Synthesis, characterization and properties of poly (vinyl alcohol)/ chemically modified and unmodified pumice composites

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ABSTRACT

Biodegradable poly (vinyl alcohol) (PVA) composites with different weight percentage of chemically modified and unmodified pumice particles were prepared by a simple and ecofriendly solution casting technique. The structure and properties of polymer composites were investigated using line profile analysis employing X-ray diffraction data (XRD), UV-visible, FT-IR spectroscopic techniques, optical microscopy, DSC and electrical property measurements. The XRD pattern indicated the amorphous domain of PVA was decreased by raising the pumice content. FTIR and UV-Visible spectrum reveals the interactive co-ordination between polar segments of PVA with the polar surfaces of pumice particles. The increase in glass transition temperature (Tg) with melting behavior by the addition pumice indicated the intermolecular interaction between the pumice and PVA from DSC analysis. From optical microscopic images, the modified/PVA composite showed an excellent uniform dispersion of pumice particle than unmodified pumice PVA composites. Composite with 5 wt. % of sample films shows the higher conductivity, dielectric constant and dielectric loss tangent properties than pure polymer, due to the increase in orderliness of the pumice particles inside the polymer chain. The overall properties of chemically modified pumice/ PVA composite were higher than the PVA/unmodified pumice samples.

KEY WORDS: poly (vinyl alcohol), modified pumice, X-ray diffraction, thermal, electrical properties.

1. INTRODUCTION

Polymer composites are prepared by various methods and among them solution blending is very simple and rapid because it needs simple equipment such as glass plate and not involved in any complicated process. The properties of the composites depend upon geometry of dispersed phase and the orientation of filler particles (Yan, 2015; Nihmath and Ramesan, 2014; Ramesan and Pradyumnan, 2011). The low cost inorganic particles with polarity and highly porous structure are usually preferred by the factorial applications. Therefore many workers are focused on cheaper alternatives such as coal, fly ash, silica gel and agricultural waste (Sareena, 2012; Sunitha, 2009; Ramesan, 2015). Pumice particles are abundant in many countries, which is one of the low cost minerals that can be used as reinforcing filler in polymer. Pumice is a highly porous volcanic glass formed during explosive eruptions which is composed of 60 % of SiO_2 (Maleki and Borghei, 2005).

Biodegradable polymer has attracted much attention in the cause of the increase in environmental pollution and quick decrease in the petroleum energy sources. Among the biodegradable polymer, poly (vinyl alcohol) (PVA) has a prominent role owing to their low cost and chemical stability (Mudigoudra, 2012). Moreover the easy processability and optical transparency for the fabrication of different PVA composite by cost efficient and environmental friendly methods. In this study, the films of PVA with different content of modified and unmodified pumice composites were prepared by a simple solution casting method. The effect of chemical modification reflects on different physio-chemical properties and electrical properties (AC conductivity, dielectric constant and dielectric loss tangent) of blend composites were investigated.

2. MATERIALS AND METHODS

2.1. Materials: PVA (molecular weight 72,000) and Cetyl trimethyl ammonium bromide (CTAB) were purchased from Himedia, Mumbai and were used as received. Pumice powder with a particle dimension of 60 μm was received from Loba Chemi, India. Double distilled water was used as solvent in all the experiments.

2.2. Preparation of chemically modified pumice powder: The cetyl trimethyl ammonium bromide (CTAB), cationic surfactant with molecular mass 364.46 using as modified agent for pumice particles. Modified pumice was prepared by mixing appropriate amount of surfactant solution (CTAB) with required quantity of pumice powders. The mixture was stirred for 24 hour at room temperature, the solution was filtered washed several times with distilled water. Modified pumice dried at 120 ˚C for 8 hour then kept in desiccator.

2.3. Preparation of PVA/pumice and PVA/modified pumice micro-composites: Preparation of PVA/pumice and PVA/modified pumice micro-composites was done in water as solution mixing medium. For this, 0, 5, 10, 15 and 20

wt. % of unmodified pumice and chemically modified pumice was dispersed with PVA in water, it was then stirred for 24 h at room temperature. Finally this suspension was then treated in ultrasonicator bath for 20 minutes. The mixtures were poured into petri dishes and dried at 60 ^{0}C in an oven for three days. The films were peeled from the petri dishes and kept in vacuum desiccators.

