Improved Dielectric Model for Polyvinyl Alcohol-Water Hydrogel at Microwave Frequencies

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Abstract: Problem statement: The study described rigorous dielectric modeling for Polyvinyl Alcohol (PVA)-water hydrogel mixture at microwave frequencies. **Approach:** A commercial open-ended coaxial sensor was used to measure the dielectric constant, loss factor and ionic conductivity, σ of PVA-water hydrogel mixture ranging concentration of 80-100% water content. **Results:** The sensor was operating between 0.13 and 20 GHz at and above of room temperature $(25\pm1)°C$. Indirectly, the relaxation time, τ, activation energy, Q and entropy change, ΔS of the hydrogel mixtures are determined based on linear fitting of measured data using Debye and Arrhenius approaches. **Conclusion/Recommendations:** Two main relaxation processes were found ranging 2-10 and 10-20 GHz, respectively. Dielectric dispersion is suggested to describe by combination of Cole-Davidson (CD) and Debye (Dy) processes. The results are discussed qualitatively based on bound states of water in hydrogel mixtures.

Key words: Dielectric constant, loss factor, PVA-water hydrogel, relaxation times

INTRODUCTION

Recently, the Polyvinyl Alcohol (PVA)-water hydrogel was used on medical application, such as healing agent, due to the composition of the hydrogel is very similar to the human body skin. In addition, there are non-toxic, non-carcinogenic and bioadhesive characteristics. Because of those properties, PVA is capable of simulating natural tissue and can be readily accepted by human body. In general, this medical application was interest for water content in the hydrogel is about 80% and the temperature is between 25-65°C.

In macroscopic observation, the mechanical characteristics, such as dielectric of polymer molecules are often considered. The dielectric properties can be used to explain the orientation of the molecules or relaxation mechanism in the polymer hydrogel (Sengwa and Kaur, 2000). However, the polarization molecules in polymers are complex due to many body interactions between binding molecules. Thus, a lot of the dielectric equation was modified from the ideal Debye theory, such as Cole-Cole (CC), Davidson-Cole (DC) and Havriliak-Negami (HN) as well as Kohlrausch-Williams-Watts (KWW) distribution function, in order to represent and describe the properties of the polymer hydrogel.

In this study, a detailed macroscopic dielectric relaxation behavior of water in a PVA hydrogel was investigated and reported. The variable of environmental conditions considered are the water content, m.c, frequency, f under several temperature, T condition*s*. Then, the dielectric properties as a function of frequency and percentage water content in hydrogel were formulated. Finally, the bonding states of water molecules in hydrogel were discussed based on relaxation time, τ and mean activation energy, Q.

MATERIALS AND METHODS

Preparation of PVA-Water mixtures: Up to 11 different samples of Polyvinyl Alcohol (PVA), $\overline{M}n = 72000$ weights (1-15 g) were mixed with 60 g of water in a small beaker, respectively. During the process of preparation sample, the water was heating indirectly between 65-90°C by mixing the PVA continuously little by little until dissolution is

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completed. After that, the mixture samples were kept at room temperature (25±1)°C. The percentage of water content in PVA-water mixture is calculated from the formula:

$$m.c = \frac{m_{Water}}{m_{PVA} + m_{Water}} \times 100\% \qquad (1)$$

where, m_{PVA} and m_{Water} are the weigh of PVA and water (in g), respectively.

