High Dielectric Permittivity and Percolative Behavior of Polyvinyl Alcohol/Potassium Dihydrogen Phosphate Composites

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ABSTRACT: A new kind of anhydrous, transparent, and flexible potassium dihydrogen phosphate (KH_2PO_4 or KDP)/polyvinyl alcohol (PVA) composite in the form of film (0.10 mm) has been prepared by solution casting technique. KDP is well dispersed in the polymer matrix as observed from the microstructural studies. Frequency and temperature dependent dielectric properties of the composites have been studied with varying KDP concentrations. The PVA/KDP composite films exhibited extraordinarily high relative permittivity $\varepsilon' \sim 430$ (80 times higher compared with pure PVA and even higher than KDP) near the percolation threshold ($\phi_C = 2.5$ wt % KDP) with low dielectric losses (~ 0.15) at 1 kHz and room temperature. Such flexible, low loss and high dielectric permittivity material has enormous importance for application in devices. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 2363–2370, 2012

Key words: composites; dielectric properties; filler; film

INTRODUCTION

Polymer-based composite with excellent dielectric performance is a very popular topic of research in material science receiving increasing attention in recent years.[1–3] Many new materials are being produced using polymer and ultrafine particle as fillers dispersed in the polymeric matrix. There are several applications of polymer composites based on their optical, electrical, and mechanical properties.[4–6] Polymer composites could find applications as electrolytes in fuel cells, supercapacitors, smart windows, electrochromic devices (ECDs), and in microfluidic systems for drug delivery.[7–9] Some polymers are presently used for energy storage applications because of their interesting features such as high-electric breakdown field, low dielectric loss, easy processing, and low cost.[10] As usual, the dielectric permittivities of common polymers are very low (<10). Thus, a key issue is to enhance dielectric permittivity of such polymers while retaining other excellent mechanical performances. One approach is to introduce high dielectric permittivity ceramic fillers such as $BaTiO_3$, $CaCu_3Ti_4O_{12}$, and lead magnesium niobate–lead titanate into polymers[11–13]; but these ceramic/polymer composites have some disadvantages such as high mass density, more porous and poor flexibility due to high concentration of inorganic fillers. Another strategy is to fabricate percolative composite capacitors by adding conductive fillers (e.g., metal particles, carbon fibers, and conductive polymers) into polymers.[14–16] However, the dielectric loss of these percolative composites is usually quite high due to the insulator–conductor transition near the percolation threshold. More recently, an interesting report described a polymer composite dielectric film containing hybrid particles with organic carbonaceous shells coating on silver (Ag) cores. A percolating nanocapacitor networks with interparticle barriers originated by the organic carbonaceous shells, which syncretizes with the polymer matrix, leads to high dielectric permittivity and low dielectric loss.[17,18] But the percolation threshold for Ag particles in the composites is still high. Hence, to reduce the percolation threshold, appropriate choice of the filler as well as the polymer matrix is of considerable importance. Properties of composite materials greatly depend on the nature of the matrix and the filler, their compatibility, nature of the size combining units, and their relative properties.

Solution casting method is one of the easiest methods for the preparation of polymer composites requiring simple equipment and is less time consuming. During the past years, great advancement has been achieved in capacitor technology.[19] In this field, composite films have often been used as dielectric materials in engineering capacitors because of their combination of remarkable properties, such as low dielectric loss, good stability and flexibility,

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high volume resistivity, low water absorption rate, and low shrinking rate. Polyvinyl alcohol (PVA) with low dielectric permittivity ($\sim$ 5.2) has been widely used for polymer composites due to its easy processability, good chemical stability, film forming ability, and high transmittance. Relative permittivity ($\varepsilon' \sim 10^3$) of several polymer composites such as PVA/BaTiO$_3$,[20] PVA/PANI/Fe$_2$O$_3$,[21] PVA/ZnO,[22] etc. have been reported and most importantly the high relative permittivity values of these materials are almost independent over a wide range of temperature. However, loss factors of such composites are quite high. Dutta et al.[23] studied dielectric properties of PVA based PANI composites showing enhanced relative permittivity($\varepsilon' \sim 1.1 \times 10^3$) with high loss ($\sim$ 8.33 for $\phi_{PANI} = 0.05$) but sharply dropped in the high frequency region. Large dielectric loss results in great heat production when the polymer composite films are used as dielectric material in the capacitor. Therefore, one must seek a new polymer material with improved dielectric permittivity for usage in capacitors.

