



“Dielectric relaxation studies of biodegradable polymeric films based on composition of Gelatin and PVA”

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Abstract

The dielectric properties of PVA are considered to be a good tool for studying the polarization as well as molecular relaxation mechanisms dealing with the dynamics of mobile groups. Hence it is very important to examine the dielectric properties of PVA as a result of the variation of its molecular motion, which is affected directly by gelatin concentrations. PVA-gelatin polymer electrolyte films with different percentage of gelatin have been prepared by casting method. At microwave frequency (9.03 GHz) and at temperature 308K, the dielectric permittivity, dielectric loss, loss tangent, dielectric conductivity, relaxation time, extinction coefficient and refractive index of films were studied as a result, all of them increases with the increase in gelatin percentage.

Keywords: PVA, gelatin, dielectric permittivity, dielectric conductivity, loss tangent, refractive index

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1. INTRODUCTION

Plastics represent, however, an integral part of contemporary life and their share in both commodities and high-tech applications is expected to increase in future. Conventional polymers such as polyethylene and polypropylene persist for many years after disposal. Built for long haul, these polymers seem inappropriate for applications in which plastics are used for short time periods and then disposed. Furthermore, plastics are often soiled by food and other biological substances, making physical recycling of these materials impractical and generally undesirable. In contrast, biodegradable polymers disposed in bioactive environments degrade by the enzymatic action of microorganisms such as bacteria, fungi and algae. Their polymer chains may also be broken down by nonenzymatic processes such as chemical hydrolysis. Biodegradable polymers are often derived from plant processing of atmospheric CO₂. Biodegradation converts them to CO₂, CH₄, water, biomass, humic matter and other natural substances. Biodegradable polymers are then naturally recycled by biological process. The worldwide consumption of biodegradable polymers has been increasing for last decade, because biodegradable polymers are designed to degrade upon disposal by the action of living

organisms. Extraordinary progress has been made in the development of practical processes and products from polymers such as starch, cellulose, gelatin and lactic acid. The need to create alternative biodegradable water soluble polymers for down-the-drain products such as detergents and cosmetics has taken an increasing importance.

PVA is a non-toxic, water-soluble synthetic polymer, which has been employed in biomaterial technology for the pharmaceutical and biomedical areas due to its excellent film-forming, emulsifying and adhesion properties [1]. The PVA is obtained by hydrolysis of poly (vinylacetate), then different types of PVA can be produced depending on the degree of hydrolysis involved. The degree of hydrolysis of PVA can affect the physical properties of this polymer and its films [1].

Gelatin is a natural polymer that is prepared by partial hydrolysis of collagens, and is a well-known organic nitrogenous colloidal protein, which lacks some amino acids, as tryptophane [2,3]. A large number of glycine present in the gelatin (almost one in the three residues, arranged after every third residue), proline and 4-hydroxyproline residues. A typical structure is -Ala-Gly-proline-Arg-Gly-Glu-4Hyp-Gly-Pro.

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Gelatin is a heterogeneous mixture of single or multi-stranded polypeptides, each with extended left handed proline helix conformations and containing between 300 and 4000 amino acids [4]. The use of biobased polymeric materials as one of the components in the production of plastic items presents several advantages connected with their origin and amenability to biodegradation [5]. Among biopolymers, proteins have shown to be versatile materials that combine many characteristics relevant for technical applications such as good processability both in the melt and solution and also good film-forming properties [6]. Proteins are well known example of biodegradable polymers. Proteins contain hydrolysable linkages but do not have regular and equivalent repeating units along their polypeptide chains and are mostly amorphous. All these structural characters of protein make it easier for enzymes to facilitate biodegradation. Proteins are often used for the formation of products such as coatings, capsules in pharmaceutical and food industries, adhesive, surfactants and plastic items. However, the higher price of proteins and proteinaceous materials as compared to some other biopolymers, especially starch and cellulose, has limited research on their technical applications.