Dielectric measurements: The HP 85070B open-ended coaxial sensor was used to determine the dielectric properties of PVA-water mixtures. The measurement apparatus consists of a computer controlled HP 8720B Vector Network Analyzer (VNA). In this study, air, metal short and deionized water were used as three dielectric references for calibration at aperture of open-ended coaxial sensor ranging 0.13-20 GHz at (25±1)°C. After calibration, the sensor was immersed into the hydrogel sample to measure its relative permittivity.
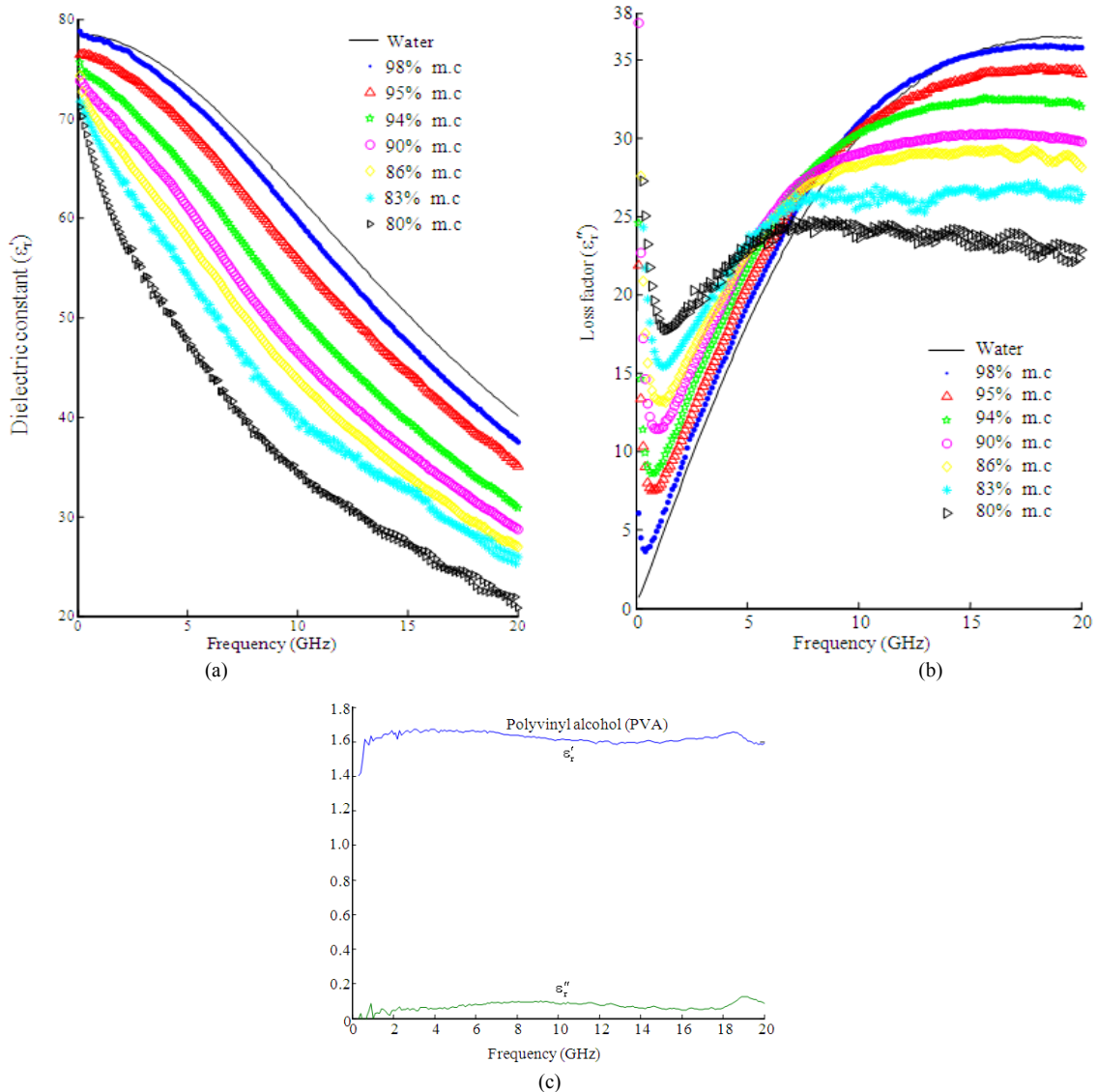

Fig. 1: Variation in measured of (a) dielectric constant, ε_r' ; (b) loss factor, ε_r'' with frequency at room temperature (25±1)°C for various water content, m.c in PVA hydrogel; (c) The measured permittivity of Polyvinyl Alcohol (PVA) powder ranging 0.13-20 GHz