Recently proton conductivity of PVA-ADP (NH$_4$H$_2$PO$_4$) composites has been studied for their use in solid ECDs.[24,25] Conductivity showed interesting enhancement of conductivity with variation of ammonium dihydrogen phosphate (ADP) concentration, the origin of which has not been clarified. Similar behavior might be exhibited by other hydrogen-bonded materials. Hydrogen-bonded KH$_2$PO$_4$ is one of them which can be chosen as filler of PVA (C$_2$H$_4$O)$_x$ for making a suitable polymer composite. By changing the potassium dihydrogen phosphate (KDP) concentrations (ϕ_{KDP}), it could be possible to adjust the dielectric properties of the composites, which motivated us to make the simple combination of PVA insulating matrix and KDP fillers at different weight fractions by standard solution casting procedure.[26] It is known that percolation is a promising way to improve the relative permittivity of polymers, because it improves the relative permittivity dramatically as the concentration of the filler approaches the percolation threshold.[27,28] Moreover, this percolative approach requires much lower concentration of the fillers compared with traditional approach of high dielectric permittivity particles in a polymer matrix. Therefore, this material possesses advantageous characteristics over the conventional polymer composites. To the best of our knowledge, no elaborate study on such new polymer-inorganic composite (PVA-KDP) has been made to explore the possibility of new applications showing interesting properties. It is also advantageous that both PVA and KDP are low cost and water soluble materials to form composite of different composition.

Our plan in this article is to prepare anhydrous and transparent PVA/KDP films with PVA as host

and to study their frequency and concentration dependence of dielectric and electrical transport properties at variable temperature. Detailed characterization of the KDP/PVA films has also been made using XRD, SEM, EDX, etc. Introduction of the KDP fillers in the polymer matrix has generated a novel two-phase KDP/PVA electroactive polymer composite (EAPCs), which displayed a high dielectric permittivity ($\varepsilon' > 400$) over a low critical content ($\phi_C = 2.5$ wt %) of KDP. The observed high dielectric permittivity with low dielectric loss of the prepared composite films makes them attractive for device fabrication.

EXPERIMENTAL

Preparation of the PVA/KDP composite films

Conventional solution casting method was applied to prepare flexible transparent PVA/KDP composite films of our investigation. Initially 2 g of PVA and 0.1 g of KDP were separately dissolved completely in 100-mL distilled water taken in carefully cleaned glass beakers, kept in magnetic stirrer for 5 h at room temperature. For making KDP/PVA composites, different concentrations of KDP (0–4 wt %) were mixed with requisite volumes of the two solutions in separate beakers. The mixed solutions with different concentrations of KDP were sonicated each for about 30 min and then stirred for an additional 2 h at 45°C for ensuring homogenous and uniform mixing of KDP into PVA matrix. The final solutions were then poured into the casting glass plates for few days for air drying at room temperature. The films were then taken out from the glass plates. The final disk-shaped transparent films for different ϕ_{SDP} were prepared each having 12 mm in diameter and about 0.10 mm in thickness. The concentration of KDP fillers was varied systematically to investigate the influence of KDP compositions on the dielectric and electrical properties of the polymer composite. For electrical measurement, electrodes were painted on both sides using good quality silver paste.

Measurements and characterization

The X-ray diffraction (XRD) pattern of pure PVA and that of the composite films with different concentrations of KDP were performed with SEIFERT XRD 3000P diffractometer by using CuK$_\alpha$ radiation. The size of the KDP fillers and grain morphology of polished surface of the pure polymer and the composite films were examined by field emission scanning electron microscopy (FESEM Model No: JEOL JSM 6700 F). Elemental analysis such as distribution of different elements, e.g., C, O, P, and K. in the PVA matrix was studied by energy dispersive X-ray
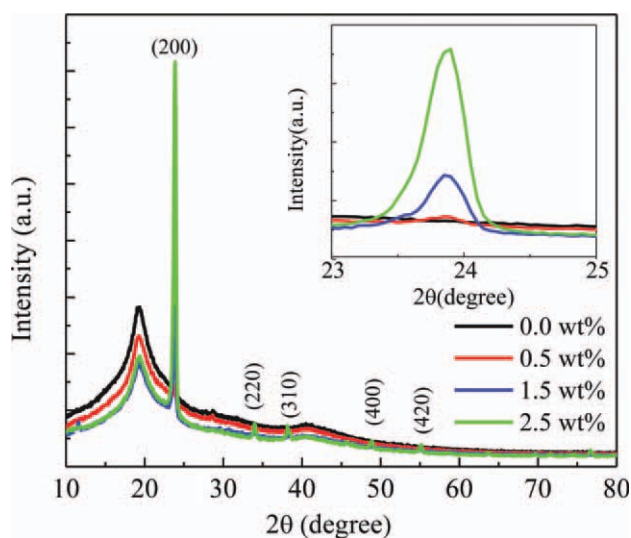
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Figure 1 XRD pattern of pure PVA and PVA/KDP composite films with different concentrations of KDP at room temperature and the inset shows the same for 2θ in the range of 23–25° following the same trend with intensity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(EDX). Spectrophotometric measurements of pure PVA and PVA/KDP solutions were done in the wavelength range from 190 to1100 nm using double beam spectrophotometer (model no: EI 2375). Fourier transform infrared (FTIR) spectroscopy studies of pure PVA and the composite films were carried out using SHIMADZU-8000 spectrometer in the range 400–4000 cm^{-1}. An impedance/gain-phase analyzer (HP4192A, 1 kHz to 10 MHz) was used for the measurements of capacitance and ac impedance at different frequencies and temperatures.