Chiellini *et al.* [7,8] elaborated biodegradable films based on PVA and waste gelatin, with sugar cane bagasse as the filler and Maria *et al.* [9] and Bergo *et al.* [10] developed the same types of film but without the filler. The chemical structure (responsible for functional group-stability, reactivity, hydrophilicity and swelling behaviour) is the most important factor affecting the biodegradability of polymeric materials. Other important factors are inter alia, physical and physico-mechanical properties, e.g. molecular weight, porosity, elasticity and morphology (crystalline, amorphous) [11,12]. However, more data on the physical properties of films based on blends of PVA and gelatin, produced by casting, are necessary. Thus the objective of this study is the development of biodegradable films based on blends of gelatin and PVA, with no plasticizer and the characterization of their dielectric studies on

behaves of the parameters like dielectric permittivity, dielectric loss, ac conductivity, relaxation time, loss tangent, extinction coefficient and refractive index.

2. EXPERIMENTAL

Polymeric films of virgin PVA and filled PVA with gelatin were prepared in the laboratory by solution cast method [13-16], gelatin was taken in the percentage weights viz., 2%, 4%, 6%, 8% and 10% and subjected to measure their dielectric parameters at microwave frequency in X-band, using the technique developed by Dube and Natarajan [17]. The average thickness of all prepared films were of the order of 100 μm .

3. RESULTS AND DISCUSSION

Figures 1-7 show the variation in the dielectric permittivity (ϵ'), dielectric loss (ϵ''), relaxation time (τ), ac conductivity (σ'), loss tangent ($\tan\delta$), extinction coefficient (k) and refractive index (n) of pure PVA and its composite films, prepared in different concentrations of gelatin at microwave frequency of 9.03 GHz and at temperature 308K. While Table 1 depicted the evaluated values of all dielectric parameters for all the PVA/gelatin composite specimen under investigation.

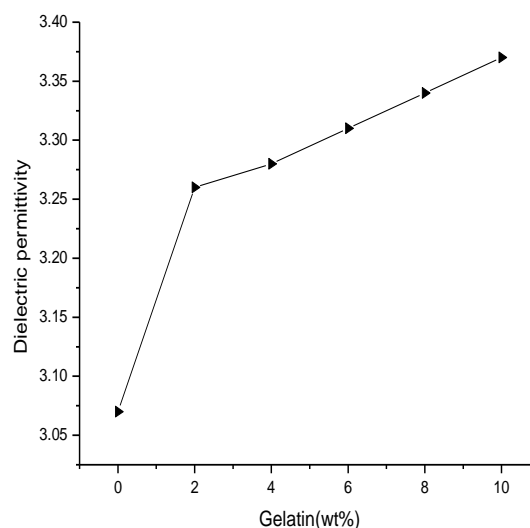


Figure 1 :- Variation of dielectric permittivity (ϵ') with doping percentage of Gelatin in PVA

Table 1:- Dielectric parameters, dielectric permittivity (ϵ'), dielectric loss (ϵ''), ac conductivity (σ'), relaxation time (τ), loss tangent ($\tan\delta$), extinction coefficient (k) and refractive index (n), carried out for PVA and PVA/gelatin composite films at 9.03 GHz frequency and at temperature 308K

Sample	Dielectric constant ϵ'	Dielectric loss ϵ''	ac conductivity σ' (Sm ⁻¹)	Relaxation time τ (10 ⁻¹²) Sec.	Loss tangent $\tan\delta$	Extinction coefficient k	Refractive index n
PVA	3.07	0.72	0.36	4.1	0.23	0.11	1.76
PVA+2%gelatin	3.26	0.99	0.50	5.4	0.31	0.15	1.83
PVA+4% gelatin	3.28	1.32	0.66	7.1	0.40	0.19	1.85
PVA+6% gelatin	3.31	1.51	0.76	8.1	0.46	0.22	1.86
PVA+8% gelatin	3.34	1.78	0.89	9.4	0.53	0.25	1.89
PVA+10% gelatin	3.37	2.19	1.10	11.5	0.65	0.30	1.92

