

Surface and dielectric studies of PVC-PVP blend films for green electronics

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In the present communication, an attempt has been made to prepare and study surface and dielectric properties of polyvinylchloride-polyvinylpyrrolidone blend films. Surface properties such as water absorption, contact angle, surface free energy of the films have been measured to investigate the interaction of blend films with water. These measurements reveal that on increasing the weight percentage concentration of polyvinylpyrrolidone in polyvinylchloride, hydrophilicity of the films increases. The surface free energy increases with increasing concentration of polyvinylpyrrolidone in polyvinylchloride, which indicates that these films tend to adsorb more moisture and dust particles from atmosphere thereby affecting its ageing and rendering it degradability. Further the dielectric properties in the low frequency range (1 kHz – 2 MHz) have been studied. The results show that the dielectric constant, loss tangent and ac conductivity of blend films increase as the weight percentage concentration of polyvinylpyrrolidone is raised. Amongst various compositions of polyvinylchloride-polyvinylpyrrolidone films studied, it is the blend film having 50% weight concentration of polyvinylchloride and polyvinylpyrrolidone each which exhibits improved mechanical flexibility, better degradability and modulated dielectric properties. This biodegradable low-cost composition can find application in field of green electronics.

Keywords: Polyvinylchloride, Polyvinylpyrrolidone, Water absorption, Contact angle, Dielectric constant, ac conductivity

1 Introduction

Polymer films with well-defined surface and bulk properties find a large number of applications in green electronics, automotive, construction, cosmetic, pharmaceutical and biomedical arenas due to their low cost, light weight, easy processability, excellent chemical resistance and non-corrosive nature¹⁻³. The characterization of surface properties especially the surface free energy of polymer films is critically important in a number of industrial applications and also has an influence when used in biomedical field. Surface free energy has a direct impact on the ageing property of polymer film and it strongly depends on the surface morphology, chemical composition and the presence of hydrophilic/hydrophobic functional groups on the surface of films⁴. The water absorption of polymeric materials is a less investigated but very important property which plays a crucial role in several applications of polymers such as personal care products, coatings and membranes used in biomedical field, biodegradable substrates used in the field of green electronics, insulation of underwater cables, etc.³. Recently, polymers with hydrophilic surfaces are used as electrochemical double layer capacitors, gas sensing, supercapacitors and biocompatible/biodegradable

coatings⁵. Dielectric spectroscopy is a strong tool for studying the bulk properties of polymeric blended films. So, a considerable interest is seen in studying water absorption, contact angle, surface free energy of polymer blend films and relate them with dielectric properties of films as their relationship opens up broad range of applications^{6,7}.

Polyvinylpyrrolidone (PVP), a conjugated polar polymer is known to have a growing pharmaceutical, biomedical importance and possess good electrical properties. PVP also offers high hydrophilicity and biocompatibility^{8,9}. However, films made of PVP alone are not practically as useful as they dissolve in water very easily and also become quite brittle on aging resulting into their poor processability. Combining PVP with other polymers could give better quality flexible/processable films and modify its surface, dielectric and mechanical properties¹⁰. To make PVP amenable, here it is proposed to blend it with polyvinylchloride (PVC). PVC, a synthetic polymer finds its applications in diversified fields as blood tubings, blood bags, consumer goods, cable insulation, etc. PVC is a proton donating polymer, while PVP is proton accepting polymer^{11,12}. It is expected that the donor-acceptor capabilities of these polymers could result into a blend film with modulated dielectric and surface properties.

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In the present communication, an attempt to prepare and study PVP rich PVC-PVP blend films was made with the aim of designing tailor made water absorption, wettability, mechanical flexibility and dielectric properties of polymer film for their prospective applications in the green electronics, agriculture, pharmaceutical, cosmetics and biomedical fields.

2 Experimental

2.1 Materials

Polyvinylchloride (PVC) of average molecular weight 62,000 gm/mol supplied by Sigma Aldrich was used as an insulating matrix. Polyvinylpyrrolidone (PVP) supplied by Loba Chemie having average molecular weight of 40,000 g/mol is used. Tetrahydrofuran purchased from HPLC is used as solvent.

