
Chapter 9

Conclusions and Scope for Future Research Work

This chapter outlines the conclusions of work done on $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and La, Nb, Sn and Zr doped $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ / Poly(vinylidene fluoride) composites prepared by melt extrusion method. Future work which can be done on the high dielectric permittivity polymer ceramic composites is also proposed in the present chapter.

- CCTO and Nb, Sn, Zr doped CCTO were prepared by conventional solid state technique. $\text{Ca}_{(1-3x/2)}\text{La}_x\text{Cu}_3\text{Ti}_4\text{O}_{12}$ ($x=0.05$) was prepared by semi-wet route.
- CCTO and La, Nb, Sn, Zr doped CCTO and PVDF composites were prepared by melt extrusion method. Films of these composites were made using compression molding machine at 200°C under a load of 5 tons. Thickness of these films was kept $100\ \mu\text{m}$.
- X-Ray Diffraction patterns confirmed the formation of single phase desired ceramics as well as composites. No change in XRD patterns have been noticed either in the ceramic or in the composites indicating no major structural change.
- Scanning Electron Microscopy shows that the PVDF exhibits spherulitic morphology. With ceramic dispersion, the spherulitic morphology of PVDF is changed significantly. At low filler concentration, ceramic particles are well dispersed in the PVDF matrix while at higher filler concentration, the inter particle distance decreases, finally leading to the formation of well connected network structure.
- Thermograms recorded for the pure PVDF and composites show that pure PVDF is stable up to 400°C and complete degradation of the polymer occurs at around 500°C . Ceramic fillers shift the degradation temperature to higher side i.e. from 442°C in PVDF to 464°C , 473°C , 480°C , 475°C and 466°C in case of PVDF-

50CCTO, PVDF-50LaC, PVDF-50NbC, PVDF-50SnC and PVDF-50ZrC composites respectively. It shows that addition of ceramic filler in PVDF matrix improves the thermal stability of the composites.

- Considerable increase is observed in the value of Young's modulus of the composites. For PVDF the Young's modulus is 810 MPa, which increases to 960, 1450, 1033, 1020, 1202 MPa in the case of PVDF-50CCTO, PVDF-50LaC, PVDF-50NbC, PVDF-50SnC and PVDF-50ZrC composites respectively. This increase in Young's modulus with increase in weight percent of the filler can be attributed to the interaction between the stiffer ceramic filler and the flexible PVDF matrix making composites stiffer as compared to pure PVDF. With increase in the ceramic content the composite is becoming stiffer due to increase in the resistance to the free movement of polymeric chains. This is also a reason for decrease in the elongation at the breaking point with increasing concentration of the ceramics in the PVDF matrix.
- Dielectric permittivity of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) considerably improves on doping with La, Nb, Sn and Zr. Dielectric permittivity of CCTO is 3100 at 100 Hz and 40°C which increases to 8850, 25500, 7050 and 21000 for LaCCTO, NbCCTO, SnCCTO and CCTZO respectively at the same frequency and temperature. CCTO as well as doped CCTO exhibits high value of ϵ' due to formation of barrier layers at the grains-grain boundaries interfaces. In the case of composites ϵ' is 3 for PVDF, which increases to 54, 60, 98, 74 and 88 for PVDF-50CCTO, PVDF-50LaC, PVDF-50NbC, PVDF-50SnC and PVDF-50ZrC at 100 Hz and 40°C . Dielectric permittivity increases with increasing temperature and decreasing frequency and vice versa. The composite materials always have microheterogenities due to the presence of two or more phases in electrical contact. There exists a difference in the conductivity of the dispersed phase/phase and the matrix. This gives rise to interfacial or space charge polarization due to blocking of the charge carriers at the polymer-ceramic interface. Space charge polarization involves displacement of charge carriers over large distance. Hence it

cannot follow the alternating field at high frequency. This gives rise to rapid decrease in ϵ' with increase in frequency in the low frequency region.

- Dielectric loss ($\tan\delta$) of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) is 0.86 at 100 Hz and 40°C which decreases to 0.13 and 0.32 in case of La doped CCTO and Sn doped CCTO respectively, while it remains unchanged for Zr doped CCTO at the same frequency and temperature. In the case of Nb doped CCTO, it increases to 1.68 at 100 Hz and 40°C . For PVDF it is 0.08, in the case of the composites, this increases to 0.21, 0.34, 0.24, 0.22 and 0.10 for PVDF-50CCTO, PVDF-50LaC, PVDF-50NbC, PVDF-50SnC and PVDF-50ZrC at 100 Hz and 40°C . Therefore, a slight increase in loss has been observed with ceramic dispersion. In the composites a dielectric relaxation is observed at low frequency in the composites. Another dielectric relaxation is observed in the intermediate frequency range. Relaxation at lower frequency is attributed to Maxwell Wagner polarization in the composites and the one in the intermediate frequency range can be attributed to α_c relaxation associated with molecular motion of the polymer chains in the crystalline regions of PVDF. The glass transition relaxation α_a of PVDF occurs beyond 1 MHz. With increase in temperature these relaxations shift to higher frequency.
- To understand the nature of dielectric relaxation, use is made of modulus spectroscopy. It is observed that M' value decrease with the increase in the ceramic content. This indicates increase in the dielectric permittivity with the increasing content of the ceramics. It is observed that in PVDF and the composites, there is a steep rise in the value of M' at a particular frequency. This corresponds to a dielectric relaxation. A corresponding peak is observed in the M'' vs $\log f$ plot at the same frequency. It is observed that this relaxation appears in PVDF as well as in the composites at around 100 Hz and 40°C . This relaxation peak shifts to lower frequency in the composites. This is due to restricted mobility of the polymeric chains because of their interaction with the filler particles. This relaxation is due to α_c relaxation associated with molecular motion of the polymer