2.4. Characterization: X-ray powder diffraction (XRD) measurements of polymer composite films were performed at room temperature on a Bruker AXS D X-ray diffractometer equipped with a back monochromator operating at an accelerating voltage of 30 kV and a copper cathode as the X-ray source (λ= 1.5406 Å). The scanning rate was 10^0 /min over a range of 10–80^0. Hitachi U-3000 spectrophotometer is used to record the ultraviolet visible (UV–vis) absorption spectra of aqueous solution of PVA with different loading of modified and unmodified pumice incorporated polymer composites. The interactions between PVA polymer chain with modified and unmodified pumice was proved by Fourier Transformation Infrared spectroscopy by using JASCO (model 4100) spectrophotometer. The surface structural morphology of the samples was taken by using Trinocular microscope Model Axio Lab.A1 attached AxioCam ERc5s Carl Zeiss Micro imaging GmbH Analyzer. The DSC studies were carried out on a V2 6D TA instrument model DSC 2010. Initial scans were taken from 50 to 100ºC to remove the thermal history effects and then cooled to room temperature. The samples were heated at a rate of 10^0C/min in a wide range of temperature suitable for the given sample. The AC conductivities and dielectric properties of the composites were measured by Hewlett–Packard LCR Meter, fully automatic system in a frequency range 10^2–10^6 Hz at room temperature.

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction studies (XRD): XRD analysis has been routinely used for crystalline phase identification based on the diffraction peak position and pattern. X-ray curve of pumice particles given in Figure 1. It shows four major diffraction peaks at 2θ= 19.4, 26.4, 29.3 and 40. 3º along with few diffraction peaks, which is mainly due to the presence of silanol and alumina groups in the pumice particles, indicating the crystalline nature of the pumice particles (Ersoy, 2010).
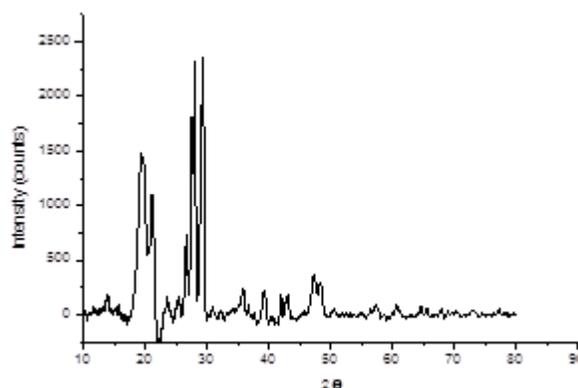
Figure.1.XRD of pumice powder

       Figure 2 shows the XRD pattern of pure PVA with modified pumice. In this a characteristic broad peak of PVA centered at 19.40º indicating the presence of semi- crystalline phase corresponding to a plane (1 0 1) in pure PVA matrix (Bhargav, 2009). The XRD of PVA/ pumice composite exhibit the characteristic peak of PVA with the diffractions of pumice. When the loading of pumice increases to 15 wt. %, the intensity of crystalline peaks is also found to be increases.

       Figure 3 represent the X-Ray diffraction profile of PVA with 5 and 15 wt. % of unmodified pumice particles. In this a broad diffraction peak of PVA is centered at 2θ = 19°, corresponding to the amorphous part of PVA. In addition, there are two diffraction peaks in PVA with 5 wt. % observed at 2θ = 28.8°and 40.0° indicates the semi-crystalline part of the composite. This systematic arrangement of pumice inside the macromolecular chain of PVA is mainly due to the strong intermolecular complex formation between hydroxyl group in PVA and polar silanol group in pumice.