2.2 Sample preparation

Free standing films of pure PVC and PVP were made by solution cast method. THF was used as solvent to prepare the films. PVC film was successfully casted. Pure PVP film could be casted but with great difficulty and it lacked mechanical flexibility. In order to get PVP rich robust and flexible film, the blends of PVC and PVP were made by gradually increasing the weight percentage concentration of PVP as 10%, 20%, 30%, 40%, 50%, 60% and 80 % in PVC. However, it was observed that PVC film with 60% and 80% weight concentration of PVP could not be formed. Therefore, films of pure PVC and PVP and blend films with 10%, 20%, 30%, 40%, 50% concentration of PVP in PVC were selected for further studies. All the films were prepared at room temperature. The average thickness of the films was of the order of 0.08 cm.

2.3 Characterization techniques

2.3.1 Morphological and structural characterizations

Polymer morphology is a microscale property that is largely dictated by the amorphous or crystalline portions of the polymer chains and their influence on each other. The morphology of PVC, PVP and PVC-PVP films were examined using scanning electron microscope (SEM) (JEOL JSM 6360) with acceleration voltage of 20 kV. For this purpose, thin layer of platinum (50 Å) was deposited on the film using physical vapour deposition. X-ray diffraction (XRD) data was obtained using a Bruker AXS D8 Advance Powder X-ray diffractometer. The XRD patterns were recorded in the 2θ range of 10° - 90° with

step width 0.020° and step time 64 seconds using $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$).

2.3.2 Water absorption, contact angle and surface free energy measurement

The samples were air dried at 323 K up to a constant weight. They were then immersed in a static deionized water bath. The specimens were taken out of the water after a certain time period, wiped with tissue paper to remove traces of water on their surface and reweighed. The percentage of water absorption (WA%) was calculated by the weight difference between the samples exposed to water and the dried samples according to the equation discussed elsewhere¹³.

The surface wettability of the films was tested by measuring the contact angle (θ) of a water droplet of 1 μL placed on the film surface using the contact angle meter equipped with a CCD camera (Contact Angle meter, Rame-Hart instrument, USA) at ambient temperature and surface free energy was calculated from contact angle data¹⁴.

2.3.3 Mechanical flexibility

The mechanical flexibility of the polymeric films can be measured by measuring its folding endurance¹⁵. The folding endurance is determined by folding the film repeatedly at 180° angle of the plane at the same place until it breaks. The film exhibiting folding endurance value of 300 or more is considered to have excellent flexibility¹⁶.

2.3.4 Low frequency dielectric measurements

Agilent precision LCR meter and Agilent solid test fixture having electrodes of diameter (0.5 cm) were used for measurements of dielectric parameters in the frequency range of 1 kHz to 2 MHz. Frequency dependent values of parallel capacitance C_p and parallel resistance R_p , with sample were measured for evaluating the dielectric parameters at room temperature. The real part ϵ' and the imaginary part ϵ'' of the complex permittivity, loss tangent $\tan\delta$, ac conductivity σ_{ac} , real part M' and imaginary part M'' of complex electric modulus and real part Z' and imaginary part Z'' of complex impedance of the films were determined from equations discussed elsewhere¹⁷.

3 Results and Discussion

3.1 SEM and XRD analysis

To investigate the morphology of PVC, PVP and PVC-PVP blend films, scanning electron microscopy was performed and their images are shown in Figs 1-3.

The surface of PVP film exhibited certain degree of roughness as compared to surface of PVC-PVP blend film. X-ray diffraction is used to observe different types of polymers phases (crystalline, semi-crystalline and amorphous). In order to investigate the microstructure evolution of PVC-PVP blend film, XRD analysis was performed. Figure 4 shows the XRD pattern of PVC, PVP and PVC-PVP blend film. The XRD pattern of PVP shows sharp and intense peaks. However, PVC and PVC-PVP blend films show broad humps of low intensity exhibiting their amorphous nature.

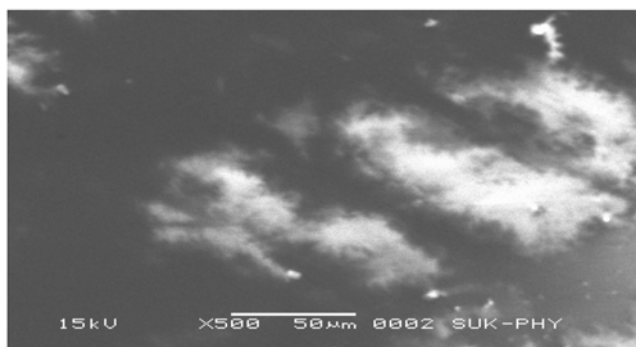


Fig. 1 — SEM image of PVC film.

