

Electrical and Dynamic Mechanical Analysis of Nano Alumina Addition on Polyvinyl Alcohol (PVA) Composites

Archana Nigrawal*, Navin Chand

Advanced Materials and Processes Research Institute, Bhopal (formerly RRL Bhopal), (CSIR), Bhopal-462064, India

*archananigrawal@yahoo.co.in

Abstract- This paper reports the Dielectric, a.c. conductivity and DMA results of nano alumina filled PVA composites. Dielectric, a.c. conductivity, Dynamical mechanical measurements were performed on these composites. Effects of temperature and frequency variation on dielectric constant (ϵ'), dielectric dissipation factor ($\tan \delta$) and on a. c. conductivity ($\sigma_{a.c.}$) were determined. With the increase of nano alumina content, the dielectric constant increased. $\tan \delta$ peak temperature shifts towards higher temperature side for all samples in both the cases of dielectric and DMA. This shows that increase in nano alumina concentration initially increased the relaxation temperature towards higher temperature. The detailed analysis of the results showed that dielectric dispersion consists of both dipolar and interfacial polarization. The Linchenecker model fits well for the dielectric data obtained experimentally for these composites.

Keywords- PVA; Nano Alumina; Dielectric; Ac Conductivity; Composite

I. INTRODUCTION

Nanoscale fillers are different from conventional micron-size fillers due to their small size and corresponding increase in surface area. It is expected that the addition of nanoparticles into polymers would enhance the electrical properties of filled polymers [1]. As compared to the other nanomaterials such as carbon nanotubes, alumina is cheaper and has the ability to be functionalized for nanocomposites fabrication.

Development of dielectric materials for applications in communication systems such as substrates, cellular phone, etc. has been rapidly progressing in the past few years [2]. An advantage of using these materials is that they make the size reduction of microwave components possible, in comparison with traditional metallic products.

The large surface area of the filler can be utilized depending on the type of property. For example, it may also result in a composite of high electrical resistivity due to the electrical resistance associated with the interface.

PVA is a hydrophilic, semi-crystalline polymer that has much attraction due to its excellent biocompatibility, nontoxicity. These properties have paved a way to the use of PVA in a wide range of applications such as medical, cosmetic, food, pharmaceutical and packaging industries. Inorganic materials can effectively improve the thermal stability and mechanical properties of PVA, thus broadening the scope of applications of PVA [3]. The dielectric behavior of polypyrrole composite films is studied in a work where PVA was incorporated as host material in the conducting composite polymer having PPy [3].

Nano-sized fillers may exhibit better electrical characteristics. Alumina is a hard spherical material, has properties like high stiffness, thermal conductivity and dielectric characteristic. Alumina has excellent size and shape capability, which is beneficial for engineering production. It is typically used for high temperature electrical insulators, high voltage insulators, electronic substrates, thermometry sensors, and grinding media [4].

Recently in a paper poly(vinyl alcohol) (PVA)–poly(ethylene oxide) (PEO) blend filled with montmorillonite (MMT) nanoclay up to 10 wt.% concentration were synthesized by aqueous solution-cast technique and characterised for their electrical properties [5].

Development of PVA-based nano-composites has been an emerging method to improve PVA's properties. PVA nano alumina nanocomposites materials with improved electrical properties may offer a viable alternative for the applications to than conventionally nano filler filled PVA materials. In our recent paper mechanical properties of the bio composite films having different wt % of treated sisal fibre powder with and without nano alumina powder were determined, and it was observed that addition of nano alumina increased the tensile strength remarkably and T_m of PVA was little affected on adding untreated sisal fibre powder. Addition of nano alumina reduced the ΔH of sisal fibre powder filled PVA composites [6].

In a paper polyimide/nano- Al_2O_3 hybrid films were prepared and characterized by transmission electron microscope (TEM) and infrared spectrum (IR). The dielectric behaviours of the composites were investigated as a function of the concentration of the Al_2O_3 nanoparticles. They reported that as the nano- Al_2O_3 loading increases, the volume resistivity and the electrical breakdown strength show a little decline, while the dielectric constant of the hybrid films increases, which was attributed to the significant interfacial zone between the polyimide and the filler [7].

There is no paper in the literature on electrical properties of nano alumina–PVA composites. In this study nano alumina filled PVA composites were prepared and characterized for their electrical and dynamic mechanical properties.

II. MATERIALS AND METHODS

Biodegradable PVA Hydrolysed (98-99%) used in this study was obtained from Sigma Aldrich having an average mol.wt-146000 and MP. 200°C. Nano alumina was obtained from Sigma Aldrich of size <50 nm, CAS1344-28-1.

Composite preparation

PVA composites were prepared by solution casting method. PVA solution was prepared by heating the desired quantity of PVA powder in distilled water at 80°C for 2 hrs on a hot plate magnetic stirrer. Three different PVA composites were prepared having 0.5, 1 and 1.5 wt % of nano alumina powder to the solution for 3 hrs on a hot plate magnetic stirrer. In a separate PVA solution desired quantities different concentration of nano alumina were added and films were casted. Stirred gel was poured on a petri dish to make film. Sample designation, wt.% of samples is listed in Table1.