RESULTS AND DISCUSSION

Figure 1 shows the room temperature XRD pattern of pure PVA and that of the PVA/KDP composite films with different concentrations of KDP. It is shown that PVA has a semicrystalline structure with the peak at 2θ = 19.35°.The intensities of the PVA peaks in the composites are reduced significantly after the addition of different concentrations of KDP. A sharp and highly intense peak at 2θ = 23.9° and few low intense peaks are observed in the composite
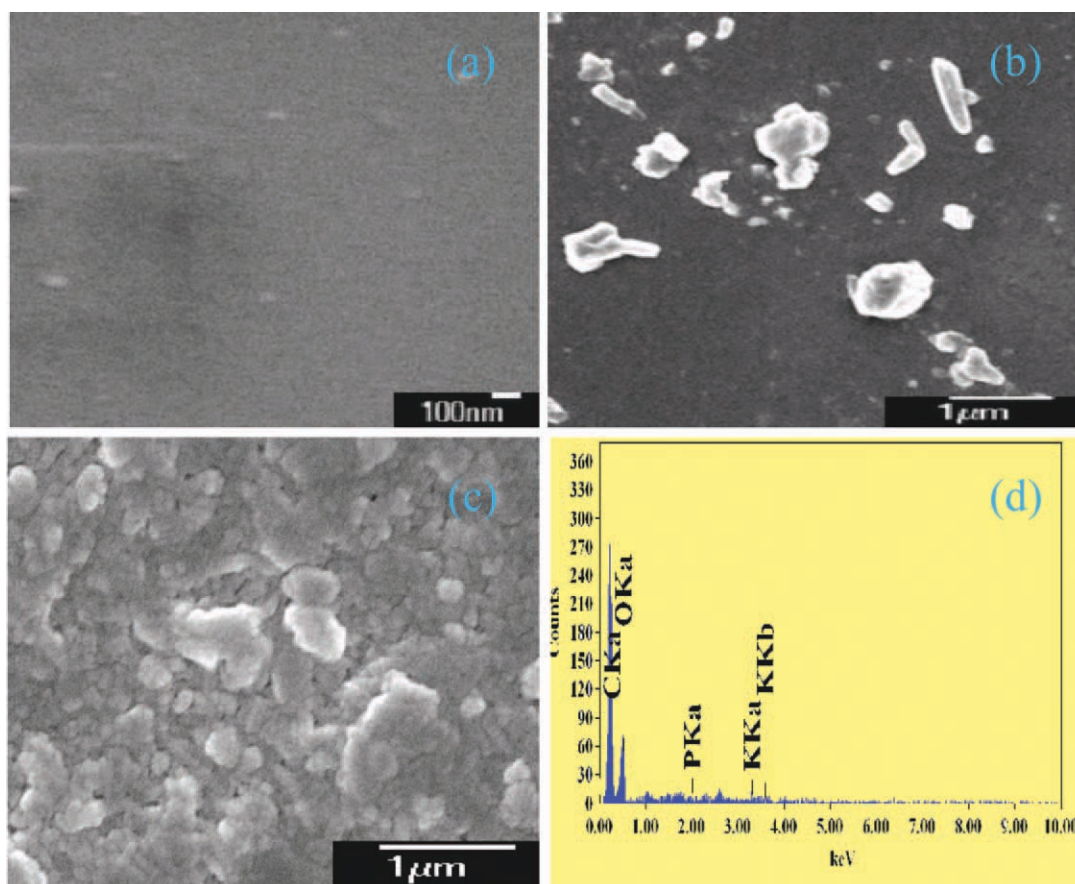