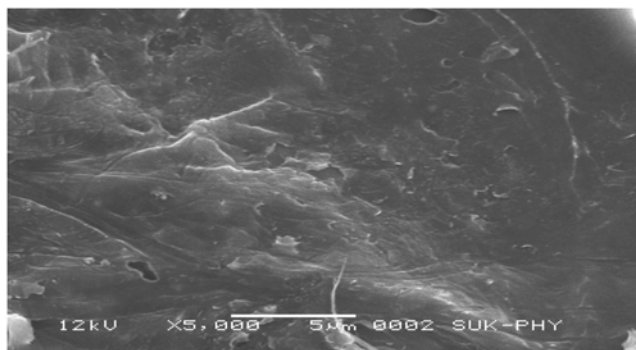


Fig. 2 — SEM image of PVP film.

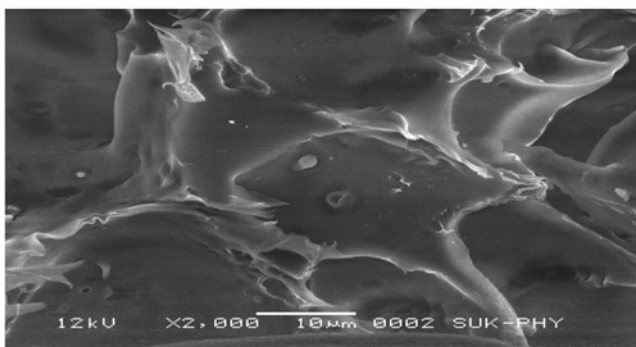


Fig. 3 — SEM image of PVC-PVP blend film.

3.2 Water absorption, contact angle and surface free energy studies

The water uptake characteristics of PVC, PVP and PVC-PVP blend films at room temperature are studied for a fixed period of time. Values of water absorption (WA%) as a function of percentage concentration of PVP in PVC film is plotted as shown in Fig. 5. It was observed that the water absorption of the PVC-PVP blend films increases with the increasing percentage concentration of PVP in PVC. This behavior was expected since the water absorption of these blend films is mainly due to the presence of PVP, which is soluble in water even at room temperature¹⁸. The PVC-PVP blend film with 50% weight concentration of PVP dissolved in water.

The increase in water absorption will make the film easier to dissolve in water as the absorption of water

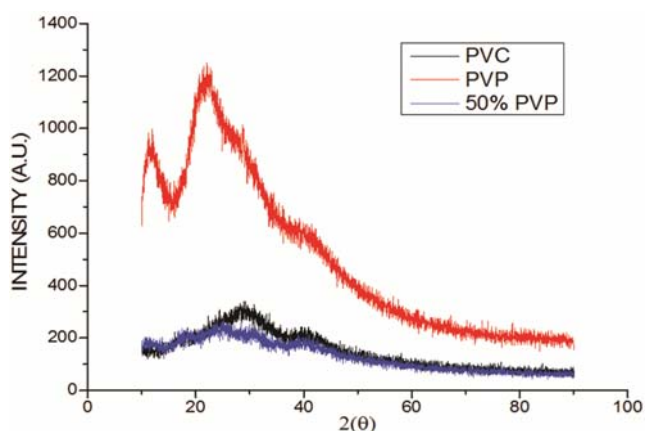


Fig. 4 — XRD patterns of films.