PVA with 15 wt. % unmodified pumice has very perfect crystalline peaks are formed at $2\theta = 27.84$ and 27.94^{0}. It is interesting to observe that the diffraction peaks of the PVA/modified pumice particles appear to be more packing with standard diffraction pattern as compared to PVA/unmodified pumice. This is because of the surface modifications on pumice particles improves the adhesion between the polymer and the filler surfaces (Elashmawi, 2013).
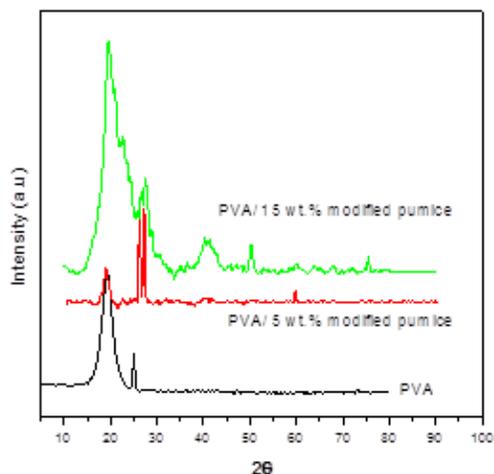
Figure 2. XRD of PVA/modified pumice
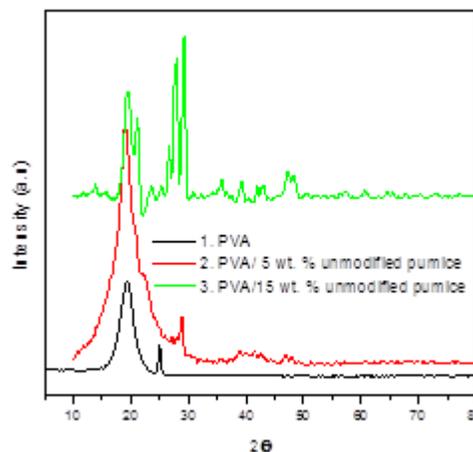
Figure 3. XRD of PVA/unmodified pumice

3.2. UV-Visible spectroscopy: UV–VIS spectra in the wavelength range of 190–800 nm of various concentration of modified and unmodified pumice with are shown in Figure 4 and 5 respectively. Both graphs have a sharp and strong absorbance in the region of 205 -215 nm. This is attributed to the $n \rightarrow \pi^{*}$ transitions of PVA. The main absorption for all curves showed that the intensity of the absorption peak of PVA is decreases by the addition of pumice particles. Moreover the composite with 5 wt. % of sample show the maximum absorption and the absorption of composite is slight shifted towards lower wavelength region with respect to pure PVA. These shifts indicate the coordinate affinity between pumice and PVA segments. The observed spectra in PVA with unmodified pumice particle have no noticeable peak shift. This is due to the poor complexation between the pumice particles and polymer.
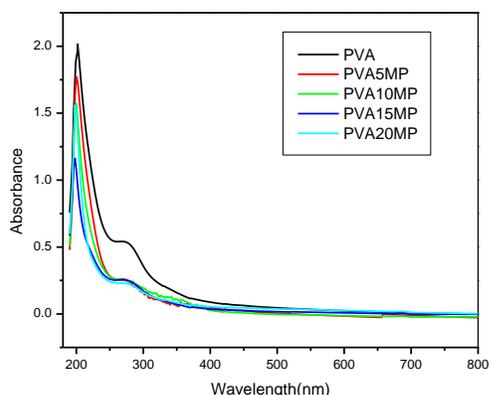
Figure 4. UV-Visible spectrum of PVA / different content of modified pumice
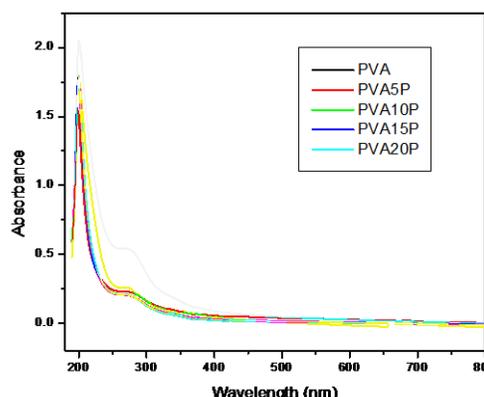
Figure 5. UV-Visible spectrum of PVA with various content of unmodified pumice