TABLE I SAMPLE DESIGNATION OF NANO ALUMINA FILLED PVA COMPOSITES

wt.% of Nano Alumina	Sample Designation
0.00	PVA
0.5	Sample 1
1.0	Sample 2
1.5	Sample 3

A. Dielectric Measurements

Capacitance (C) and $\tan \delta$ values of nano alumina filled PVA composite samples were measured by using a Hewlett - Packard, LCR Meter, model 4274 A, in the temperature range from 30 to 150 °C and frequency range from 1 to 10 kHz with a constant heating rate at ± 1 °C/min. Dielectric constant (ϵ') was evaluated by using the following relation:

$$\epsilon' = C/C_0$$

Where C and C_0 were the capacitance values with and without sample, respectively; C_0 is given by $[(0.08854 A)/d]$ pF,

Where A (cm^2) is the area of the electrodes and d (cm) is the thickness of the sample. $\tan \delta$ (dissipation factor) is defined as follows.

$$\tan \delta = \epsilon''/\epsilon'$$

Where ϵ'' is the dielectric loss.

a.c. conductivity of nano alumina composite samples was calculated by using the following relation:

$$\sigma_{a.c.} = \epsilon_0 \omega \epsilon' \tan \delta$$

where $\tan \delta$ is the dissipation factor, ω is the angular frequency, which is equal to $2 \pi f$ (where f is the frequency).

B. Density Measurements

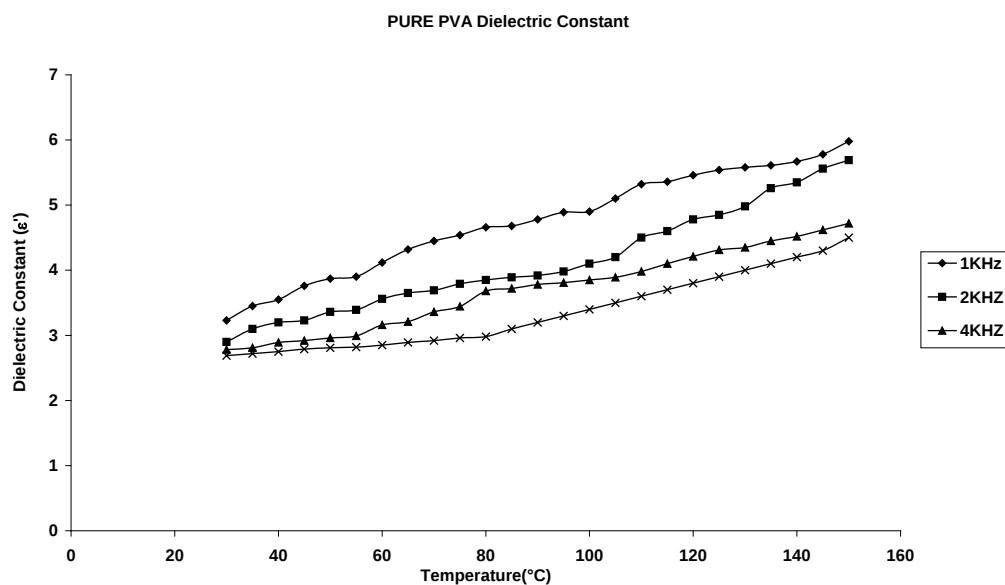
Density values of the nano alumina filled PVA composites were determined by using a Mettler Toledo precision balance based on Archimedes principle.

C. Dynamic Mechanical Analysis (DMA)

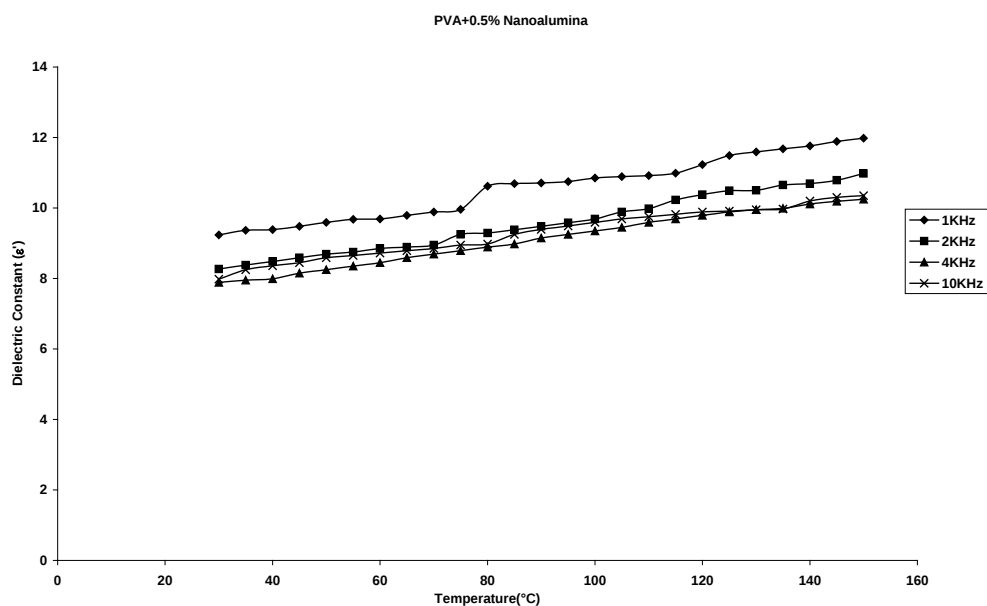
Dynamic mechanical analysis was carried out with a Dynamic mechanical spectrometer model (DMS 6100 SSI Nanotechnology Inc). Measurement of the storage modulus (E'), loss modulus (E'') and $\tan \delta$ of the samples was carried out under compression mode at 1, 2, 5 and 10 Hz frequencies in the temperature range from 30°C to 190°C.