RESULTS AND DISCUSSION

Analysis of data: In general, the relative permittivity of water ($\varepsilon_r' \approx 80$) is far greater than PVA ($\varepsilon_r' \approx 1.6$) (Fig. 1c), consequently, the dielectric properties of water content in PVA-water mixture is dominated. Figure 1a and b show the variation in dielectric constant, ε_r' and loss factor, ε_r'' of hydrogel with frequency at room temperature, $(25\pm1)°C$ for various percentage water content, m.c. In general, the curve of dielectric constant, ε_r' of hydrogel mixtures is disperse broader and showed lower maxima of loss factor, ε_r'' compared with pure water. The decrease in relative complex permittivity of the hydrogel mixture is caused by the displacement of polymer PVA molecules in water.

Dielectric modeling: The relative complex permittivity, ε_r of hydrogel may be calculated by using a sum of two relaxation processes, which is the combination of Cole-Davidson (CD) and Debye (Dy) processes. However, dispersion also exists at very low frequencies (≤ 2 GHz) for dielectric constant, ε_r' which has not been investigated in this study. Moreover, the loss factor, ε_r'' at lowest frequencies (≤ 3 GHz) is assumed entirely caused by conductivity, σ and characterized as $\varepsilon_r'' = \sigma/2\pi\varepsilon_o f$. Finally, the relative complex permittivity of hydrogel is expressed as:

$$\varepsilon_r = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_1}{\left[1 + \left(j\omega A_1 \tau_1\right)\right]^{A_2}} + \frac{\varepsilon_1 - \varepsilon_\infty}{1 + \left(j\omega\tau_2\right)} - \frac{j\sigma}{2\pi\varepsilon_o f} \qquad (2)$$

where, A_1 and A_2 are the empirical constant, which are determined by optimized with measured data.

Finding relaxation time, τ, static permittivity, ε_s and ε_1: The static permittivity, ε_s and relaxation time, τ of hydrogel mixture can be predicted easily by linear Eq. 2 (Robert, 1988):

$$\varepsilon_r' = -\left(\omega\varepsilon_r''\right)\tau + \varepsilon_s \qquad (3)$$

From (3), we observed that the gradient of variation in ε_r' with $-\omega\varepsilon_r''$ is represented by the relaxation time, τ, as well as the point at ε_r'-axis, when $-\omega\varepsilon_r'' = 0$ gives the value of ε_s. The height of the intermediate plateau from the line in Fig. 2 represented as ε_1. The intersection between the line and ε_r'-axis gives the value of ε_s. However, the Fig. 2 contains two linear slopes represented two major dispersions, which is broad low-frequency dispersion and high-frequency dispersion. The estimated values of dielectric constant

(ε_s and ε_1) and relaxation time (τ_1 and τ_2) corresponding to various percentage of water content, m.c are revealed in Table 1.

Finding Optical Permittivity, ε_∞: In general, the optical permittivity, ε_∞ is independent of frequency, f and temperature, T (Nyfors and Vainikainen, 1989). Thus, the ε_∞ of hydrogel is assumed as mixture expression:

$$\varepsilon_\infty = v_{water}\varepsilon_\infty^{water} + \left(1 - v_{water}\right)\varepsilon_\infty^{PVA} \qquad (4)$$

where, $\varepsilon_\infty^{water} = 4.9$ and $\varepsilon_\infty^{PVA} = 1.6$ are the infinite optical permittivity of pure water, dry and dry PVA powder, respectively. The fraction volume of pure water, v_{water} is calculated from:

$$v_{water} = \frac{m.c\left(\rho_{PVA}\right)}{100\rho_{water} + m.c\left(\rho_{PVA} - \rho_{water}\right)} \qquad (5)$$
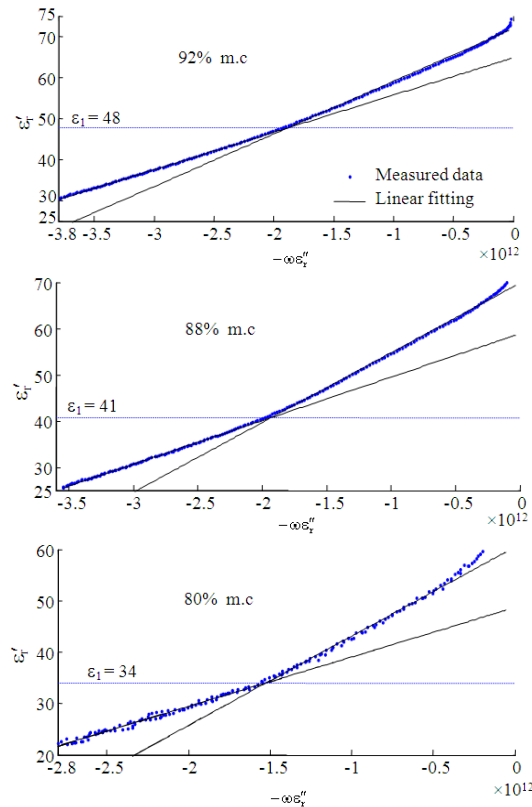

Fig. 2: The ε_r' versus $-\omega\varepsilon_r''$ for various water content, m.c, which plotting slope is represented the relaxation time, τ of PVA-water hydrogel at $(25\pm1)°C$

Table 1: The estimated values of dielectric static (ε_s and ε_1), relaxation time (τ_1 and τ_2) and conductivity, σ for various percentage of water content, m.c at room temperature based on fitting data in Fig. 2 and 3

Water (g)	PVA (g)	m.c (%)	$\sigma(\Omega^{-1}\,m^{-1})$	τ_1 (ps) (1st fitting)	τ_2 (ps) (2nd fitting)	ε_1	ε_s (1st fitting)
60	1.0	98	0.04	11	8.9	73	78
60	2.0	97	0.10	12	8.8	68	77
60	3.0	95	0.15	12	8.5	55	76
60	4.0	94	0.19	12	8.9	48	73
60	5.0	92	0.20	13	9.1	48	72
60	6.0	91	0.28	13	9.0	47	72
60	7.0	90	0.30	14	9.0	45	71
60	8.0	88	0.34	14	8.7	41	69
60	10.0	86	0.41	14	9.0	39	68
60	12.0	83	0.50	15	8.4	37	65
60	15.0	80	0.60	18	9.0	34	61

*: 1st fitting of measured data is from 2-10 GHz; 2nd fitting of measured data is from 10-20 GHz

Where:

ρ_{water} = 0.9959 g mL^{-1}

ρ_{PVA} = 1.26 g cm^{-3} are the apparent density of water and dry PVA powder at room temperature, respectively and m.c is the percentage of water content in the PVA hydrogel

Finding conductivity, σ: The conductivity term, σ is determined by optimizing with measured loss factor, ε_r'' at low frequency (≤ 5 GHz) with (1). The estimated values of conductivity, σ are listed in Table 1, as well as plotted as Fig. 3. The conductivity data increases in linear form with water content, m.c in the mixtures as revealed in Fig. 3. However, the apparent conductivity itself is independent of frequency. The linear scope may be calibrated directly in percent of water content, m.c. The obtained fitted parameters as a function of water content, m.c (%) for (1) are listed in Table 2.

Macroscopic analysis: The measurement results by using HP coaxial sensor and calculated values of (1) can be compared between Fig. 1a and b and 4. Clearly, the calculated values in Fig. 4 are quite consistent with measured data in Fig. 1a and b. The values of relaxation time, τ obtained from Fig. 4 are available in Table 1. The relaxation time, τ is higher at low frequencies (below 10 GHz) and decrease with water content m.c, in hydrogel due to the orientation polarization of polar molecules is slowed down by the binding of water molecules and PVA in the mixtures. The water molecules are directly attached by swelling into the groups of polymer molecule in the main chain and replaces cross-links between PVA molecules. It is a main factor to limit its movement and relaxation time, τ increase compare with free water molecules. In addition, the water molecules can also be hydrogen bonded with hydrophilic groups (-OH) in the side chain of the PVA molecule. This type of bond is caused by predominantly Coulombic forces and has little effect on the rigidity of the structure.
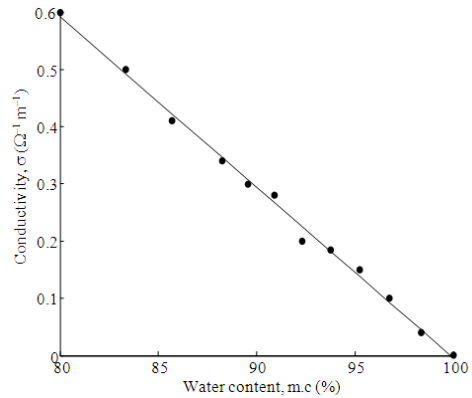