3.3. FT-IR spectroscopy: The elucidation of the molecular structure of polymers and its composites was done by Fourier transform infrared spectroscopy (FTIR). Figure 6 and 7 shows FTIR absorption spectra of PVA with and without different concentrations of modified and unmodified pumice respectively. All spectra exhibited characteristic bands of stretching and bending modes of OH, C–H, CH_2, C=O and C=C groups. The bands at 3320 and 1635 cm^{-1} are assigned to O–H stretching and bending vibration of hydroxyl group stemmed from the presence of PVA,

respectively. The band at 3475 cm^{-1} became smaller with shoulder at 3460 cm^{-1} after adding both pumice and modified pumice. This gives a clear indication about the specific interaction of pumice particle in the polymer matrices. The band at about 1091 cm^{-1} corresponds to C–O stretching of acetyl groups present on the PVA backbone. But this peak is absent by the addition of filler particles. The result indicates that the polar groups are the active cites during synthesis and a strong interaction between these groups leads to slight shift of absorption frequencies.
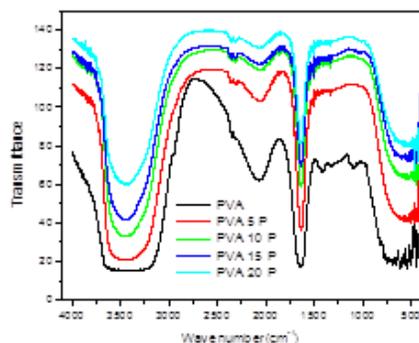
Figure.6.FTIR spectra of PVA/modified pumice   **Figure.7.FTIR spectra of PVA/unmodified pumice**
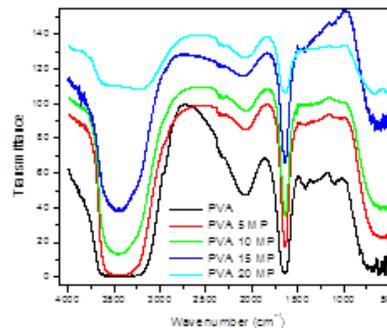
From the spectra it can be noticed that the addition of pumice powder causes some observable changes in the spectra of the composite in the range 1000- 400 cm^{-1}. It induces a new absorption band at 769 cm^{-1}, is due to the interaction between pumice particles and the polymer chain.

3.4. Optical microscopic images: The optical images of PVA and PVA with different content of unmodified and modified pumice composites are given in Figure 8. PVA/unmodified pumice composite show surface irregularities as compared to PVA with chemically modified pumice particles. The remarkable changes in the optical images of modified pumice/PVA is due to the chemical modification on pumice particles (treatment with cationic surfactant CTAB) lowers the surface energy of pumice surfaces and there by improves the interaction between polymer and filler particles. When the concentration of pumice became 15 wt.% (Fig. 7 (b) and (d)), the agglomeration of filler particles can be clearly evident from the figure.
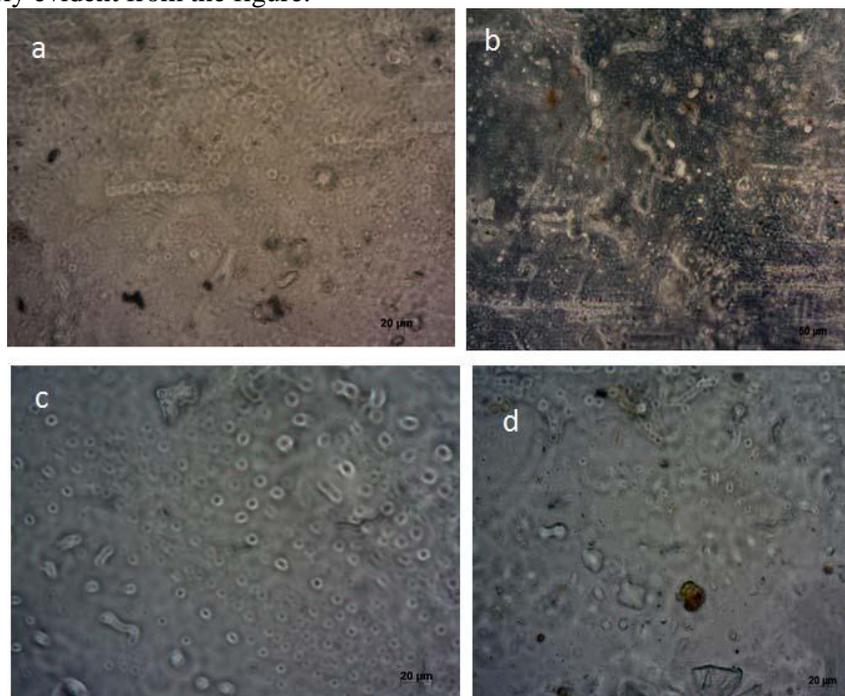
Figure.8.Optical images of PVA with unmodified pumice (a) 5 wt. % (b) 15 wt. % and modified pumice (c) 5 wt. % (d) 15 wt. %