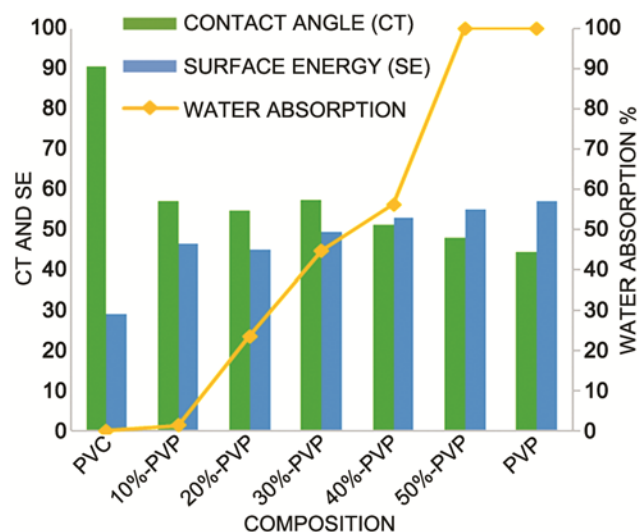


Fig. 5 — Water absorption, contact angle and surface free energy measurements of films under investigation.

on to the hydrophilic group mainly occurs through hydrogen bonding or weak electrostatic interactions and the film can be easily dissipated with the water molecules¹⁹. It was this combination of PVC-PVP, i.e., 50% weight concentration of PVC and 50% weight concentration of PVP which exhibited both the mechanical flexibility which is the characteristic feature of PVC the host matrix and the degradability which is a distinctive property of PVP. Wettability studies were performed by measuring contact angles in order to investigate the ability of the PVC, PVP and PVC-PVP blend films surface to make an intimate contact with water. Figure 5 shows the contact angle and surface free energy of films. It is revealed from the graph that the contact angle of blend films decreases on increasing the amount of PVP in PVC²⁰. The contact angle data was further used to calculate the surface free energy (SFE) of polymer films. Various methods are available to calculate surface free energy from contact angle data^{4,21}. In the present study, surface free energy was determined using Neumann method. Neumann has derived following equation for determination of surface free energy from single liquid contact angle measurement²¹:

$$(\gamma_s / \gamma_l)^{0.5} \exp \{ -\beta_1 (\gamma_l - \gamma_s)^2 \} = 0.5 (1 + \cos \theta) \quad \dots (1)$$

Where γ_s is the SFE of a solid, γ_{sl} is the SFE corresponding to the solid-liquid interface, γ_l is the SFE of a measuring liquid, and θ is the contact angle between the solid and the measuring liquid and $\beta_1 = 0.0001247$ has been determined experimentally²¹.

The surface free energy was found to be increasing with increase in weight percentage concentration of PVP in PVC. Blend films with higher values of surface energies tend to adsorb more moisture from atmosphere and will have short life time. Amongst all the compositions of blend films PVC film with 50% weight concentration of PVP was found to be the most hydrophilic film with high surface free energy value thereby reducing its age.

3.3 Folding endurance

The flexibility of films was determined by measuring their folding endurance. For this each film was repeatedly folded at 180° angle of the plane at the same place until it breaks. The number of times the film could be folded at same place without breaking gives the value of folding endurance. The results of average folding endurance are given in Table 1. The folding endurance values of PVC-PVP blend films were >200 rendering them flexibility as compared to PVP film.

3.4 Low frequency dielectric studies

The variation in real part of the complex permittivity (ϵ'), i.e., dielectric constant of pure PVC, PVP and PVC-PVP blend films as a function of frequency is shown in Fig. 6. It is observed that the ϵ' values of all samples decrease on increasing frequency. The values of ϵ' are higher at low frequencies, due to the Maxwell-Wagner interfacial polarization effects within the bulk of the sample and the electrode polarization effects, but as the frequency of the applied field is increased, the ϵ' values begin to decrease. At high frequencies, the periodic reversal of the electric field occurs fast. Due to this there is no excess ion diffusion in the direction of the field resulting in decrease²² in values of ϵ' . ϵ' values for the blend films are almost intermediate between its values for pure PVC and PVP in the measured frequency range. Similar behaviour was observed by Rawat *et al.* in PVP-PAM blend films²³.

The dependence of loss tangent $\tan \delta$ on frequency is shown in Fig. 7. The loss tangent $\tan \delta$ spectra show dispersion in the measured frequency range²⁴. Further at 2 MHz the ϵ' values of some of the blend films are in the range of 2-3 and the $\tan \delta$ values are less than 0.07. These films can be used as low dielectric constant materials in the low frequency region²⁵.