Fig. 3: Variation in conductivity, σ with percentage of water content, m.c in PVA-water hydrogel with linear fit

Table 2: The relationship between each of parameters in Eq. 1 with water content, m.c (%)

Dielectric parameters of PVA-water hydrogel in Eq. 1
($80\% \leq m.c \leq 98.5\%$; 100%); (0.13 GHz$\leq f \leq$20 GHz); 25°C

$\varepsilon_s = 1.18833 \times 10^3\,(m.c)^3 - 0.330562(m.c)^2 + 31.4052\,(m.c) + 944.058$

$\varepsilon_1 = -9.15419 \times 10^{-4}(m.c)^4 + 0.341051\,(m.c)^3 - 47.3823\,(m.c)^2$
$\quad + 2.91189 \times 10^3(m.c) - 6.67939 \times 10^4$

$\varepsilon_\infty = v_{water}\varepsilon_\infty^{water} + \left(1 - v_{water}\right)\varepsilon_\infty^{PVA}$

where: $\varepsilon_\infty^{water} = 4.9$ $\varepsilon_\infty^{PVA} = 1.6$

$\tau_1 = -2.52953 \times 10^{-15}\,(m.c)^3 + 6.8418 \times 10^{-13}\,(m.c)^2 - 6.18714 \times 10^{-11}$
$\quad (m.c) + 1.88378 \times 10^{-9}$ s

$\tau_2 = 8.5 \times 10^{-14}$ s ; $\sigma = -2.96099 \times 10^{-2}(m.c) + 2.95783$ $\Omega^{-1}m^{-1}$

$A_1 = 5.61583 \times 10^{-4}\,(m.c)^2 + 0.0893697(m.c) + 4.311717$

$A_2 = 0.0535328(m.c) + 6.687$

However, the relaxation time of hydrogel is approximately equal to the relaxation of free water (8.4 ps) for frequencies above 10 GHz. Obviously, energy above 10 GHz is large enough to break the hydrogen bond between water molecules and hydrophilic groups of PVA. In fact, the overall effect on water structure is extremely complex.
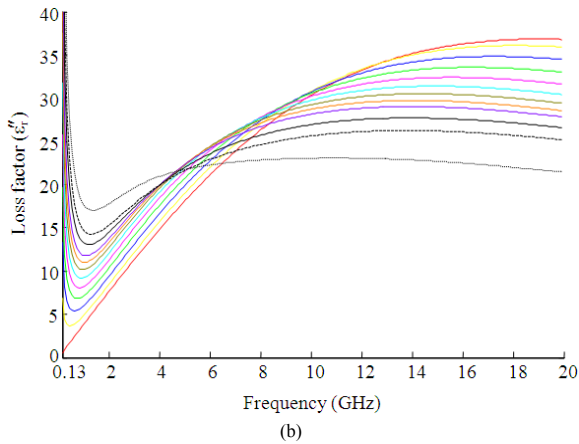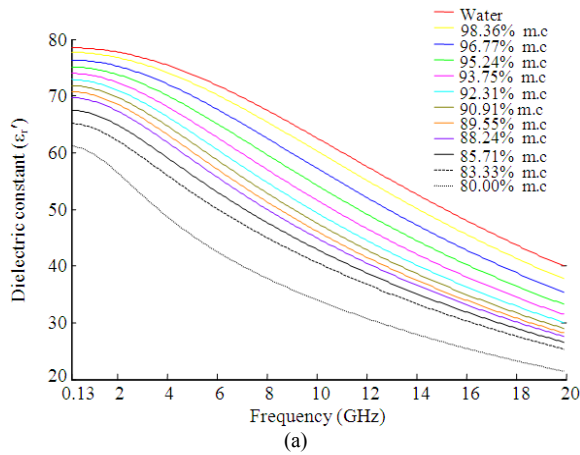
(a)