Figure 2 SEM images of the polished surface of (a) 0.0 wt %, (b) 1.5 wt %, (c) 2.5 wt %, KDP/PVA composite films, and (d) EDX spectroscopy of 2.5 wt % KDP/PVA composite film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The Weight Percentages of the Individual Elements in the KDP/PVA Composite Obtained from EDX Study for ϕ_{KDP} = 2.5 wt %

Elements	C	O	P	K
wt %	51.04	48.03	0.64	0.29

film with 2.5 wt % KDP. The presences of such peaks in the composite are not due to PVA but due to KDP filers because at this critical concentration (2.5 wt %), the KDP grains are highly oriented in the film. Inset shows the same for 2θ in the range of 23–25° following the same trend with intensity. It represents clearly a low intense sharp peak (blue color) and high intense sharp peak (green color) for 1.5 and 2.5 wt % KDP, respectively.

Figure 2(a–c) shows the SEM images of the pure PVA and PVA/KDP composite films having 1.5 and 2.5 wt % KDP, respectively. Figure 2(a) represents the pure PVA matrix having no any filler. In Figure 2(b), many small clusters of KDP are observed but those clusters are not connected, whereas in Figure 2(c), the grains of KDP are dispersed in the PVA matrix homogeneously and aggregate to form large particle clusters and become self-connected and forming a network spans in the polymer matrix. Thus semiconducting paths due to KDP filler are formed, which significantly raises the relative permittivity and conductivity of the percolative composite.

Figure 2(d) displays the EDX spectra of 2.5 wt % KDP/PVA composite film. The area on which the EDX study has been made is shown in the corresponding SEM image in Figure 2(c). The EDX study was made to detect the presence of C, O, P and K peaks. The weight percentages of the mentioned elements in the composites, shown in Table I, are in good agreement with the expected concentrations of the elements.

Absorption spectra of pure PVA and the corresponding PVA/KDP solutions with different concentrations of KDP at room temperature are shown in Figure 3(a). It is observed that the pure PVA solution exhibits almost similar (but not identical) characteristics to that of PVA/KDP composite solutions with various concentrations of KDP. The absorption spectra of pure PVA solution exhibits narrow band with sharp peak at 974 nm, whereas the PVA/KDP solutions with different concentrations of KDP exhibit relatively narrower band peaking at ∼ 972 nm. The narrower band indicates the particle size distribution is quite narrow in the PVA matrix. The slight shift in the lower wavelength and narrowing of the surface absorption band upon incorporation of the KDP particles into PVA is induced by agglomeration of the KDP particles and change of the dielectric properties of the surrounding environment. More-

over, it is also observed that the absorbance of the composite solutions increases with increasing the concentration of KDP, which is due to increasing the amount of salt within those solutions.

FTIR spectra of pure PVA and the composite films with different concentrations of KDP at room temperature are shown in Figure 3(b). The broad high absorption peak at 3438 cm^{-1} is assumed to arise from the O—H stretching frequencies of PVA and water hydroxyl groups. Peaks at 2928, 1116, and 844 cm^{-1} are attributed to the C—H stretching, C—H—O bending and C—O stretching, respectively, due to the characteristics of the KDP filler. The band at 1740 cm^{-1} was attributed to the carbonyl functional groups in the films and the intensity of this band in the composite films decreases. It is also noticed that the addition of the phosphate causes the shift of
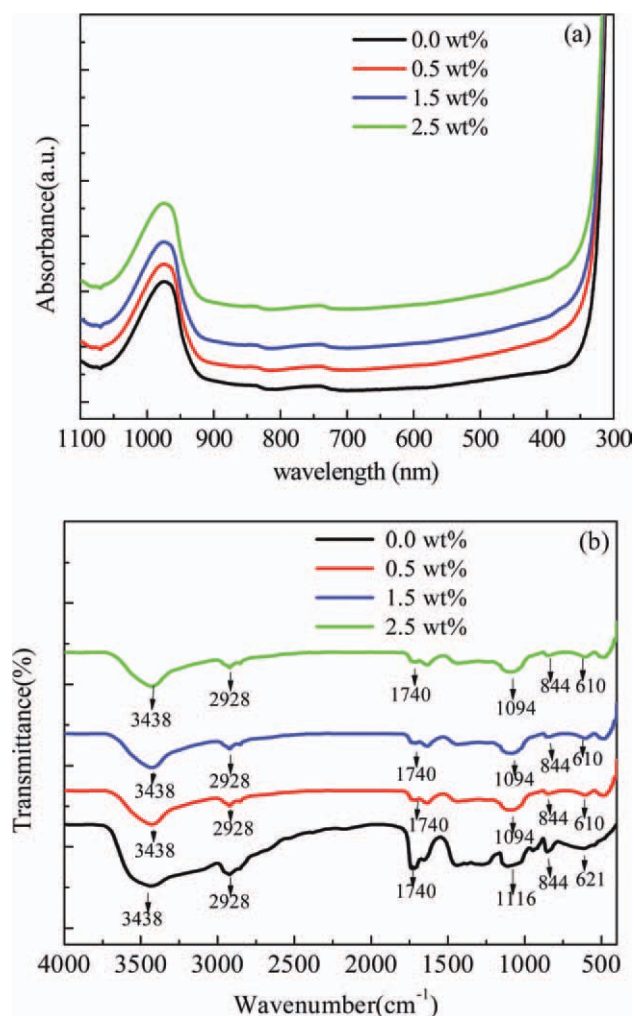