Table 1 — Folding endurance of polymer films.

| Composition | Mean folding endurance (n =3) |
|-------------|-------------------------------|
| PVC | 348 |
| PVP | 04 |
| 10% PVP | 308 |
| 20% PVP | 296 |
| 30% PVP | 281 |
| 40% PVP | 255 |
| 50% PVP | 248 |

n =number of repeated observation

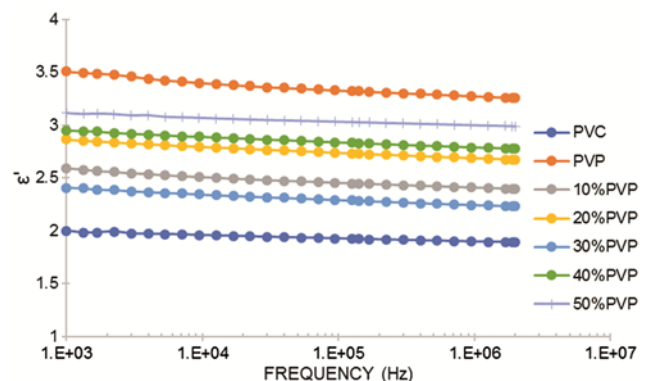


Fig. 6 — Variation of real part ϵ' of the complex permittivity of films with frequency.

Frequency dependent spectra of AC conductivity σ_{ac} for pure PVC, PVP and PVC-PVP blend films are shown in Fig. 8. The AC response of all the samples exhibits a frequency independent conductivity up to 10^4 Hz. However, an insignificant increment in σ_{ac} values between $10^5 - 10^6$ Hz is observed. It is observed that on increasing the PVP content in PVC the values of σ_{ac} increases²⁶. This probably is due to the dipole-dipole interaction between C-Cl of PVC and C=O of

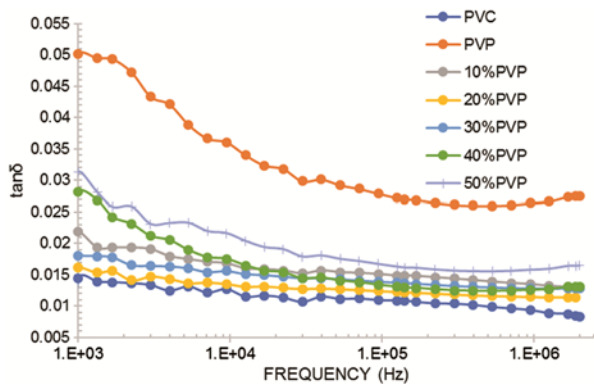


Fig. 7 — Variation of loss tangent $\tan\delta$ of films with frequency.

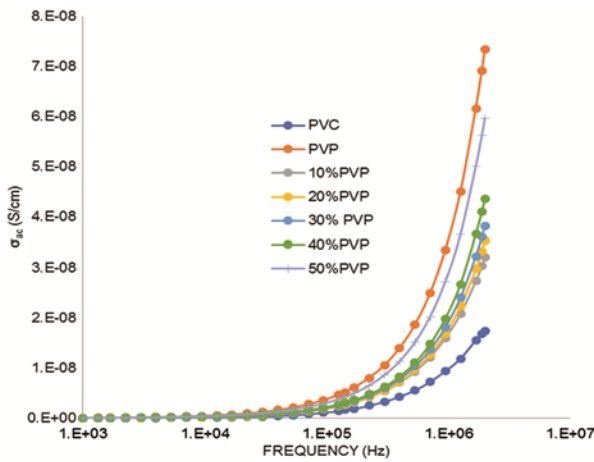


Fig. 8 — Variation of AC conductivity σ_{ac} of films with frequency.

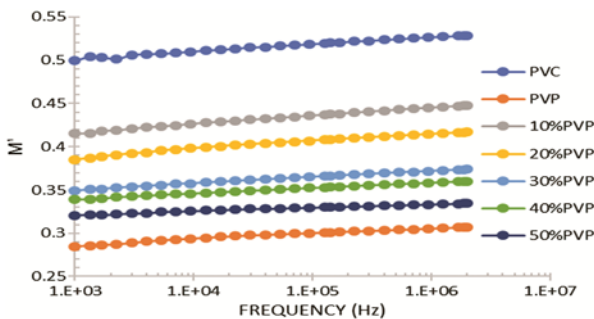


Fig. 9 — Variation of real part of electric modulus of films with frequency.

PVP which results in decreased association of PVP chains and good dispersion²⁷ of PVP in PVC.