(b)

Fig. 4: Variation in calculated of dielectric constant, ε'_r and loss factor, ε''_r with frequency at room temperature $(25\pm1)°C$ for various water content, m.c in PVA hydrogel

Temperature effects analysis: Figure 5 shows the ε'_r versus $-\omega\varepsilon''_r$ plot for pure water at various temperature, T. The measured relaxation time, τ of bulk water ranging 25-60°C can be obtained from fitting of Fig. 5 by using (2) are tabulated in Table 3. It is expected that the hydrogen bonds are broken at high temperature, which leads to increase in mobility of side chains or decreases of the relaxation time, τ. The relaxation time, τ of water and PVA hydrogel are plotted as Arrhenius (Hasted, 1973) plots in Fig. 6. The linear relationships in Fig. 6 indicate that the temperature dependence of the relaxation time can be described by (6):

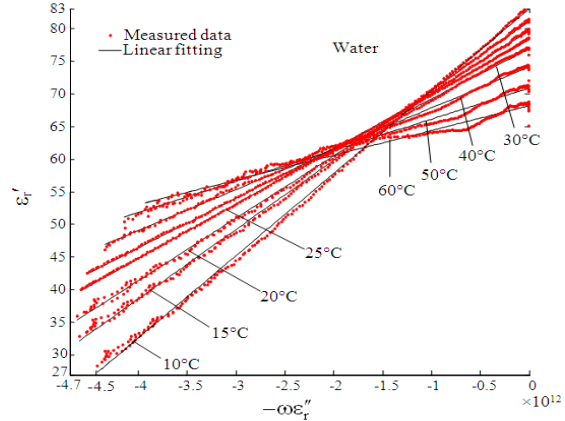$$\ln(\tau) = Q\left(\frac{1}{R(T+273)}\right) + \ln(\tau_o) \qquad (6)$$

Fig. 5: The measured ε'_r versus $-\omega\varepsilon''_r$, which plotting slope is represented the relaxation time, τ of water at 10, 15, 20, 25, 30, 40, 50 and 60°C

Table 3: The estimated values of relaxation time, τ for pure water and PVA hydrogel under several temperature, T

Sample	T (°C)	τ(ps) This study	Kaatze, (2005)	Hasted, (1973)
Water	10	13.0	12.68	12.60
	15	11.0	10.84	-
	20	9.6	9.37	9.30
	25	8.4	8.28	-
	30	7.6	7.31	7.20
	40	6.3	5.82	5.80
	50	4.8	4.75	4.80
	60	3.8	4.01	3.90
97% m.c Hydrogel		This study		
		2-10 GHz	10-20 GHz	
	25	12.0	8.80	
	30	9.5	8.00	
	35	8.9	7.40	
	40	8.0	6.30	
	45	7.9	6.10	
	50	7.9	5.80	
83% m.c hydrogel		This study		
		2-10 GHz	10-20 GHz	
	25	16.0	8.30	
	30	15.0	8.00	
	35	14.0	7.40	
	40	13.0	6.60	
	45	13.0	6.40	
	50	13.0	6.20	
80% m.c hydrogel		This study		
		2-10 GHz	10-20 GHz	
	25	18.0	9.70	
	30	17.0	8.90	
	35	15.0	8.30	
	40	15.0	7.90	
	45	14.0	7.50	
	50	14.0	7.50	

Where:

$$\tau_o = \frac{h}{k(T+273)}\exp(-\Delta S/R) \qquad (7)$$

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Where:

R = the gas constant (R = 8.3143 J mol^{-1} K^{-1})

k = The Boltzman constant (k = 1.38066×10^{-23} J K^{-1})

h = The Phanck constant (h = 6.62608×10^{-34} J sec^{-1})

