5) Hysteresis behaviour of Barium Titanate ($BaTiO_3$)/Polyvinylidene fluoride (PVDF) composite.

J.of. Material Science letters (in press).

(6) Resistivity behaviour of Barium Titanate ($BaTiO_3$)/Polyvinylidene fluoride (PVDF) composite.

J.of Material science Letters (in Press).

(7) Surface effect by SEM studies on Barium Titanate ($BaTiO_3$)/polyvinylidene fluoride (PVDF) composites.

J.of Material science Letters (communicated).

(8) SEM studies on Barium Titanate ($BaTiO_3$)/Polyvinylidene fluoride (PVDF) composites.

J.of Material science letters (communicated).

(9) Pyroelectric, Dielectric, Resistivity and Hysteresis behaviour of Barium Titanate ($BaTiO_3$)/Polyvinylidene fluoride (PVDF) composites and correlation by SEM studies.

J.of Material science letters (communicated).

(10) Off-valency additive effect and its influence on curie peak of Barium Titanate ($BaTiO_3$)/Polyvinylidene fluoride (PVDF) composite.

J.of Material science letters (communicated).

(11) XRD studies on Barium Titanate ($BaTiO_3$)/Polyvinylidene fluoride (PVDF) composites in the range from 98° to 103°.

J.of Material science letters (communicated).

(12) XRD studies on Barium Titanate ($BaTiO_3$)/Polyvinylidene

fluoride (PVDF) composites in the range from 10° to 50°.
J.of Material Science letters (communicated).

(13) Electrothermographic behaviour of Poly (methyl methacrylate) and Leucomalachite green mixed system.
J.of.Material science letters, 3, 1065-1068,1984 (not included in the thesis).

(14) Dielectric behaviour in Lead Zirconate Titanate (PZT)/Polyvinylidene fluoride (PVDF) composite.
Paper presented at 2 nd International conference on conduction and Breakdown in solid dielectrics, Erlangen, West Germany, 7-10 July'86. p.227-231. (not included in the thesis).

(15) Effect of Internal stresses and conductivity in Barium Titanate ($BaTiO_3$)/Polyvinylidene fluoride (PVDF) composites and other polymer/ceramic composites.
J.of.Material science letters (communicated).

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