



Study of Structural and Conduction Behaviour in Ionic Liquid based Polymeric Electrolyte Membrane with Layered Filler

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ABSTRACT

Ionic liquids (ILs) are salts with low melting point close to room temperature. They have interesting solvent properties and are able to dissolve some polar molecules. Polyvinyl formal-IL (1-Ethyl-3-methylimidazoliumtosylate) nanocomposite electrolyte with layered filler was synthesized by solution cast technique. Changes in surface morphology have been observed using optical microscopy and scanning electron microscopic (SEM) images. Variation of dielectric constant, dielectric loss, tangent loss and modulus spectra with frequency and temperature were studied with the aid of impedance spectroscopy.

Key words: Polyvinyl formal (PVF), Polymer salt complexation, Ionic Liquid, Graphite filler, NCPEs

INTRODUCTION

Recently ionic liquid (IL) based polymer electrolyte membranes have become more attractive for the technological and medical application [1-2]. They have excellent properties of low melting point, non volatility, non flammability, high thermal stability and high conductivity. The ionic behaviour of polymer composite electrolyte depends on type of salt, their concentration and addition of filler. Poly vinyl formal (PVF) based composite electrolyte has been less studied among different polymer electrolyte systems. PVF is a polar, colorless, water soluble and porous structure polymer. It is produced from partially hydrolyzed poly vinyl acetal and formaldehyde (with 1-3 glycol and 1-2 glycol structure)[3]. Ionic liquid are a promising class of new materials with a bright technological future. Ionic liquids are liquids at room temperature composed entirely of ions and less viscous fluid. It shows tremendous promise as replacement for harmful organic solvents. The IL exhibits large electrochemical window and meets the requirement of plasticizing salts with improved thermal mechanical properties and flexibility [4-5]. The addition of IL in polymer matrix enhances the flexibility as compared to the conventional salts. Most recently ionic liquid based electrolyte has been successfully used in different electrochemical devices. To enhance the quality of electrolyte, the dispersion of filler is an important option. Use of layered fillers /clays [like MMT (Montmorillonite), Mica and graphite] shows promising result in polymer electrolyte due to their high aspect ratio and surface area [6-8]. In the layered filler, stacking of layer leads to Vander Waal gap between the layer called the inter layer or gallery. Isomorphous distribution within layer generates negative charges that are counter balanced by cations present inside the galleries.

The dispersal of MMT clay in hydrophilic polymer matrix enhances its potential application in medicine, pharmacy and also in electrolytes. The polymeric grade MMT clay is 2:1 phyllosilicate, which is also called inorganic polymer, and chemically it is a metal silicate [9]. The dispersion of small amount of MMT clay in a suitable polymeric solvent has swelling properties. Swelling of the clay is mainly due to the solvent intercalation (absorption) in the clay galleries and also because of the adsorption of solvent molecules on the hydroxylated aluminates clay surface through H-bond interaction, which results into the clay exfoliation. The intercalated and exfoliated clay sheets in polymeric solvent results in to the organic – inorganic composites of highly complicated structure, which is responsible for the improved thermal, mechanical, and electrical properties of the polymer clay composites. Another layered filler is carbon (graphite). Graphite is an allotrope of carbon, and it has layered structure. The addition of small volume fraction of graphite provides moderately high surface area leading to excellent performance of composite polymer electrolyte in terms of conductivity and interfacial stability. This filler has effect on particle size distribution, morphology, surface characteristics and most importantly color[10]. The aim of this work is to synthesize the IL based polymer composite electrolyte with layered filler and study their ionic and structural behaviour comparatively by different experimental techniques like XRD, SEM, IR and Impedance spectroscopy.