Electric modulus formalism has been used for interpretation of relaxation phenomena. The difficulties arising in the analysis of dielectric spectra due to the nature of electrode, the electrode-specimen electrical contact and the injection of space charges and absorbed impurities can be suppressed using complex electric modulus spectra^{28,29}. The spectra of real part (M') and imaginary part (M'') of complex electric modulus for pure PVC, PVP and PVC-PVP blend films are shown in Figs 9 and 10. From Fig. 9 it is observed that values of M' increase with increasing frequency which confirms that the measured dielectric properties of films are free from contribution of electrode polarization effects²⁷. The M'' spectra (Fig. 10) of the investigated films show dispersion in the experimental frequency range.

Complex impedance spectroscopy is used to separate the electrode polarization effect and the bulk material properties¹⁷. The shape of the impedance spectra of a material gives the information about the electrode polarization which occurs due to formation of electric double layer (EDL) capacitances by the free charges that build up at the interface between the dielectric material and the electrode surfaces.

Moreover, it also gives an idea about the current carriers whether they are electrons or ions¹⁷. Figure 11 shows the complex impedance plots (Z'' versus Z') of all samples under investigation, which have arcs of semicircles starting from the origin of the plot and inclined at different angles to the real axis.

It is observed that the ionic conducting materials exhibit two different arcs in the complex plane plots. One corresponding to the electrode polarization and the other gives an idea about the bulk material properties²⁴. The complex impedance plots for our samples exhibited single arcs over the entire

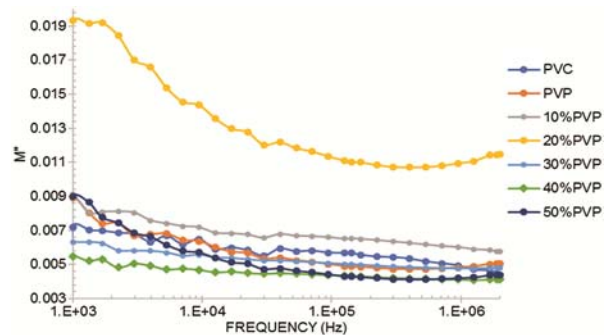


Fig. 10 — Variation of imaginary part of electric modulus of films with frequency.

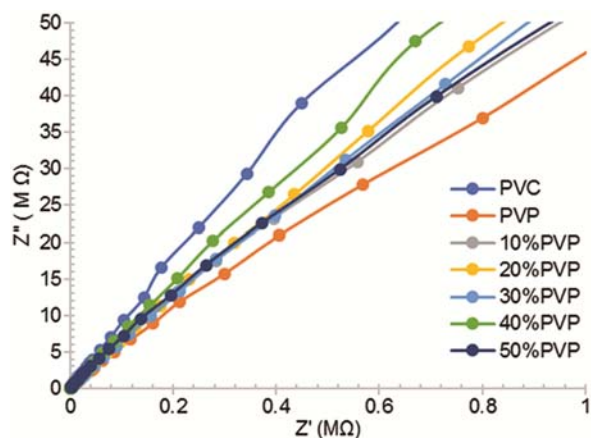


Fig. 11 — Complex impedance plots of films.

experimental frequency range, which correspond to the properties of bulk material and that the blend films have good electrical contacts with the electrodes thereby eliminating the formation of EDL capacitances. The large values of imaginary part Z'' of complex impedance as compared to the real part Z' confirm good capacitive behavior of these films^{17,24}.

4 Conclusions

In the present communication blend films of PVC with various percentage weight concentrations of PVP from 10% to 50% were prepared and studied. The water absorption, and surface free energy increased with increase in percentage weight concentration of PVP in PVC and the contact angle was found to be decreasing thereby increasing its hydrophilicity. The films with high values of surface free energy will have strong tendency to adsorb moisture from atmosphere and will age faster as compared to blend films with low value of surface free energy. PVC-PVP blend film with 50% weight concentration of PVC and PVP each was found to exhibit better mechanical flexibility and was also soluble in water rendering it degradability. The ϵ' values of the blend films are in the range of 2-3 and the $\tan\delta$ values are less than 0.07 suggesting their applications as low dielectric constant materials in the measured frequency range. The large values of imaginary part Z'' of complex impedance as compared to the real part Z' confirm good capacitive behaviour of these films. PVC-PVP blend films with variable ageing property and low dielectric constant values can be used in green electronics and biomedical fields.