The dielectric permittivity (ϵ'), of composite films increases on increasing gelatin contents into PVA lattice. The ϵ' for pure PVA was found 3.07 and for different gelatin composition into PVA, ϵ' varies from 3.26 to 3.37. The higher value of ϵ' on doping is due to the presence of additional charge carriers and restrictions of their movement in the polymer chain, local accumulation of charge will give rise to interfacial polarization.

Therefore, due to intra and intermolecular interactions [18,19], ϵ' increases on doping of gelatin, as shown in Figure 1 Ahmed and Hanafy [20] investigated the dielectric constant of PVA-gelatin blends at lower frequency range and at different temperature regions, 290K to 460K. The dielectric permittivity (ϵ') for pure PVA was found within 12.0-4.0 for the frequencies between 100 Hz-1000 KHz, at temperature 310K and for 25 wt% presence of gelatin into PVA, ϵ' varies from 15.0 to 9.0 for the same frequency region and at temperature 310K.

The results carried out by Ahmed and Hanafy show decreasing trend for the value of ϵ' , on increasing frequencies from 100 Hz to 1000 KHz for pure PVA and PVA/gelatin blend films. Since our results were evaluated at the frequency 9.03 GHz, which is quite higher as compared to the frequencies used by Ahmed and Hanafy, and temperature 308K. Our dielectric permittivity (ϵ') for pure PVA and PVA-gelatin composite films are accordingly. ϵ' for pure PVA and PVA-gelatin composite films decreases at microwave frequencies and increases with the addition of gelatin into PVA matrix.

Figure 2 shows the variation of dielectric loss (ϵ'') with dopant concentration. ϵ'' for pure PVA and doped PVA with gelatin, was found in

the range 0.72-2.19. Dielectric loss (ϵ'') is a direct function of relaxation process [13,16] and the origin of this relaxation is due to the local motion of polar groups. ϵ'' for pure PVA is increased on doping of gelatin into PVA. The increase in ϵ'' may be due to the increase in the polarity of the molecules on doping for large molecule, the rotary motion of the molecules was not sufficiently rapid for the attainment of equilibrium with the field. So that more time was required for the dipole to reorient, i.e., relaxation time (τ) was increased and hence dielectric loss (ϵ'') was increased.

The relaxation time comes out for pure PVA was 4.1 ps. Value of τ increases on doping of gelatin into PVA and found in the range 5.4-11.5 ps (Fig. 3) for different concentration of gelatin into PVA matrix.

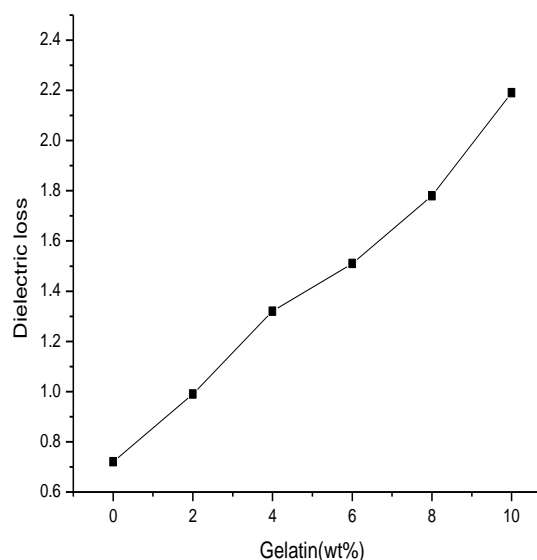


Figure 2:- Variation of dielectric loss (ϵ'') with doping percentage of Gelatin in PVA