3.5 Differential Scanning Calorimetry (DSC): Differential scanning calorimetry to study the thermal transition taking place by the interaction of different weight percentage of pumice with polymer and is as shown in Figure 9. The DSC graph of PVA (Figure 9) showed the glass transition temperature (Tg) at 73°C, whereas the pumice particles embedded PVA exhibit the glass transition temperature at 75 and 79 ºC for 5 and 15 wt. % pumice particles respectively. The increment in Tg with the raise in concentration of filler particles is due to the polar-polar interaction between the polymer chain and pumice surfaces (Ramesan and Lee, 2008). It is also evident from the figure that the melting temperature of PVA composite is further increased by the addition of pumice particles and this may be due to the strong interfacial interaction between the pumice and PVA segments.
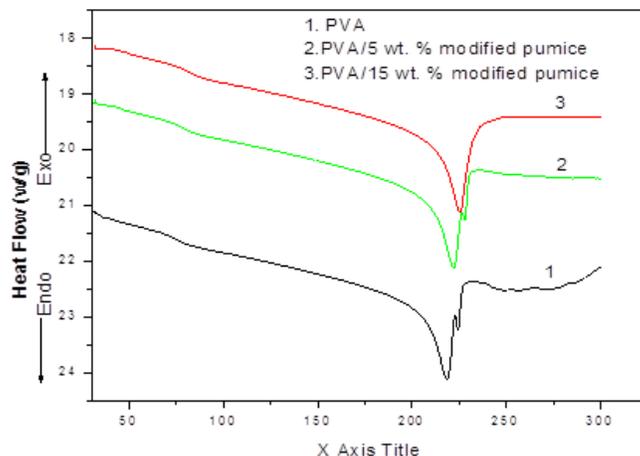
Figure.9.DSC patterns of PVA/with different content of modified pumice particles

3.6. AC Conductivity: Alternating current response as a function of frequency offers valuable information about the dynamic response of the polymeric system. Figure 10 and 11 shows the AC electrical conductivity of PVA with various amounts of chemically modified and unmodified pumice particles at different frequencies respectively.
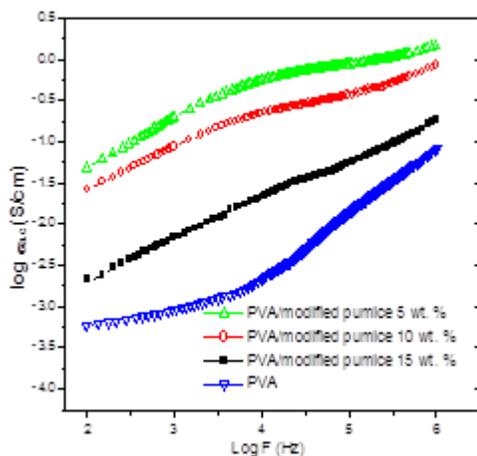
Figure 10. AC conductivity of PVA/ modified pumice
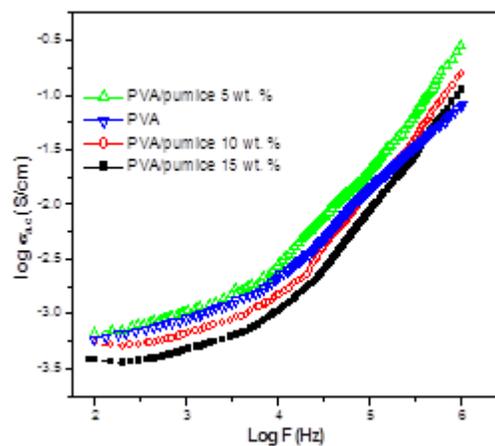
Figure 11. AC conductivity of PVA/ unmodified pumice