III. RESULTS AND DISCUSSION

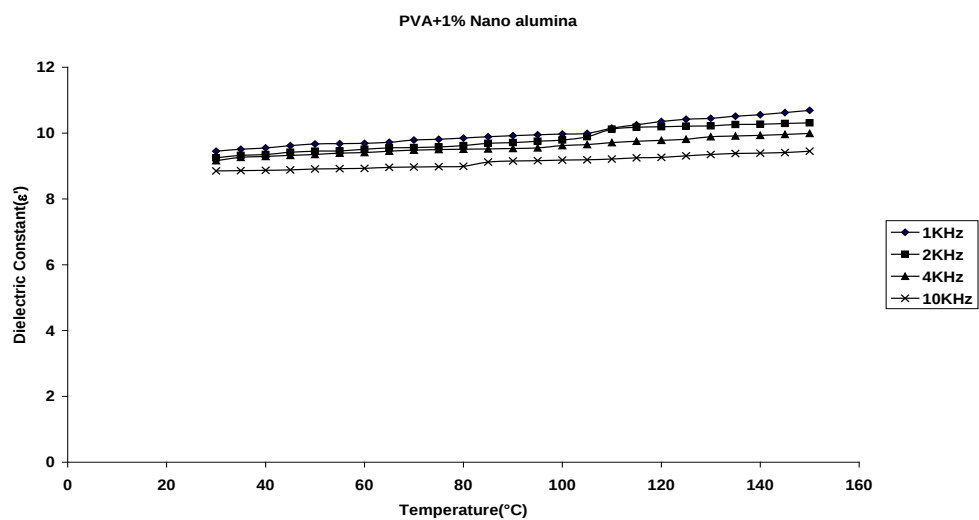
Figures 1(a-d) show the variation of ϵ' with temperature and frequency for pure PVA and samples 1, 2 and 3 respectively. At initial temperature (30°C) these plots (Figures 1(a-d)) do not show any change in ϵ' value which shows that there is no accumulation of interfacial charge within the composites. As the temperature gradually increased, it was observed that dielectric constant also increased and at 150°C, ϵ' value for the sample having higher percent of nano alumina was maximum. The increase in dielectric constant can be attributed to the fact that near the glass transition temperature, segmental mobility of the polymer chains gave high rise in dielectric constant for all the samples.



(a)



(b)



(c)

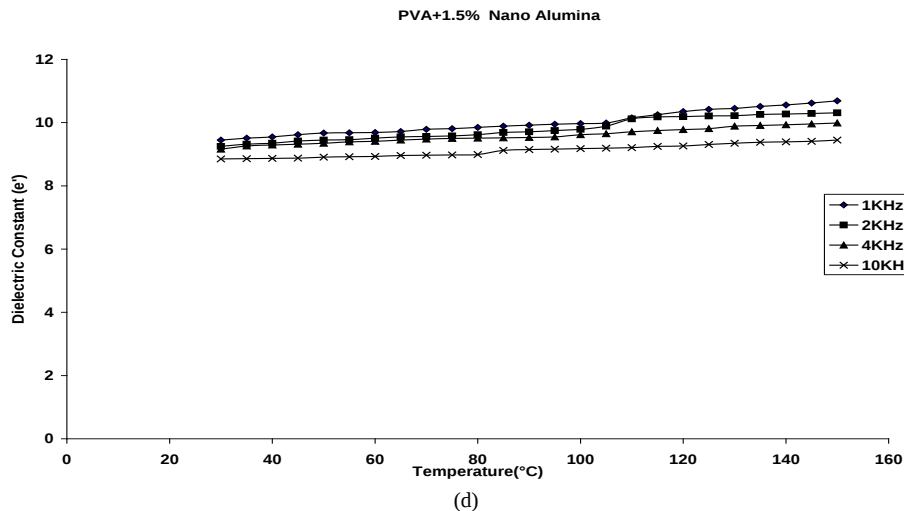


Fig. 1 (a) variation of dielectric constant with temperature of pure PVA at 1, 2, 4 and 10 kHz frequencies
 (b) variation of dielectric constant with temperature for PVA+0.5% nano alumina composite film at 1, 2, 4 and 10 kHz frequencies
 (c) variation of dielectric constant with temperature for PVA+1% nano alumina composite film at 1, 2, 4 and 10 kHz frequencies
 (d) variation of dielectric constant with temperature for PVA+1.5% nano alumina composite film at 1, 2, 4 and 10 kHz frequencies

Frequency dependent dielectric behavior of nano alumina filled PVA composite showed that the difference in ϵ' values between 1 kHz and 10 kHz at higher temperatures increased significantly. In the case of Sample 1 no major difference was observed in the variation of ϵ' which indicates that the contribution of the matrix was predominant one, because of the low concentration of filler present in the sample. The increase in ϵ' value at higher temperatures between 1 kHz and 10 kHz is due to the availability of more space for the easy rotation of dipoles and ions, and interfacial polarization occurred in the composites. Due to the interfacial polarization large local fields were generated within nano alumina PVA composite that increased the dielectric constant. In general, the greater polarizability of the molecule leads to a higher relative dielectric constant of the material. Dielectric constant values decreased on increasing frequency because when the applied field frequency increased, it was assumed that the dipoles present in the composite cannot reorient themselves fast enough and therefore dielectric constant decreases.