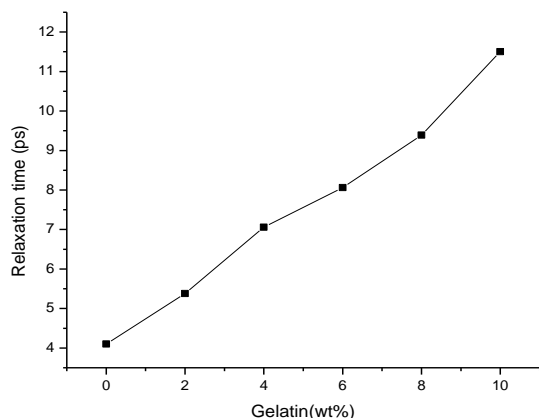


Figure 3:- Variation of relaxation time (τ) with doping percentage of Gelatin PVA

Figure 4 shows the increase in ac conductivity (σ') on doping of gelatin into PVA. The σ' for pure PVA is 0.36 Sm^{-1} and for all the PVA-gelatin composite films σ' lies in the range $0.50\text{-}1.10 \text{ Sm}^{-1}$. The conduction mechanism may be ascribed to the conjugated C=O groups produced by PVA-gelatin interaction and free C=O, which are formed by the oxidation of -OH groups of the host polymer. In fact, PVA is a polar polymer and considered as a good charge-storing dielectric by virtue of its insulating properties and high concentration of deep traps. Accordingly the subsequent trapping of gelatin molecules is expected to promote the supply of more conductive impurities, which acts as a charge sources share in PVA conductivity. The increase in ac conductivity on doping may be due to the sample softening. Thus, the charge carriers can move more easily through the sample volume, giving rise to a large current.

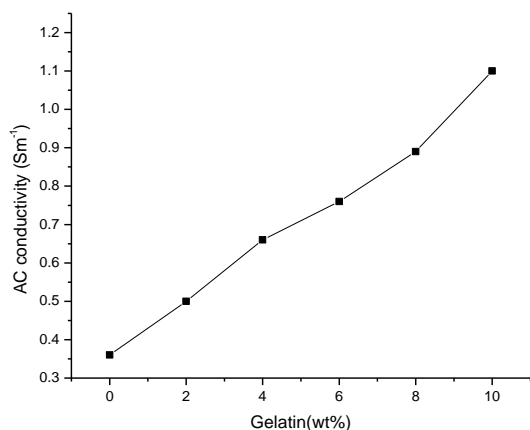


Figure 4 :- Variation of ac conductivity (σ') with doping percentage of Gelatin in PVA

Loss tangent ($\tan\delta$) has been obtained for all the investigated films and found in the range $0.23\text{-}0.65$. The origin of microwave dielectric loss is attributed to dipole absorption dispersion in the polymers, dipolar losses due to impurities and photon-phonon absorption spectra corresponding to the density of state in the amorphous regions of polymer [21]. The variation in the loss tangent ($\tan\delta$) with doping concentration is illustrated in Figure 5.

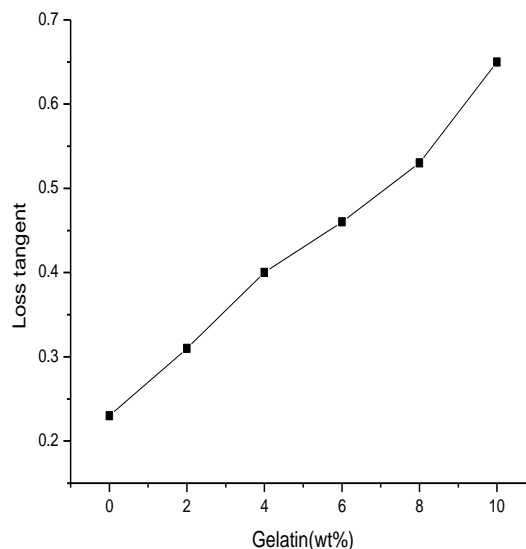


Figure 5 :- Variation of loss tangent ($\tan\delta$) with doping percentage of Gelatin in PVA

The optical constant viz., extinction coefficient (k) and refractive index (n) have been obtained by using equations used by Tanwar *et al.* [13,16]. For virgin PVA, k comes out to be 0.11 and for PVA-gelatin composite films, k varies in the range $0.15\text{-}0.30$. The values of refractive index were found in the range $1.76\text{-}1.92$, for PVA and its composite films with gelatin.