The linear slope in Fig. 6 represents the mean activation energy, Q of bulk water and gives 18.3 kJ mol^{-1} compare with literature (Nyfors and Vainikainen, 1989) value 18.8 kJ mol^{-1}. While, the estimated value of In(τ_o) is -32.877 or τ_o = 5.27×10^{-15} sec. Indirectly, the entropy change, ΔS can be determined from τ_o. The similar procedures are implemented in PVA hydrogel and the mean activation energy, Q for 96.8 and 80.0% m.c hydrogel are estimated between 12.1 and 5.45 kJ mol^{-1} for 2-10 GHz and 14.2 and 5.84 kJ mol^{-1} for 10-20 GHz, respectively, as listed in Table 4. This mean that the energy, Q released (or absorbed) per mole for the hydrogen bond are formed in PVA hydrogel, are less than the hydrogen bonds formed in pure water for entire frequency. In other word, the lower value of Q, the more stable of the hydrogel. In additional, a negative value of ΔS indicates a decrease in entropy, the less random in saturated hydrogel system.

Figure 7 shows the variation in relative permittivity, ε_r of PVA hydrogel with frequency for various temperature, T. As mention earlier, the binding between PVA chain and water molecules are very stable for high concentrated hydrogel, thus the slight higher temperature or energy is not significant to polarize the molecules in the hydrogel compared to the pure water.

This condition will cause the relative permittivity, ε_r of PVA hydrogel are evident less sensitive to higher temperature (> 30°C), especially for PVA hydrogel with low water content (< 80% m.c) as shown in Fig. 7.

(a)

(b)

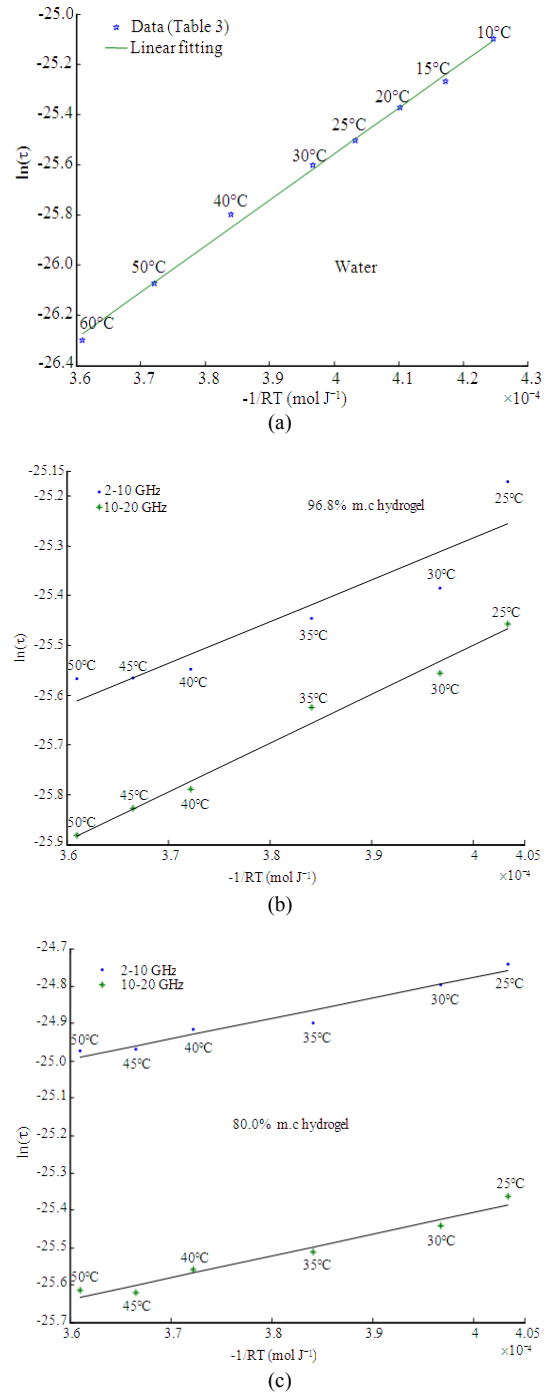(c)