In case of Polyimide/nano- Al_2O_3 hybrid composites dielectric behaviours of the composites also increased on increasing the concentration of the Al_2O_3 nanoparticles [7].

Due to the presence of polymeric matrix, some charge carriers present in nano alumina get trapped and cannot freely discharge at the electrodes, and thus space charges accumulate at the interface of conducting filler. This process is Maxwell-Wagner Sillars (MWS) interfacial polarization. Maxwell-Wagner Sillars (MWS) interfacial polarization was also reported in the case of polymer silicate nanocomposites [8].

Figure 2 shows the variation of dielectric constant with concentration of the nano alumina particle in the composites. Linchenecker model fitted for the dielectric data of the composites fits well. The Linchenecker model for dielectric constant of a composite is given as follows:

$$\epsilon' = v_1 * \ln \epsilon_1 + v_2 * \ln \epsilon_2$$

Where ϵ' is the dielectric constant of the composite. ϵ_1 is the dielectric constant of the PVA. ϵ_2 is the dielectric constant of nano alumina, v_1 is the volume fraction of the PVA and v_2 is the volume fraction of the nano alumina [8]. Experimentally and theoretically calculated ϵ' values are found in good agreement.

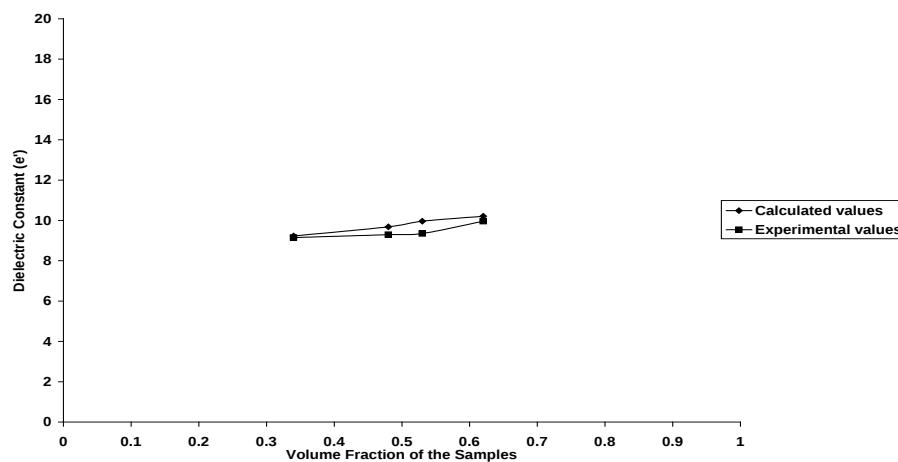
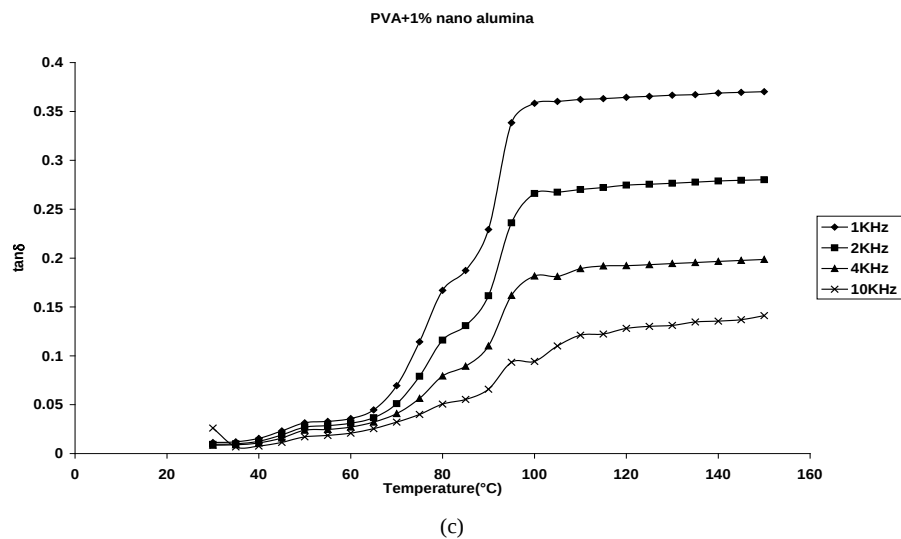
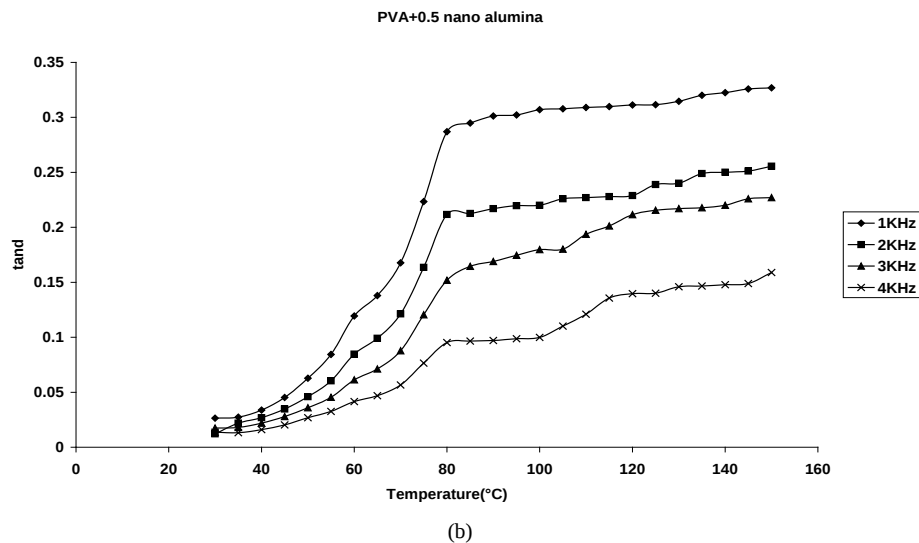
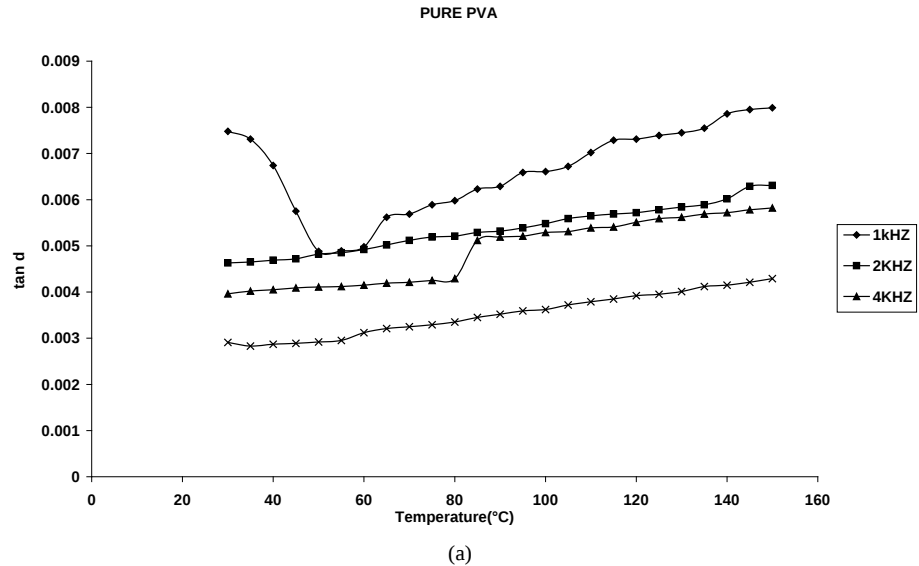