The variation in k and n with doping concentration are shown in Figures 6 and 7 respectively. The significance of k is given by the fact that after the wave has travelled over a distance equal to the wavelength of wave in the dielectric material, its amplitude decays by a factor $e^{-2\pi k}$.

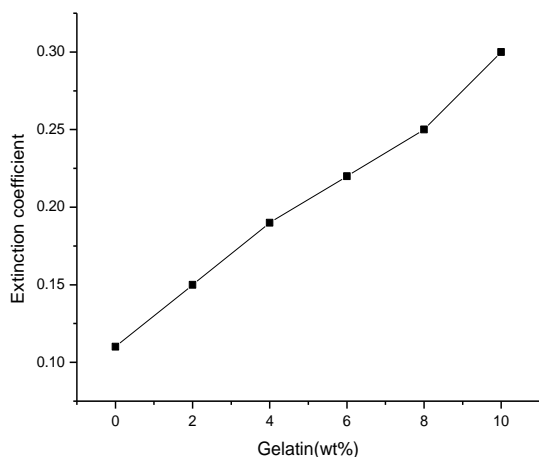


Figure 6:- Variation of extinction coefficient (k) with doping percentage of Gelatin in PVA

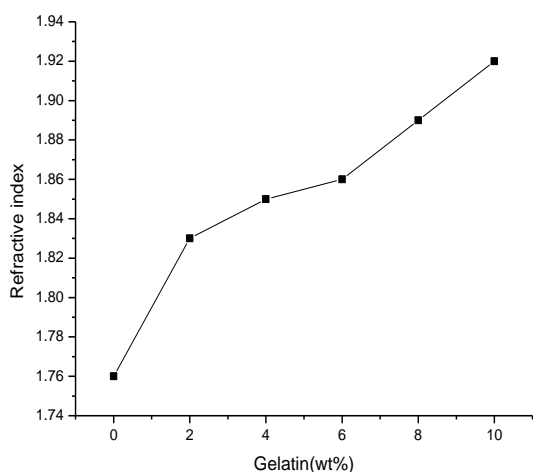


Figure 7 :- Variation of refractive index (n) with doping percentage of Gelatin in PVA

4. CONCLUSION

- The dielectric parameters carried out at microwave frequency (9.03 GHz) and at temperature 308K for pure PVA and PVA-gelatin composite films, have been found to show incremental values. The ϵ' varies from 3.07-3.37 and ϵ'' from 0.72-2.19, as gelatin content increases into PVA matrix. The loss tangent is found to vary from 0.23-0.65, thus having good microwave lossy behaviour.
- The present study of PVA host and its gelatin composite films reveal that PVA can be effectively combine with gelatin to enhance its dielectric parameters such as ac conductivity, relaxation time, extinction coefficient and refractive index obtained

for the samples under investigation, and alter their conduction behaviour.

- Blending gelatin with PVA to produce biodegradable composite materials with adequate dielectric properties could be a practical way to reduce environmental pollution.
- The increase in conductivity with increasing concentration of gelatin is attributed to decrease in the degree of crystallinity and increase in the amorphicity.
- The ac conductivity was less than that of conductor, but greater than that of an insulator at microwave frequencies. Because of this property, it can be used to construct microwave components like filters.
- Being an electrode less technique, measurements at microwave frequencies are free from electrode polarization and associated problems and thus yield real material parameters.

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