Figure 3 (a) UV-absorption spectra of pure PVA and PVA/KDP solutions with different concentrations of KDP at room temperature and (b) FTIR spectra of pure PVA and PVA/KDP composite films with different concentrations of KDP at room temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
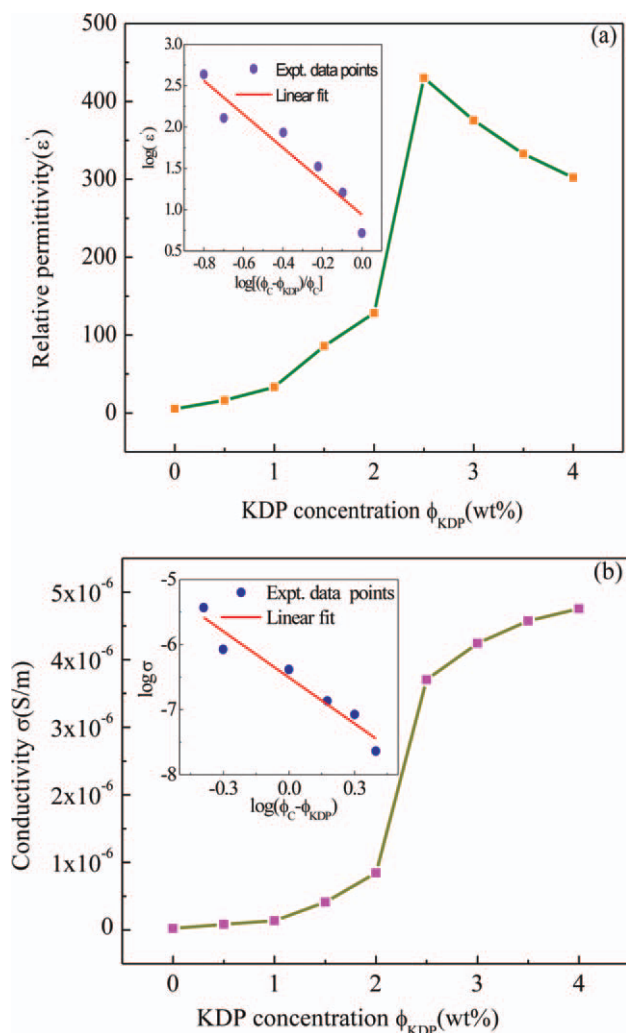
Figure 4 (a) Dependence of the relative permittivity of the composites on the KDP concentration measured at room temperature and 1 kHz and the inset shows the best fit of the relative permittivity values to eq. (1) and (b) variation of the conductivity of the PVA/KDP composites with different concentrations of KDP measured at room temperature and 1 kHz and the inset shows the best fit of the conductivity values to eq. (2). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

O—H bending vibration from 621 to 610 cm^{-1}. The peak appeared at 621 cm^{-1} in pure PVA film is absent in the composite films, which suggests that intermolecular hydrogen bonds are formed between the KDP and PVA. The peak at 1116 cm^{-1} assigned to C—O stretching of the secondary alcohol of PVA, is shifted to 1094 cm^{-1} in the composites.[24] Thus, the FTIR spectra for the composite films strictly prove the existence of chemical bonding between the KH_2PO_4 and PVA matrix.