Fig. 2 variation of dielectric constant with volume fraction of the samples

Figures 3 (a-d) show the variation of $\tan \delta$ with temperature for sample 1, 2 and 3 respectively. These plots show that $\tan \delta$ increased with increase in temperature but decreased with increasing frequency for all the samples. The increase in dissipation factor with increase in nano alumina concentration is due to the interfacial polarization mechanism occurred in the composites. In the case of Sample 1 $\tan \delta$ peak at 1 kHz appeared at 90°C, and at 110°C. This peak shifts to higher temperature side at 4 kHz and appeared at 125°C. For Sample 2 at 2 kHz $\tan \delta$ peak appeared at 125°C corresponding to 1 and 2 kHz frequencies. This peak shifted to 135°C for 4 and 10 kHz.



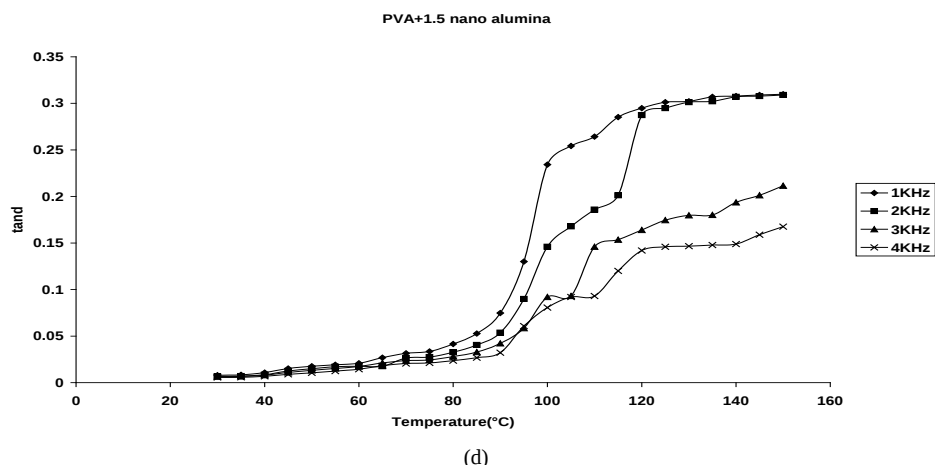
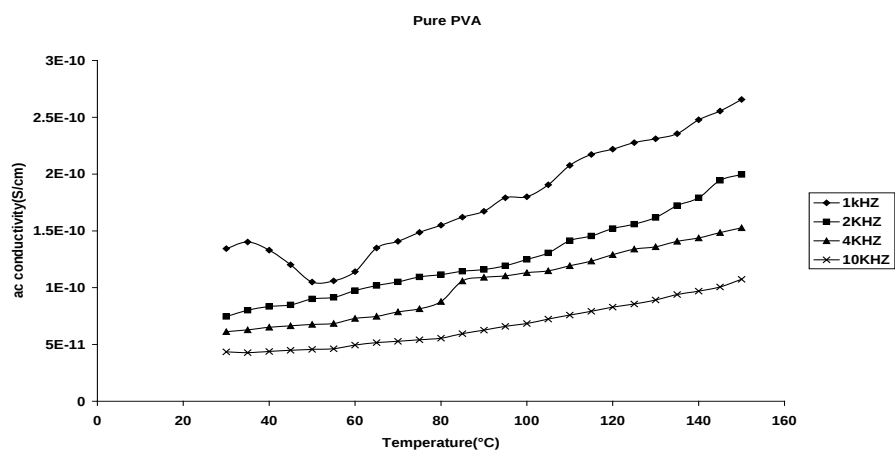


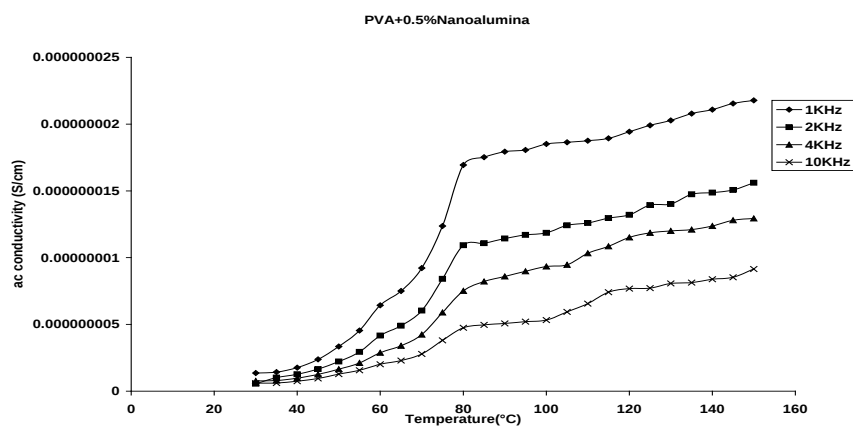
Fig. 3 (a) variation of $\tan \delta$ with temperature for pure PVA at 1, 2, 4 and 10 kHz frequencies
 (b) variation of $\tan \delta$ with temperature for PVA+0.5% nano alumina composite film at 1, 2, 4 and 10 kHz frequencies
 (c) variation of $\tan \delta$ with temperature for PVA+1% nano alumina composite film at 1, 2, 4 and 10 kHz frequencies
 (d) variation of $\tan \delta$ with temperature for PVA+1.5% nano alumina composite film at 1, 2, 4 and 10 kHz frequencies

In the case of Sample 3 $\tan \delta$ peak occurred at 115°C and at 140°C for 4 and 10 kHz frequencies. The dissipation factor attained high values, which decreased when frequency increased, illustrating the relaxation processes.

Figures 4(a-d) show the variation of $\sigma_{a.c.}$ with temperature for pure PVA and Samples 1-3. This plot shows a peak at 75°C at all the frequencies. Similarly in Sample 1, (Fig. 4b) peak appeared at 75°C at all the frequencies. In the case of Sample 2 (Fig. 4c) $\sigma_{a.c.}$ remained constant up to 95°C and then increased in $\sigma_{a.c.}$ up to 150°C. There were two peaks in $\sigma_{a.c.}$ curve between 105°C and 135°C at 1 KHz frequency. These peaks occur at 95°C and 125°C at 1 KHz for Sample 3 (Fig. 4d). Higher temperature peak is visible at all the frequencies between 125°C and 140°C. In a study temperature dependence on ac electrical conductivity of PVAPPY-FeCl₃ was reported. They observed that the ac conductivity increases with the increment of temperature and it obeys universal power law and it was driven by mobility of free charges as temperature increased [9].