It can be seen from the figure that 5 wt. % of sample shows the maximum the AC conductivity and after that the conductivity value decreases with further addition of pumice particles. In the case of unmodified PVA/ pumice composite, the conductivity of 10 and 15 wt. % of samples are lower than the bare polymer. However in modified pumice composite, the AC conductivity of 15 wt. % of sample shows the lower conductivity value than pure PVA. This is because the chemical modification on pumice powder lowers the surface energy which leads to the uniform

arrangement and distribution of filler particle in polymer matrix (Ramesan, 2001). When the loading of pumice particles reached above the critical concentration, the available surface area of the filler for the reaction decreases which ultimately result in poor conductivity. Another interesting observation is that, the conductivity of modified pumice with PVA composites is much higher than the unmodified blend composites. The silica other metal oxides present in the pumice particles contains many metal impurities, which is not favorable for the physical interaction between the organic and inorganic components.

3.7. Dielectric Constant: The variation of dielectric constant with frequency at room temperature for PVA composite and different weight percent of modified and unmodified pumice particles incorporated PVA is presented in Figure 12 and 13 respectively. The dielectric constant decreases rapidly with increase in frequency and reaches a constant value at 10^4 Hz for all the polymeric system. The high dielectric constants at lower frequencies are due to orientation polarization mechanism developed in the polymer matrix. It can be seen that the PVA/ modified pumice composite shows very high dielectric constant value than unmodified pumice/ PVA system. The high dielectric values of modified pumice composites are due to the enhanced compatibility between the pumice particles and the PVA molecules (Ramesan, 2014). Moreover, the uniform dispersion of pumice particles in to the macromolecular chain of PVA leads to a higher dielectric value for the composites. In all the cases, the dielectric constant of 5 wt. % of composite is much higher than pure PVA. The decrease in dielectric constant above 5 wt. % of sample is due to the agglomeration of pumice powders in the polymer chain and this reduces the segmental mobility of the chain and this result is in good agreement with the optical images of composites.
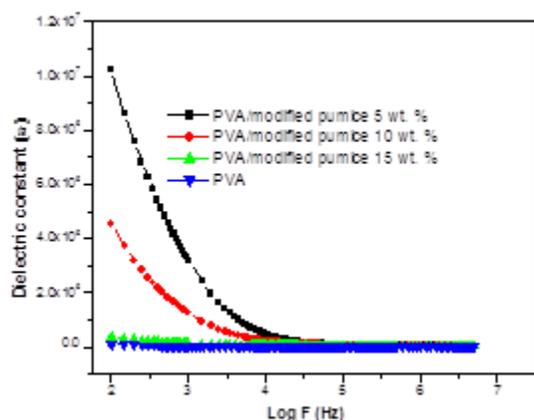
Figure.12.Dielectric constant of PVA modified pumice
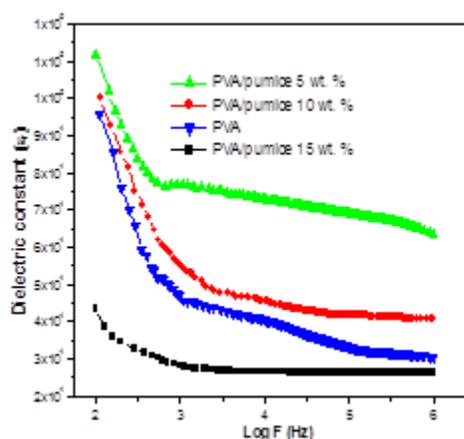
Figure.13.Dielectric constant of PVA unmodified pumice