The behavior of relative permittivity (ε') of the composite film as a function of KDP concentration at a particular frequency ($\sim$ 1 kHz) at room temperature is shown in Figure 4(a). There is gradual

enhancement of ε' with increasing ϕ_{KDP}, but there is a dramatic enhancement of ε' when $\phi_{KDP} > 2$ wt %, and ε' reaches the maximum value 430 (at 1 kHz, which is almost 80 times higher than that of the pure PVA film) when $\phi_{KDP} = 2.5$ wt %. The variation of ε' in the neighborhood of ϕ_C follows the power law[29–31] eq. (1) given below:

$$\varepsilon' = \varepsilon_p[(\phi_C - \phi_{KDP})/\phi_C]^{-t} \qquad \text{for } \phi_{KDP} < \phi_C \qquad (1)$$

where ε_p is the dielectric permittivity of PVA, ϕ_{KDP} the weight fraction of KDP, ϕ_C the percolation threshold, and t the critical exponent. Experimental values of relative permittivity are fitted to eq. (1) and its log–log plot is shown in the inset of Figure 4(a). A best linear fit of the relative permittivity data of the log–log plot of power law via eq. (1) gives $\phi_C = 2.46$ and $t = 2.02$ ($\pm 4.2\%$).

Figure 4(b) shows the variation of conductivity (σ) as a function of KDP concentration measured at room temperature and 1 kHz. The great increase in the conductivity can be seen at the KDP concentration of 2.5 wt %, which is just the percolation threshold of the system. The reason for the electrical properties of the composite can be attributed to the tunneling conduction mechanism and percolation phenomenon.[16,32,33] The conductivity can be analyzed with the critical KDP concentration, percolation threshold ϕ_C, by the following the universal Scaling Law eq. (2) as shown below:

$$\sigma = \sigma_{KDP}(\phi_C - \phi_{KDP})^{-s} \qquad \text{for } \phi_{KDP} < \phi_C \qquad (2)$$

where σ and σ_{KDP} are the conductivities of the composite and the KDP filler, respectively, ϕ_{KDP} the weight fraction of the KDP filler, ϕ_C the percolation threshold, and s the critical exponent. It can be seen from the inset of Figure 4(b) that the logσ versus log$(\phi_C - \phi_{KDP})$| plot from eq. (2) yields the best-fit line with the same value of percolation threshold ($\phi_C = 2.5$ wt %) as obtained from the relative permittivity data and the corresponding value of s is found to be 2.36($\pm 3.6\%$). The observed low value of percolation threshold is due to use of the KDP filler. The value of s greater than 2.0 for various polymer composites has also been reported earlier.[14,34] The high value of s is attributed to the extreme geometry of the filler.[35]

The variation of relative permittivity with frequency at a fixed temperature (303 K) with different concentrations of KDP filler within the PVA matrix is shown in Figure 5(a). As expected, the trend of variation of relative permittivity with frequency is the reverse of electrical conductivity. A strong frequency dispersion of permittivity is observed in the lower frequency region in comparison with the higher frequency region for all the KDP
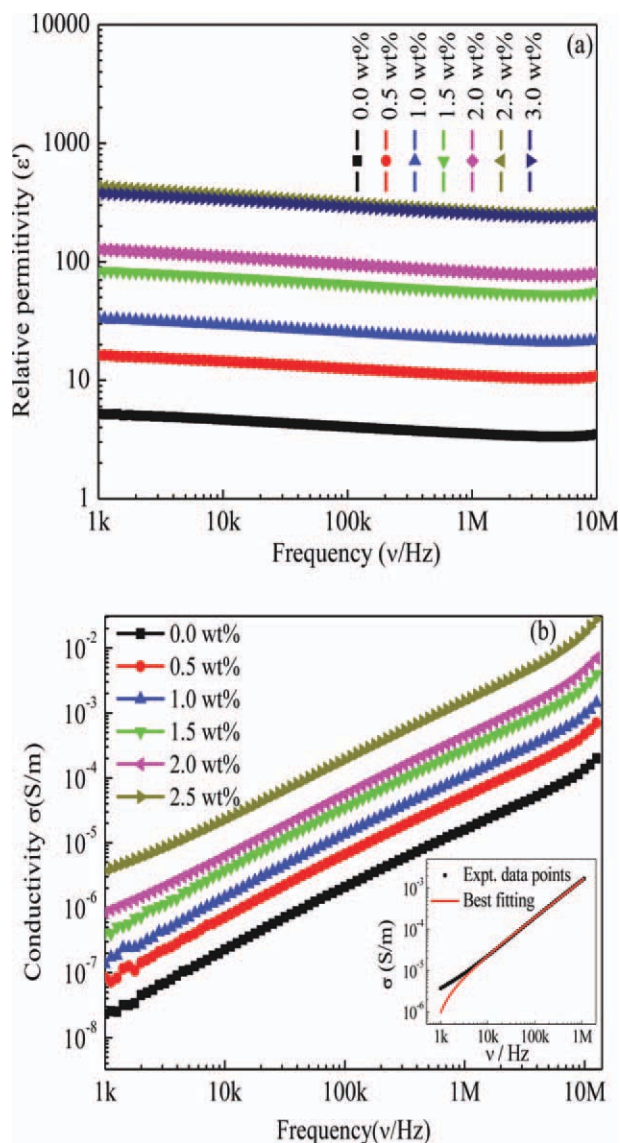
Figure 5 Dependence of (a) relative permittivity and (b) conductivity on frequency of the PVA/KDP composites with different concentrations of KDP at room temperature and the inset (b) shows the best fit of conductivity values for 2.5 wt % KDP according to Almond–West power law to eq. (3). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