(a)



(b)

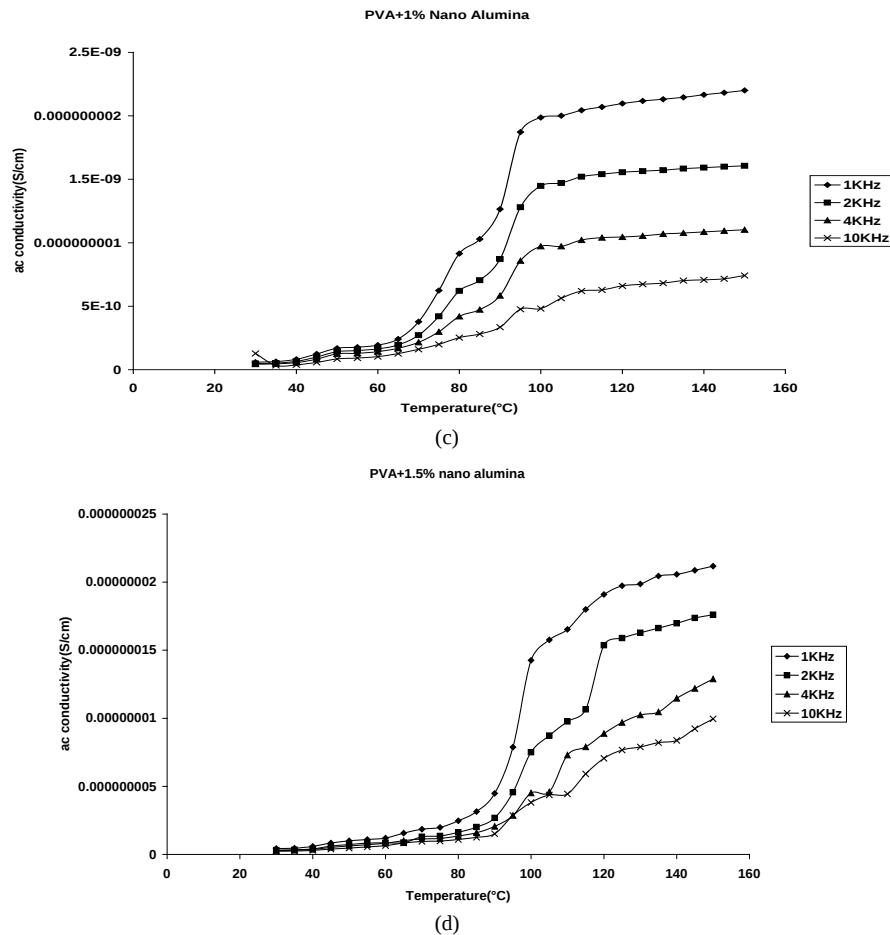


Fig. 4 (a) variation of σ_{ac} with temperature for pure PVA composites film at 1, 2, 4 and 10 kHz frequencies
 (b) variation of σ_{ac} with temperature PVA+0.5% nano alumina composite film at 1, 2, 4 and 10 kHz frequencies
 (c) variation of σ_{ac} with temperature for PVA+1% nano alumina composite film at 1, 2, 4 and 10 kHz frequencies
 (d) variation of σ_{ac} with temperature for PVA+1.5% nano alumina composite film at 1, 2, 4 and 10 kHz frequencies

Figures 5-8 show the variation of dynamic mechanical parameters such as E' , E'' and $\tan \delta$ with temperature for PVA and Samples 1-3 respectively. E' value for Sample 1 occurs at 73.9, 74.2, 75.2 and at 82.5 °C respectively corresponding to 1, 2, 5 and 10 Hz frequencies. This is due to the stiffness of alumina which increased elasticity of the nano composites. $\tan \delta$ peak temperature shifts towards higher temperature side for all samples. This shows that increase in nano alumina concentration initially increased the relaxation temperature towards higher temperature. Increase in nano alumina content from Sample 1 to Sample 3 increased the E' values from 1.28×10^8 to 6.38×10^8 Pa. $\tan \delta$ peaks shifted towards right hand side on increase in frequency. This behaviour is due to α relaxation of PVA resin. The incorporation of alumina particles resulted in some increase in the storage modulus in the whole temperature range, compared to that of the pure PVA. This can be well explained by reinforcing effect of alumina particles leading to an increased stiffness.