EXPERIMENTAL

Composite polymer electrolyte films (100-300 μm thickness) were prepared using solution cast technique. The Polyvinyl formal [(PVF) (MW. 50,000 ACROS organics)], Ionic liquid (1-Ethyl-3-methylimidazoliumtosylate) [(282.36g/mol)(Aldrich, AR grade)], Polymer grade hydrophilic montmorillonite (MMT) clay (Nanoclay, PGV), was purchased from Sigma-Aldrich, USA and graphite from graphite India Ltd. PVF dissolved in THF solvent and IL was stoichiometrically stirred for 10-15 h continuously. THF is easily miscible water-alcohol solution. Layered fillers like MMT and graphite powder were dispersed in this solution. This gelatinous polymeric solution was finally cast in Borosil glass dish. This solution cast film was dried at 30°C in B.O.D. incubator for Controlled Evaporation followed by vacuum drying to obtain the solvent free standing films of NCPE. Structural behaviour of pure PVF, polymer electrolyte and NCPEs films were studied by X-ray diffractometer (Phillips X-Pert model) in the Bragg's angle range (2θ) 15-60° using Cu-K α radiation ($\lambda=1.542\text{\AA}$). The SEM images of different composite electrolyte systems were recorded with JEOL JXA-8100 EPMA instrument at 15KV and 0.1 nAmp. The electrical characterization of the solid polymer composite electrolyte was carried out using impedance spectroscopy by applying small a.c. signal (200mV) across the sample cell with Pt-blocking electrodes. The complex impedance parameters were measured with impedance analyzer (HIOKI LCR Hi-tester, model 3522, Japan) in the frequency range 40 Hz-100 KHz. Dielectric relaxation behaviour studies were carried out by the impedance data.

RESULT AND DISCUSSION

X-ray diffraction pattern of pure PVF and composite electrolytes are shown in Fig.1. XRD pattern of pure PVF film shows a broad hump with peak at $2\theta = 20^\circ$. This shows the semi-crystalline nature of pure PVF film. After the addition of ionic liquid in PVF polymer matrix the decrease in intensity of peak and enhancement in broadness of peak area have been observed though XRD investigation upto 40 wt% IL doped electrolyte film. This leads to decrease in the crystalline behaviour of PVF. The increase in amorphousness of system is due to the polymer salt complexation. After the dispersion of MMT powder in pristine electrolyte system, broadness of electrolyte peak increases which further leads to enhancement of amorphousness of electrolytes. This provides the better medium for fast protonic conduction in electrolyte system. This shows that MMT and graphite filler in PVF matrix are modifying the structure of host polymer.

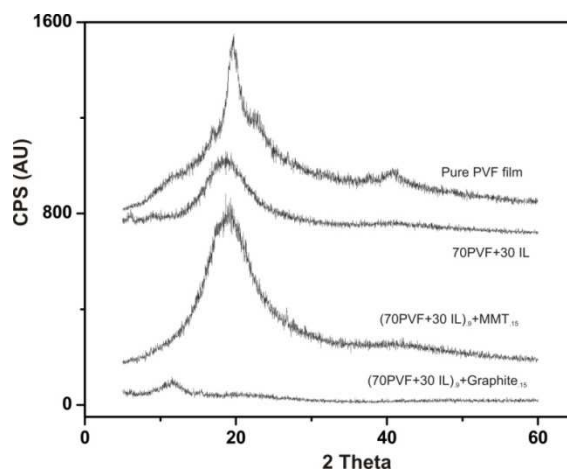


Fig. 1 XRD pattern of (0.7 PVF: 0.3IL) 0:985 -layered filler 0:015 composite polymer electrolyte system

Scanning electron microscopic image of pure PVF (Fig.2 (a)), pristine electrolytes (70PVF: 30IL), MMT and Graphite powder dispersed NCPEs are shown in Fig.2 (b, c) and Fig.2 (d). SEM image of pure PVF film shows porous behaviour and branch polymeric structure. In this image the surface morphology of polymer and composite systems are visible. On the addition of Ionic liquid in PVF polymer, the interaction of IL and polymer chain is observed. In MMT dispersed NCPE an interesting observation has been recorded that the numbers of pore per unit area have increased dramatically due to the intercalation of polymer chain with MMT filler. The SEM image is evidence of heterogeneous modification in the surface morphology of PVF-IL polymer electrolyte after the addition of layered filler (MMT and Graphite).

The FT infrared spectra of different polymer Nanocomposite electrolytes are shown in Fig.3. The prominent peaks and their assignments are given in table-1. Some salient features are as follows: On the mixing of ionic liquid, intensity of polyvinyl formal peak at 1020 cm^{-1} increases and some (peak in the range $3040\text{-}2700\text{ cm}^{-1}$) are getting decreased. Some new peaks are also generated by the interaction of PVF and IL. The addition of filler reduces the intensity and broadening of peaks of pristine and composite systems due to interference with host pristine matrix. Filler also produces some own characteristic peaks. This mutual interaction is favourable for the enhancement of amorphousness.