concentrations. The relative permittivity attains higher values at low frequencies and decreases monotonically with increase of frequency. At lower frequency of the applied voltage, all the dipoles in the polymer chain can orient themselves resulting in a higher permittivity values at these frequencies. As the electric field frequency increases, the dipole groups find it difficult to orient at the same pace as the alternating field, so the contributions of these dipole groups to the permittivity goes on reducing resulting in a continuous decrease of permittivity of the composites at higher frequencies. The relative permittivity increases dramatically near the percola-
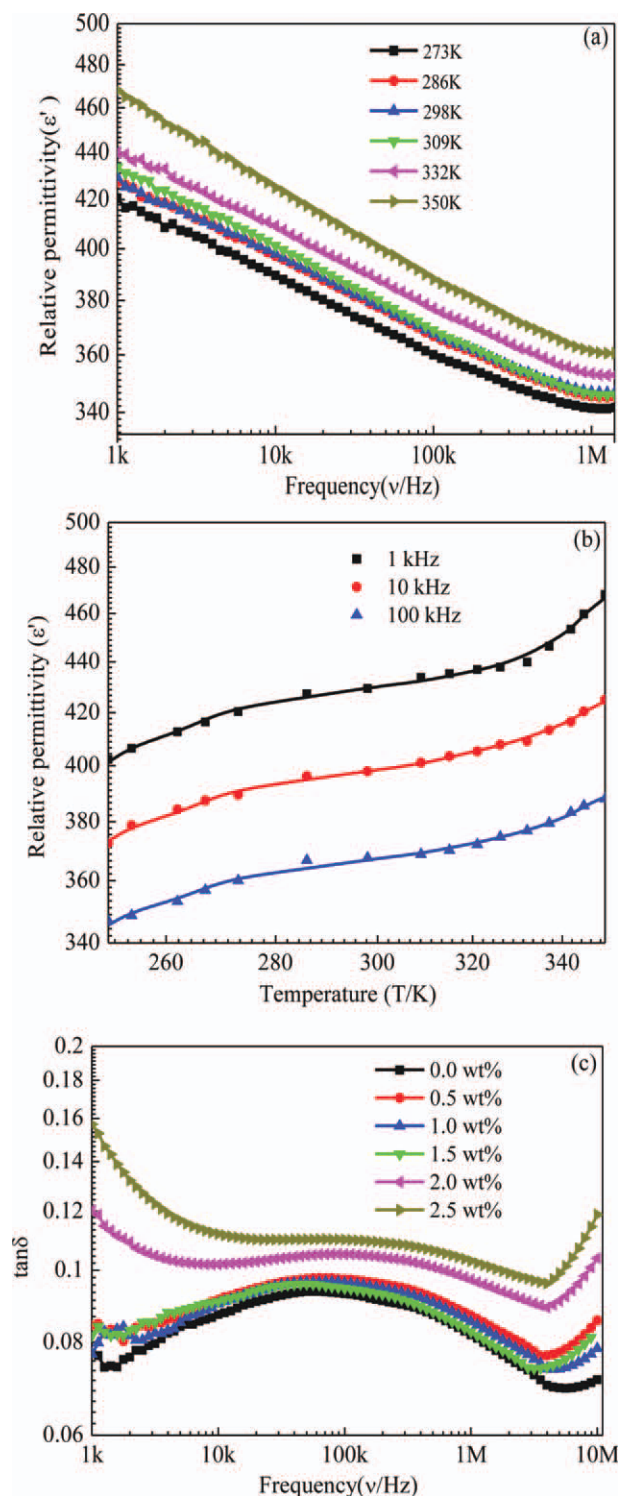

Figure 6 Dependence of relative permittivity of the PVA/KDP composite having 2.5 wt % KDP as a function of (a) frequency for different fixed temperatures, (b) temperature for different fixed frequencies, and (c) dependence of loss tangent on frequency of the PVA/KDP composites with different concentrations of KDP at room temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tion threshold. It is usually believed that the percolation threshold is an important point at which electrical property also varies a lot and hence the study of the conducting composites in the vicinity of percolation threshold is an effective way to know their electrical transport behavior.