chains in the crystalline regions of PVDF. Height of the peak in M' as well as M'' is less in the case of composites as compared to pure PVDF. This shows that the dielectric permittivity as well as the dielectric loss is more in the composites as compared to that in pure PVDF. These peaks shift to higher frequency with increasing temperature. In the composites another peak appears at low frequency and high temperature. At 40°C this peak is not observed in the composites as it may be present at lower frequency. It is not observed in PVDF also. This relaxation is of Maxwell-Wagner-Sillar (MWS) type. Maxwell Wagner Sillar polarization is always present in the multiphase systems having phases with different conductivities i.e. electrical heterogeneities.

- Relaxation times, τ was determined using the relation $\tau = \frac{1}{2\pi f}$ where f is the frequency in cycles per second at the peak position in M'' vs $\log f$ plots for α_c relaxation. Plots of $\log \tau$ vs $1000/T$ are linear in accordance with Arrhenius relationship:

$$\tau_{\max} = \tau_0 \exp\left(\frac{E_R}{kT}\right) \quad (9.1)$$

where E_R is the activation energy associated with the relaxation process, τ_0 is the pre-exponential factor, k is the Boltzmann constant and T is the absolute temperature. It is found that the activation energy for α_c relaxation increases with increasing content of CCTO. This is due to increase in the stiffness of the composites with increasing content of CCTO. It is also observed that M'' peaks shift to lower frequency with increasing content of ceramic. This is because of the restricted movement of the polymer chains as mentioned above. It is also in conformity with the increasing value of Young's modulus with increase in the content of the ceramics.

- Various models are used in the literature to predict the effective dielectric permittivity of the composites viz: Maxwell's model, Clausius-Mossotti model, Lichtenecker's or logarithmic mixture rule and the effective medium theory (EMT) model. EMT model gives the predicted values closest to the

experimentally observed values. Microstructure and microchemistry of the interfaces are also very important in determining the physical, mechanical and electrical properties of the composites. Therefore the experimental results do not match exactly with the values predicted by these models.

- Temperature-dependence of dielectric relaxation is explained by Havriliak-Negami (H-N) function.

$$\boldsymbol{\varepsilon}^* = -\mathbf{i} \frac{\sigma_{dc}}{\varepsilon_0 \omega^s} + \boldsymbol{\varepsilon}_\infty + \sum_j \frac{(\Delta\varepsilon)_j}{[1+(i\omega\tau_j)^\alpha]^\beta} \quad (9.2)$$

where, σ_{dc} is dc conductivity, ω is the angular frequency, s is an exponent ($0 < s \leq 1$), τ_j is the relaxation time of the j^{th} process, ε_0 is the vacuum permittivity, $\Delta\varepsilon$ is the dielectric strength of the j^{th} process and α and β are the shape parameters of the H-N function which define the symmetric and asymmetric broadening of the α_c relaxation peak in ε'' curve. The higher value of α for the composites as compared to pure PVDF indicates a stretched relaxation over a wider range of frequencies. Asymmetry parameter β has a value of 1 for PVDF showing the symmetry of the spectrum. For the composites, β parameter has different values due to the dispersion of ceramics particles which creates heterogeneity in the system. For composites, the relaxation time (s) calculated from H-N fit decreases with increase in temperature. The composites exhibit lower relaxation time as compared to PVDF. With increase in the temperature, the relaxation time decreases in the composites. Lower value of relaxation time at higher temperature is because of the ease of relaxation at higher temperature due to increased mobility of the polymeric chains both for pure PVDF as well as the composites.

Results of dielectric permittivity, dielectric loss, Young's Modulus and thermal degradation temperatures in different systems at 50 wt% of the ceramic filler are given in table 9.1.

Table 9.1 Values of various parameters for different composites containing 50 wt% of the filler.

Compositions	ϵ' (at 100 Hz)	$\tan\delta$ (at 100 Hz)	Young's Modulus (MPa)	Degradation Temperature ($^{\circ}\text{C}$)
PVDF	3	0.08	750	442
PVDF-50CCTO	54	0.21	960	464
PVDF-50LaC	60	0.34	1450	473
PVDF-50NbC	98	0.24	1033	480
PVDF-50SnC	74	0.22	1020	475
PVDF-50ZrC	88	0.10	1200	466

➤ **Future Scope**

Dielectric strength is an important parameter from the application point of view. This needs to be studied. Effect of the particle size of the ceramic on the dielectric as well as mechanical behavior can also be studied.