3.8. Dielectric loss: The plot of dielectric loss tangent (tan δ) vs. logarithmic frequency for PVA with modified and unmodified pumice particles are presented in Figure 14 and 15 respectively. It is clearly evident from the figure that the dielectric loss tangent of modified pumice particles incorporated PVA shows higher dielectric values than the unmodified pumice/PVA composite. Modified composites with 5 wt. % of samples shows the higher tan δ value at a frequency of 10^2 to $10^{4.5}$ Hz followed by a sharp decrease at higher frequencies, while the all samples of unmodified composite shows sharp decrease in dielectric loss with increase in frequency. The dielectric loss tangent of material generally depends upon the polarity of matrix, molecular interaction and the mobility of polymer chain (Subbaraj, 2014). The chemical modification on pumice particles improves the interfacial interaction between the filler surface and the polymer chain. The lower value dielectric loss at higher concentration of pumice particles is due to the aggregation of filler, which leads to a high viscosity of the polymer matrix (Jayakrishnan and Ramesan, 2014). The dielectric loss tangent values of unmodified pumice/ PVA composites are much lower than that of pure PVA. The poor tan δ value is mainly due to the poor interfacial interaction between the pumice powder and PVA chain.
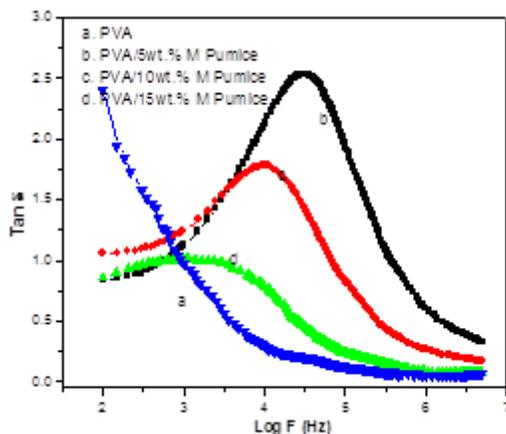
Figure.14.Dielectric loss tangent of PVA/modified pumice
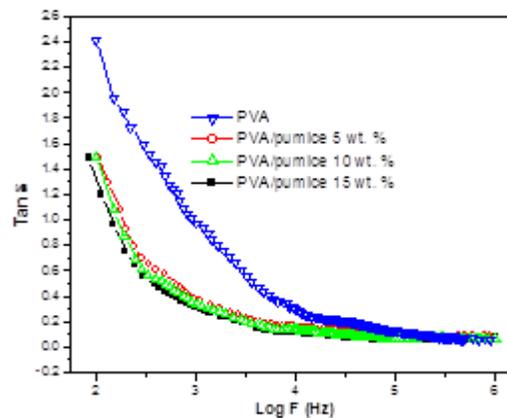
Figure.15.Dielectric loss tangent of PVA/ unmodified pumice

4. CONCLUSIONS

PVA with various contents of modified and unmodified pumice composites were prepared by a simple solution casting method and their crystalline and electrical properties were investigated. XRD studies showed that the amorphous nature of the composite was decreased due to the interaction of pumice particles with the polymer chain. UV-Visible spectroscopic studies revealed the strong intermolecular interaction between PVA with modified and unmodified pumice particle. FT-IR analysis reveals the chemical interaction between the hydroxyl groups of PVA with the silanol group in pumice particles. Optical images depicts the better surface morphology of chemically modified/ PVA composites than the unmodified PVA composite. Melting temperature and the glass transition temperature of composites were found to be increases with increase in weight percentage of pumice particles in PVA. AC electrical conductivity, dielectric constant and dielectric loss factor of pumice loaded PVA was studied as a function of frequency at different loading of fillers. The electrical properties of the composite was maximum up to 5 wt. % of pumice and with further addition of fillers, the conductivity and dielectric properties found to be decreases. The higher value of conductivity of the modified pumice composite is due to the higher compatibility between the polymer and pumice surfaces.

5. ACKNOWLEDGEMENTS

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