Figure 5(b) represents variation of conductivity with frequency at room temperature for different concentrations of the KDP filler in the composites. When the KDP concentration is increased as high as 2.5 wt %, the conductivity of the hybrid film is found to be 4×10^{-6} S/m at 1 kHz, at room temperature, and it increases with an increase in the frequency. The results confirm that conducting network was formed showing insulating to semiconducting behavior of the KDP/PVA composite film with 2.5 wt % filler. The frequency dependent conductivity σ_{ac} has been fitted according to the Almond-West type power law behavior with a single exponent[34]:

$$\sigma_{ac} = \sigma_{dc} + \sigma_0 \omega^u \qquad (3)$$

where σ_{dc} is the dc conductivity and $\sigma_0 \omega^u$ the ac contribution with $\omega = 2\pi\nu$ and u the critical exponent. Experimental data of the conductivity are fitted to eq. (3) and its best fit is shown in the inset of Figure 5(b) for the composite with $\phi_{KDP} = 2.5$ wt %, gives $u = 0.89 \pm (0.17\%)$, where the solid line indicates the best fit of exponential data to the Almond-West type power law eq. (3). The effective conductivity of the composite with $\phi_{KDP} \leq \phi_C|$ increases almost linearly with frequency demonstrating the power-law behavior.

Figure 6(a) shows the dependence of the relative permittivity on frequency for different fixed temperatures within the temperature range from 273 to 350 K. The relative permittivity increases obviously with the rise of temperature and this is more prominent at the lower frequency region than that of the higher frequency regime. Figure 6(b) shows the variation of the relative permittivity of the PVA/KDP percolative composite on temperature for different fixed frequencies viz. 1.0, 10.0, and 100.0 kHz. The decrease in relative permittivity is observed with an increase in frequency. At higher temperatures, the frequency-dependent decrease in relative permittivity is quite rapid as compared with the corresponding decrease at lower temperatures. In the low-temperature range, from 250 to 310 K, rotational motions of dipoles are frozen, so they cannot catch up with the frequency change of the electric field. This is in accordance with low dielectric permittivity of the composites.[36] On the other hand, for relatively higher temperature range 310–350 K, the movement of molecules in the composite becomes easier that alters the dipoles direction only along the applied electric field because the dipoles are freer at high

temperature and can move smoothly. Therefore, increase in dielectric permittivity with the temperature is obviously observed.[37,38]

Figure 6(c) describes dielectric loss tangent (very often used to characterize the losses) with frequency for different concentrations of KDP at room temperature. The percolative PVA/KDP composite is also found to exhibit quite low loss (~ 0.15 at 1 kHz). As ϕ_{KDP} is increased from 0 to1.5 wt %, tan δ increases gradually from 0.07 to 0.08 at 1 kHz. The insulation layer between semiconducting particles or chains prohibits the occurrence of large leakage current thereby keeping the loss factor low. However, when ϕ_{KDP} increases from 1.5 to 2.5 wt %, tan δ is enhanced abruptly from 0.08 to 0.15. This is because in this range the more conductive network of KDP hydrogen bond could form and thus induces contacts between the KDP fillers, which always result in a significant increase of the conduction loss. The relatively high dielectric loss is ascribed to the motion of free charge carriers and interfacial polarization relaxation due to the conductive KDP clusters in the composites. Such KDP/PVA composite with high dielectric permittivity and low dielectric loss suggest potential application possibility in microcapacitor as well as in electromagnetic wave absorption.[20,39]

CONCLUSIONS

Homogeneous, anhydrous, and flexible transparent films of KDP/PVA composite have been prepared by solution casting technique. The dependence of the relative permittivity of the KDP/PVA composites on the hydrogen-bonded KDP fillers over a wide range of frequency and temperature were measured. The high relative permittivity ($\varepsilon' \sim 430$) which is almost 80 times higher than that of the pure PVA with low loss (~ 0.15) at 1 kHz and room temperature is observed in the KDP/PVA composites with 2.5 wt % KDP filler can be explained using the percolation theory. Such a flexible high dielectric permittivity and reduced dielectric loss composites might be very much suitable for practical applications in devices.

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