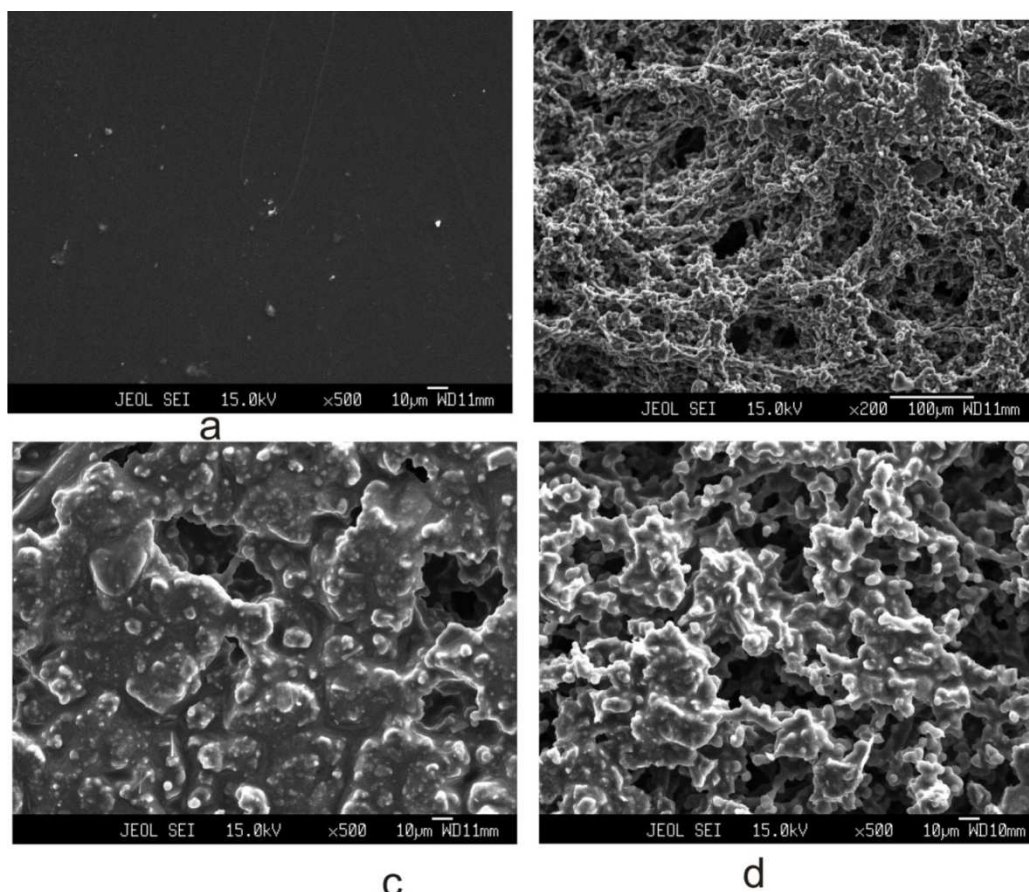


Fig. 2 SEM Image of Electrolytes (a) Pure PVF, (b) [0.7PVF: 0.3IL], (c) [0.7PVF: 0.3IL]_{0.985}: MMT_{0.015}, (d) [0.7 PVF: 0.3IL]_{0.985}: Graphite_{0.015}

Table -1 Position of IR Peaks and their Assignments

PVF (cm ⁻¹)	0.7PVF-0.3IL (cm ⁻¹)	0.7PVF-0.3IL-MMT composite (cm ⁻¹)	0.7PVF-0.3IL-graphite composite (cm ⁻¹)	Assignment of Peaks
551	553	568	571	-δ (OH)
	685	687	679	uncombined IL
	788	789		
1028	1010	1013	1014	Out of plane bending vibration of -CH bonds
			1067	C-O bond
	1180	1177	1177	Nano crystalline phase of carbon
1253		1242	1238	Tosyl function of IL - CH ₂ wagging/interaction of clay and polymer
1373				In plane bending vibration of -CH bond
			1532	Graphite G-band
	1639		1642	C=N peak
1730	1730	1730	1739	Due to -O-C=O ester carbonyl vibration of acetate unit
2850	2857	2858	2862	Symmetric and asymmetric mode of -CH, CH ₂ , CH ₃ group of
2934	2921	2957	2921	polymer backbone
3301				-OH stretching
3740	3740	3750	3743	Combination of -OH stretching vibration of vinyl alcohol

The variation of ionic conductivity with concentration of Ionic Liquid in polyvinyl formal (PVF) is shown in Fig.4. In pristine, the initial small increase in conductivity with temperature may be due to start of dissociation of Ionic Liquid in the presence of solvent, which facilitates free mobile charge carrier (cation and anion both) within the matrix. Then decrease in conductivity is observed and this behaviour can be explained with the help of effect of ion aggregation or ion accumulation on the polymer matrix. We have explained this behaviour elsewhere [11]. Similarly, the study of the effect of layered filler (MMT and Graphite) on the pristine sample is given in the same figure. The comparative look of both systems does not show the significant difference in the pattern of the variation of conductivity. The depth of decrease in temperature is relatively smaller with respect to pristine sample.