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References

- 1 Rawat A & Singh P J, *Indian J Pure Appl Phys*, 54 (2016) 170.
- 2 Abdelrazek E M, Elashmawi I & Yasin A Y, *Curr Appl Phys*, 10 (2010) 607.
- 3 Thijs H M L, Becer C R, Guerrero-Sanchez C, Fournier D, Hoogenboom R & Schubert U S, *J Mater Chem*, 17 (2007) 4864.
- 4 Deshmukh R R, Arolkar G A & Parab S S, *Int J Chem Phys Sci*, 1 (2012) 40.
- 5 Thombre J V, Rath M C, Han S H & Fulari V J, *Meth Mater Phys Mech*, 16 (2013) 118.
- 6 Madhurima V, Purkayastham D D, Sudheendran K & James Raju K C, *Correlation between dielectric permittivity and wettability for low energy surface (bismuth zinc niobate) on fused silica*, IEEE International Conference on Dielectric Liquids, (2011) 1.
- 7 Smith J R & Lamprou D A, *Trans Inst Met Finish*, 92 (2014) 9.
- 8 Rawat A, Mahavar H K, Chauhan S, Tanwar A & Singh P J, *Indian J Pure Appl Phys*, 50 (2012) 100.
- 9 Higa O Z, Rogero S O, Machado L D B, Mathor M B & Lugão A B, *Radiat Phys Chem*, 55 (1999) 705.
- 10 Hayama M, Yamamoto K I, Kohori F & Sakai K, *J Membr Sci*, 234 (2004) 41.
- 11 Andres B, Ivo K & Saha P, *Math Meth Tech Eng Environ Sci*, (2011) 431.
- 12 Waghmare R V, Belsare N G, Raghuwanshi F C & Shilaskar S N, *Bull Mater Sci*, 30 (2007) 167.
- 13 Iulianelli G, Tavares M B & Luetkmeyer L, *Chem Technol*, 4 (2010) 225.
- 14 Yuan Y & Lee T R, *Contact angle and wetting properties*, Chapter 1, Bracco G, Holst B (Edn), *Surface science techniques*, Springer Series in Surface Sciences, 51 (2013).
- 15 Karki S, Kim H, Na S J, Shin D, Jo K & Lee J, *Asian J Pharm Sci*, 11 (2016) 559.
- 16 Mukherjee D & Bharath S, *ISRN Pharm*, 2013 (2013) 1.
- 17 Sengwa R J, Sankhala S & Choudhary S, *Indian J Pure Appl Phys*, 48 (2010) 196.
- 18 Alcantara M T, Giannini D R, Brant A J C, Riella H G & Lugao A B, *Effect of different plasticizers on poly(vinyl-2-pyrrolidone) hydrogels cross-linked by radiation*, International Nuclear Atlantic Conference, 2011.
- 19 Azahari N A, Othman N & Ismail H, *J Phys Sci*, 290 (2011) 15.

- 20 Lu Y, Tang N, Lian R, Qi J & Wu W, *Int J Pharm*, 1 (2014) 25.
- 21 Żenkiewicz M, *J Achiev Mater Manuf Eng*, 21 (2007) 137.
- 22 Reddy C V S, Han X, Zhu Q Y, Mai L Q & Chen W, *Microelectron Eng*, 83 (2006) 281.
- 23 Rawat A, Mahavar H K, Tanwar A & Singh P J, *Bull Mater Sci*, 37 (2014) 273.
- 24 Tomar R & Sharma Chirag R, *IJSETR*, 3 (2014) 3023.
- 25 Sengwa R J & Choudhary S, *Bull Mater Sci*, 35 (2012) 19.
- 26 Pandey A K, *J Chem Bio Phys Sci*, 3 (2013) 1489.
- 27 Lohse D J, Russell T P & Sperling L H, *Interfacial aspects of multicomponent polymer materials*, Springer, 1997.
- 28 Sengwa R J & Choudhary S, *Express Polym Lett*, 4 (2010) 559.
- 29 Sengwa R J, Choudhary S & Sankhla S, *Express Polym Lett*, 2 (2008) 800.