Fig. 6: Arrhenius plots for bulk water and PVA hydrogel

Table 4: The estimated values of mean activation energy, Q and relaxation coefficient, τ_o for pure water and PVA hydrogel for frequency range of 2-20 GHz

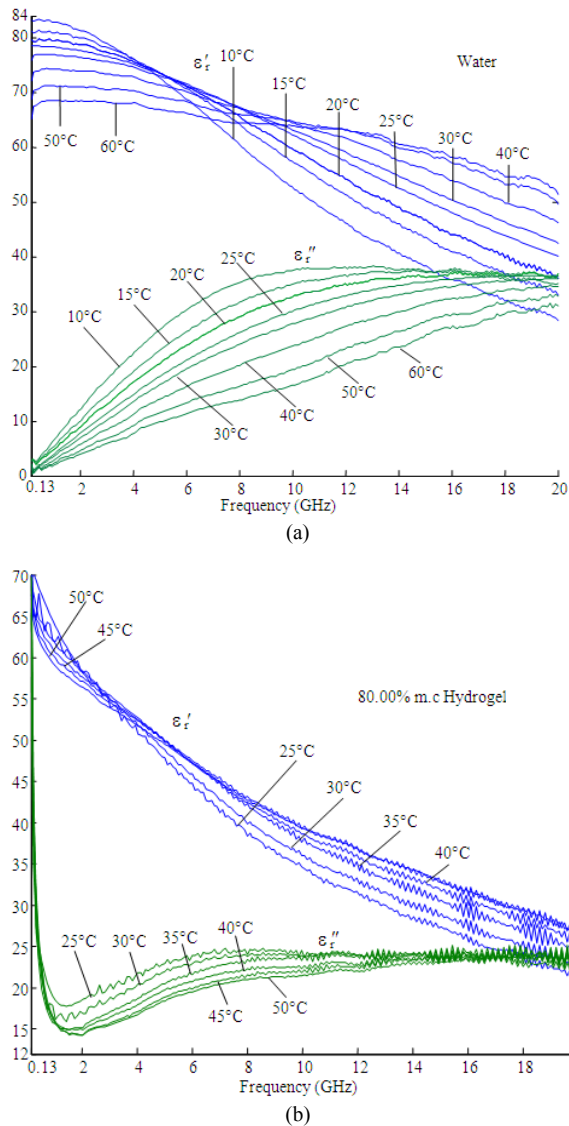| Sample	f (GHz)	Q (kJ mol^{-1})	ln(τ_o)	(ps)(τ_o)	T (°C)	ΔS (J (K mol)$^{-1}$)
Water	2-20	18.0	-33	0.0053	25	28.0
					40	28.0
					60	28.0
97% m.c hydrogel	2-10	12.0	-30	0.0810	25	5.7
					40	5.3
					60	4.8
	10-20	14.0	-31	0.0280	25	14.0
					40	14.0
					60	14.0
83% m.c hydrogel	2-10	5.1	-27	0.020	25	-21.0
					40	-21.0
					60	-22.0
	10-20	7.0	-28	0.4900	25	-9.3
					40	-9.7
					60	-10.0
80% m.c hydrogel	2-10	5.5	-27	2.0000	25	-21.0
					40	-21.0
					60	-22.0
	10-20	5.8	-28	0.9000	25	-14.0
					40	-15.0
					60	-15.0

Fig. 7: Variation in relative permittivity, ε_r of (a) water and (b) 80% m.c PVA hydrogel with frequency for various temperature, T

CONCLUSION

In this study, a linear fitting method was used to replace complicated numerical routine for finding out the calculating dielectric parameters. The linear polynomial fitting is used to estimate the values of dielectric static, ε_s relaxation time, τ and mean activation energy, Q as well as entropy change, ΔS. The rigorous dielectric model which is consists of two relaxation processes, is created successfully to describe the electric properties of the PVA hydrogel mixture.

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