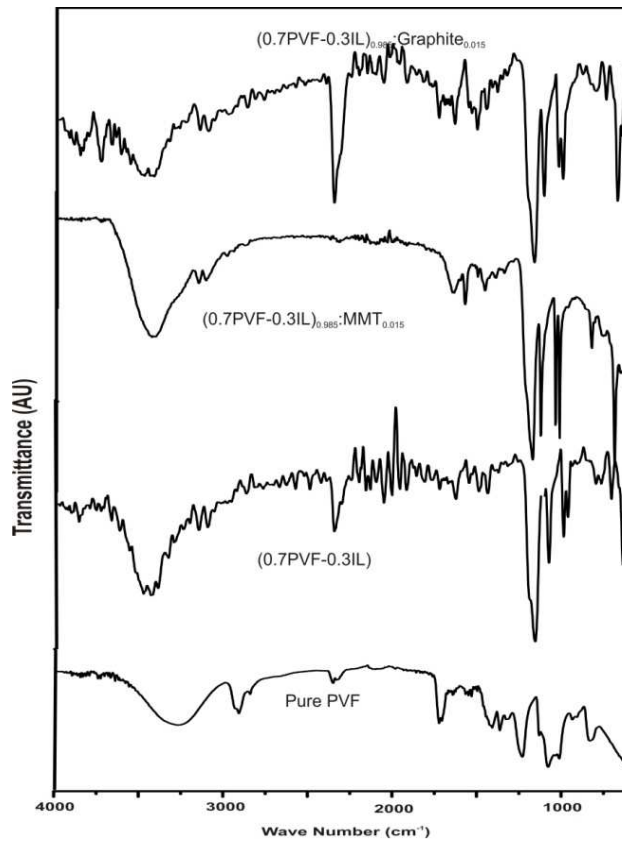


Fig. 3 IR Spectrum of composite polymer electrolyte systems

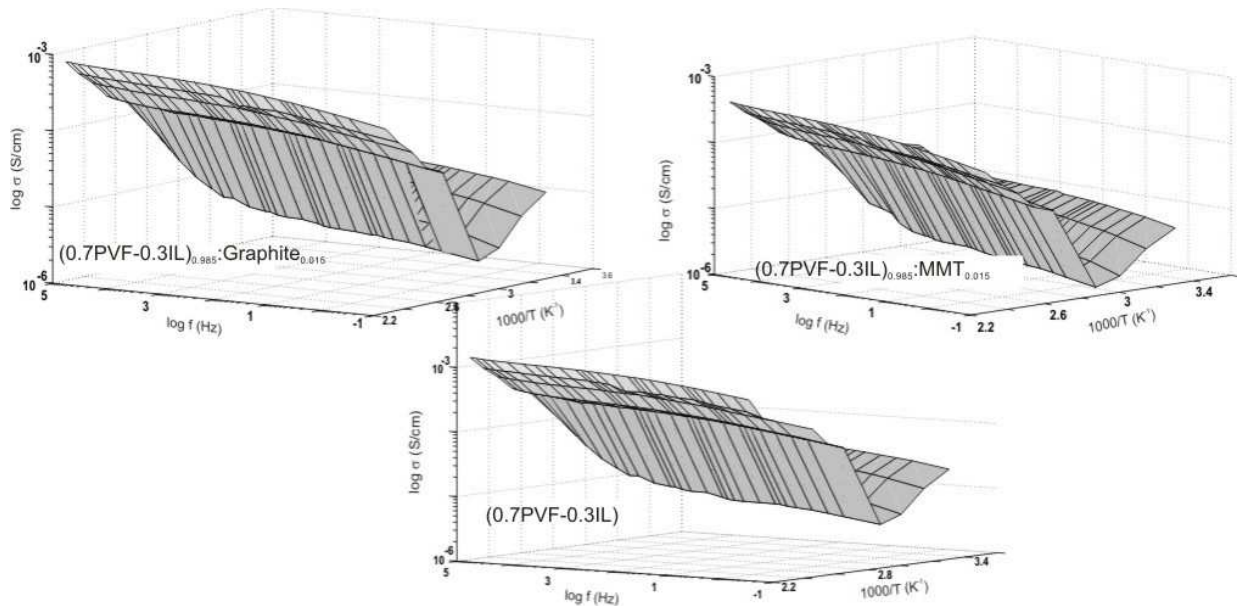


Fig. 4 Variation of conductivity with temperature and frequency

In the frequency range 300 Hz to 4MHz, the conductivity behaviour is similar to Jonscher’s Power law relation at room temperature. The frequency dependent conductivity in solid polymer electrolyte system is expressed in the Universal power law.