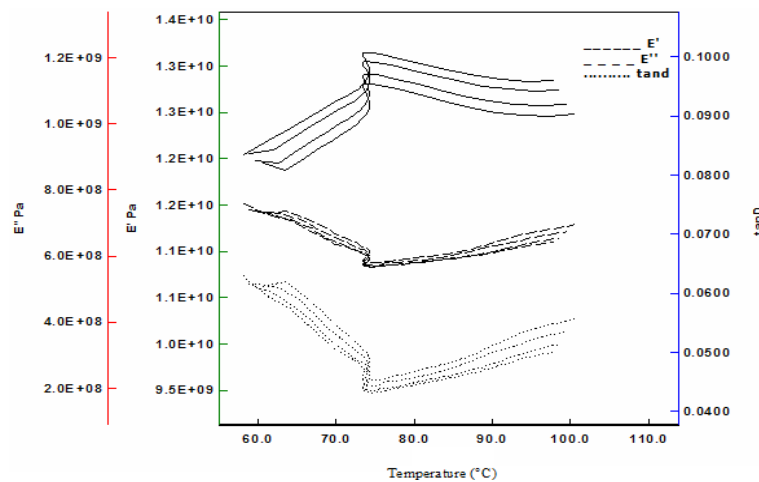


Fig. 5 DMA plot of PVA composites film

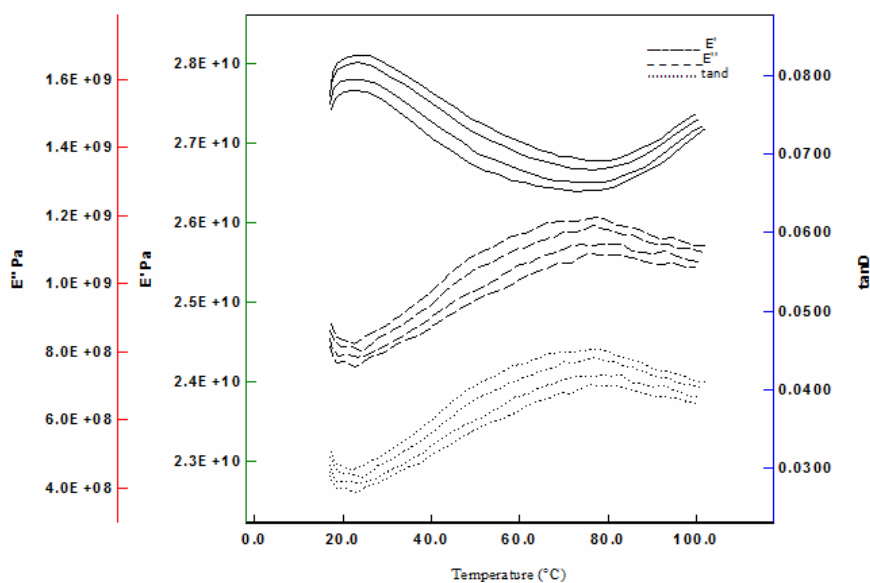


Fig. 6 DMA plot of PVA+0.5% nano alumina composite film

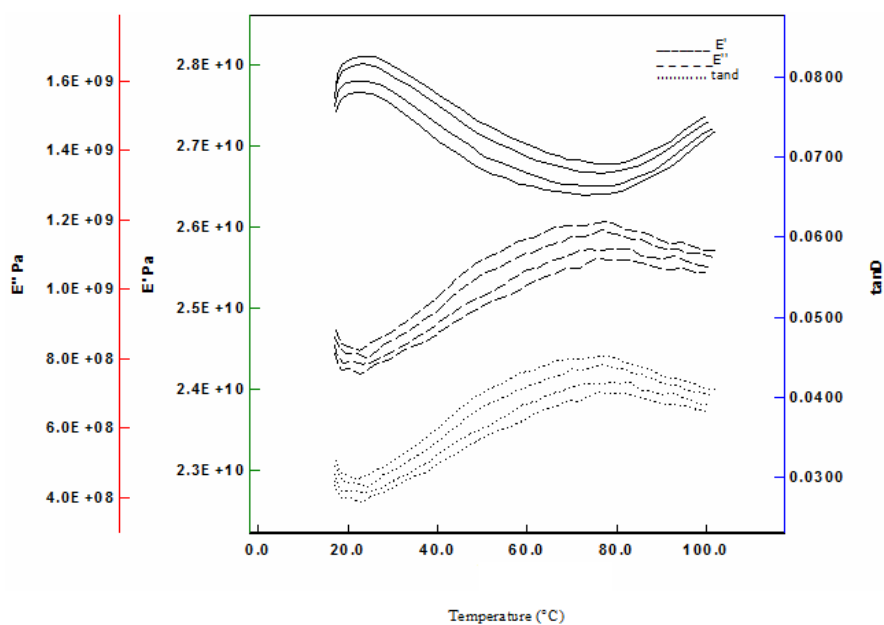


Fig. 7 DMA plot of PVA+1% nano alumina composite film

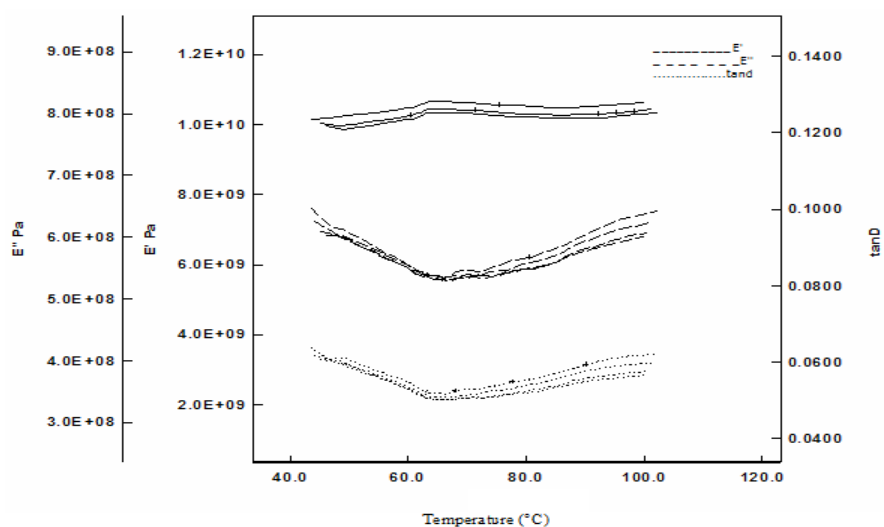


Fig. 8 DMA plot of PVA+1.5% nano alumina composite film

IV. CONCLUSIONS

It was found that dielectric constant increases with increase in nano alumina content and follows the Linchenecker model. $\tan \delta$ plots for the composites exhibit relaxation peaks. The peaks observed in case of dielectric data closely matches with that of DMA plots.

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