$$\sigma_{ac} = \sigma_0 + A\omega^n \tag{1}$$

where, σ_0 is the dc conductivity (extrapolation of the frequency dependent region to zero frequency gives the d.c. ionic conductivity), A is pre-exponential factor and n is the fraction exponent laying between 0 & 1. With the rise in temperature of sample the change in a.c. conductivity is prominently observed with frequency. This means that the charge carriers are sufficiently free to follow the changing electric field and therefore conductivity is frequency dependent. The increase in conductivity at higher temperature might be due to presence of more free ions in NCPE.

The variation of dielectric relaxation behaviour with frequency at room temperature of pure PVF, pristine electrolyte and NCPEs system are shown in Fig.5. This initial higher value of ϵ' and ϵ'' might be due to existence of an electrode and interfacial polarization- This effect in the pristine and composite electrolyte system is similar to Maxwell-Wagner- Sillars effect[12]. Fig.6 shows the variation of dielectric loss tangent ($\tan\delta$) as a function of frequency for pure PVF, electrolyte and NCPEs system at room temperature. From this figure it has been observed that $\tan\delta$ increases with doping of salt in pure polymer. This is due to increase of free mobile charge carriers available at 30wt% salt concentration and it follows to decreasing pattern achieving at higher frequency which shows the dipole relaxation changing with frequency. This is directly a manifestation of polymer chain mobility and its interaction with relaxing dipoles present in the polymer-salt complex. Such a type relaxation phenomena termed as β -relaxation may be attributed to the dipole-polymer segment interaction effect observed normally at room temperature. This peak may be attributed to segmental diffusion motion in amorphous region due to polar groups present in side chain of polymer. The loss occurring due to such interaction depends on a number of factors i.e. the number/ type of constituents in the matrix, the number of repeat units and its mobility, molecular (intra/ inter) interaction and their relaxation time.

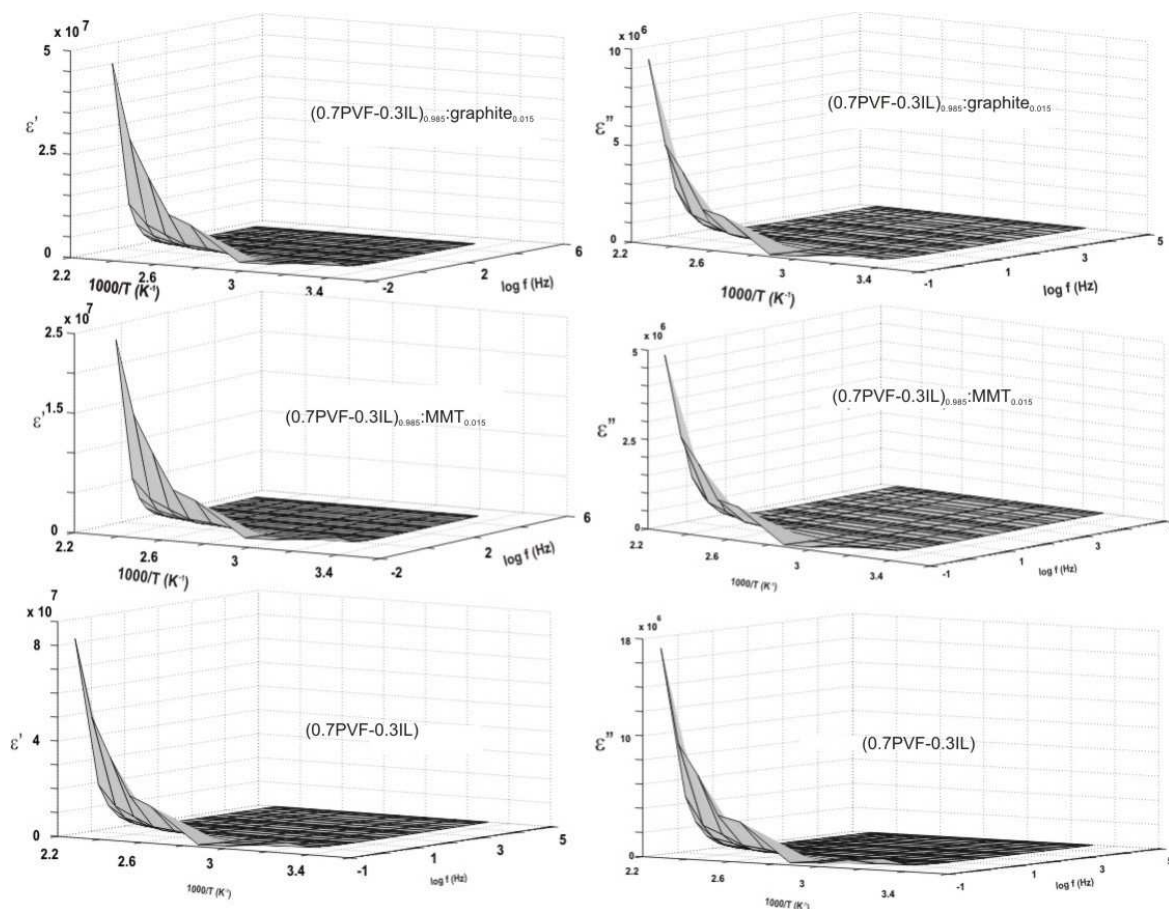


Fig. 5 Variation of Dielectric function with temperature and frequency

CONCLUSION

Experimental observations of PVF based pristine electrolytes and NCPEs has been focused on the following results. The X-Ray diffractogram shows that Ammonium acetate salt changes the amorphousness of pure PVF polymeric matrix. The increase in number of pores in surface morphology has been observed in SEM image. Dispersion of layered filler powder in electrolyte is able to enhance conductivity. Dielectric relaxation study shows the Electrode polarization and frequency dispersion at low frequency regime β -relaxation process is observed in tangent loss studies of NCPE.

Acknowledgements

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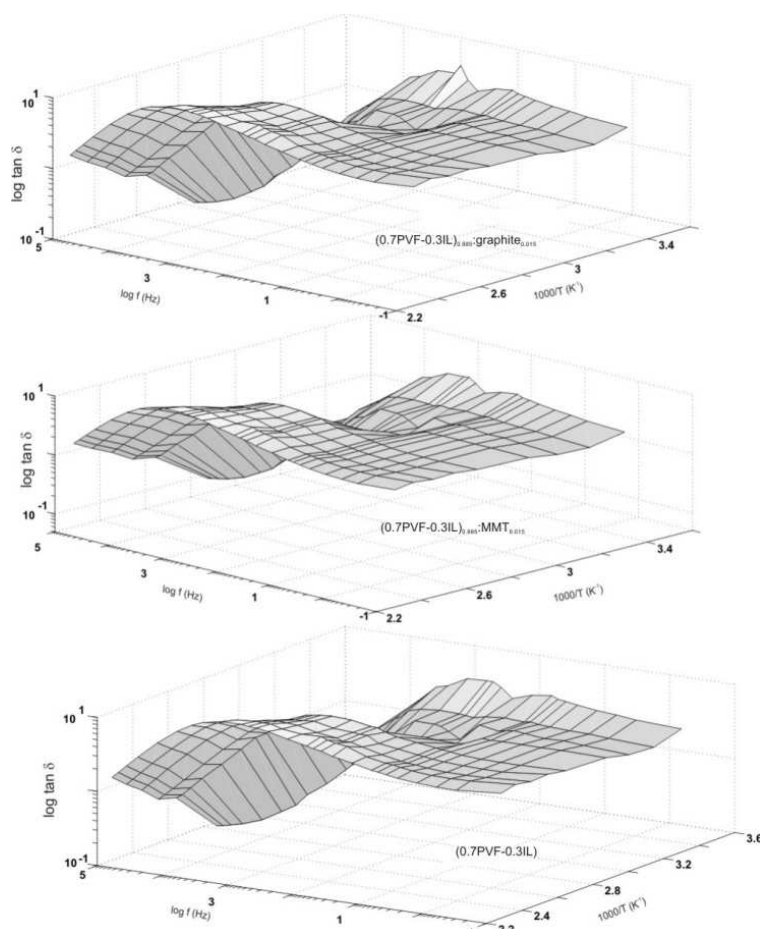


Fig. 6 Variation of Dielectric loss tangent with temperature and frequency

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