

Influence of granular strontium chloride as additives on some electrical and mechanical properties for pure polyvinyl alcohol

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Abstract. A matrix composed of polyvinyl-alcohol (PVA) mixed with different concentration ratios of the granular strontium chloride ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$) were prepared by casting technique method at room temperature (about 30°C). The electric and dielectric properties such as a.c. electrical conductivity by a conventional method, using Keithly 616 digital electrometer, dielectric constant, and dielectric loss were measured. Calculated equilibrium properties such as lattice constant, bulk modulus and elastic constants are in good agreement with experimental results. The calculated activation energy values agree well with experiment only when the SrCO_2 molecules are allowed to displace under strain, indicating the importance of inner strain relaxation. From the elastic constants, theoretical values of the Young's modulus, shear modulus, Poisson's ratio, of SrCl_2 are obtained. In addition mechanical properties such as Young's modulus, creep relaxation, and energy stored properties for these samples were also determined at room temperature.

Keywords. Polyvinyl-alcohol (PVA); granular strontium chloride, SrCl_2 ; a.c. electrical conductivity; dielectric constant; dielectric loss; Young's modulus; creep relaxation curve.

1. Introduction

The purpose of this article is to review the available experimental evidences pertaining to electric, dielectric and mechanical properties on a matrix composed of polyvinyl-alcohol (PVA) mixed with different concentration ratios of granular strontium chloride ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$).

Electronic transport in conjugated polymers (CPs) has become an increasingly interesting area of research, partly because of the unique electronic properties of CPs and partly because these materials possess great potential for device application, such as Schottky junctions, batteries, displays, sensors, and microelectronics (Skotheim 1986; Stafsform *et al* 1987; Heeger *et al* 1988; Cao *et al* 1989; Macdiarmid and Epstein 1989). Therefore, much attention has been paid to synthesizing various composite materials in which conducting polymers are embedded in some insulating polymer matrices with higher mechanical properties (De Paoli *et al* 1984, 1985; Niwa and Tamamura 1984; Bocchi and Gardini 1986; Roneali and Garini 1988).

By changing the polymer structure, composition, or molecular weight, it is possible to achieve pronounced changes of dielectric properties in broad intervals from insulators to ferroelectrics or organic semiconductors (Svorcik 2001). Firstly, some attention has been focused

on polyvinyl alcohol (PVA) for more than 75 years because of its unique chemical and physical properties as well as its industrial applications (Sakurada 1985). Also, the possibility of replacing the metals of semiconductor inorganic materials with recently discovered conducting polymer has led to intensive interest in such materials (Baughman *et al* 1982; Bloor and Movagher 1983). In the present work, thorough characterization of the electrical conductivities of PVA/ SrCl_2 samples were prepared at room temperature and measured at different temperatures. By changing the polymer structure, composition, or molecular weight, it is possible to achieve pronounced changes of dielectric properties in broad intervals from insulators to ferroelectrics or organic semiconductors (Pollak 1971). Also the dielectric properties were considered as important complementary efforts contributing to a better understanding for the mechanism of transport of such materials. For dielectric materials, usually d.c. and also a.c. conduction at high frequencies are studied to have electronic characteristics (Chiao *et al* 1972).

Also as in mechanical properties, the elastic material deforms under stress but returns to its original size and shape when the stress is released. There is no permanent deformation. Some elastic strain, like in a rubber band, can be large, but in rocks, it is usually small enough to be considered infinitesimal. Many elastic materials obey Hooke's law behaviour: the deformation is proportional to the stress. This is why spring balances work: twice the weight results in twice the deformation. Thus, rocks typi-

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cally deform elastically by 10^{-6} per bar of stress. This is a useful quantity to remember. Elastic strain in rocks is tiny—even ten kilobars typically results in only one percent deformation—if the rock does not fail first. Polymers and composites used for the renewal of civil infrastructure will be exposed to complex infrastructure service environment conditions of a range of combinations of stress, time, temperature, moisture, radiation, chemical, and gaseous environments and are expected to perform for fifty years or more. The lack of understanding of the fundamental parameters controlling long-term materials performance necessarily leads to over-design and in-service prototype evaluations and, furthermore, inhibits greater utilization. The determination of characteristics related to creep and relaxation phenomena of these materials and the understanding of the phenomena vis-à-vis civil infrastructure renewal are critical to the further use of FRP composites in civil infrastructure (Frost *et al* 1982).

Creep is the tendency of a solid material to slowly move or deform permanently under the influence of stresses. It occurs because of long-term exposure to levels of stress that are below the yield strength or ultimate strength of the material. Creep is more severe in materials that are subjected to heat for long periods, and near the melting point. It is often observed in glasses (Kanchana *et al* 2003), and it always increases with temperature. These parameters were measured at room temperature. To the best of our knowledge, no experimental work has been reported on the effect of SrCl_2 on PVA polymer. The future application of these materials strongly depends on the success of improving their mechanical and electrical properties.

2. Experimental

2.1 Sample preparation

A matrix composed of polyvinyl alcohol (PVA) mixed with granular strontium chloride ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$) with different ratios is shown below in table 1.

The preweighed PVA powder of molecular weight, 72,000 g/mole, well dissolved using bidistilled water was then added to different amounts of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$. These mixtures using casting technique were dried in Petri dish at room temperature for some days in small closed glass chambers till it became solid sheets of thickness, 1.5 mm. Casting technique methods were considered as a process of filling open molds with these mixtures. All the products of this mixture were found to be very stable, colourless and odourless, specially for the samples of low SrCl_2 concentration. Only samples with very high quality from these matrices were selected and used for both electrical and mechanical measurements. The product films of these samples were divided into six individual groups

which were denoted by symbols Sr1, Sr3, Sr5, Sr7, Sr9, and Sr11 corresponding to the ratios of polyvinyl alcohol (PVA) mixed with granular strontium chloride ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$) as shown in the above table.

2.2 Electrical measurements

RLC bridge of type (3531 Z HiTESTER, Japan) was used for electrical measurements. The stress-strain behaviour in the case of uniaxial extension was measured at room temperature using a material tester (Ametek, USA) connected with a digital force gauge (Hunter spring ACCU Force II, USA, 0.01 N resolution) to measure the stress force.

3. Results and discussion

The physical properties of the samples of composites from polyvinyl alcohol (PVA) and granular strontium chloride ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$) such as a.c. conductivity, capacitance, dielectric constant, and dielectric loss with temperature, $\sigma_{ac}(T)$, $C_p(T)$, $\epsilon_r(T)$, $\epsilon_r(T)$ and with frequency, $\sigma_{ac}(f)$, $C_p(f)$, $\epsilon_r(f)$, $\epsilon_r(f)$ were measured carefully. Also mechanical properties such as Young's modulus, creep curves and others were studied at room temperature.

3.1 Electrical measurements

3.1a *Variation of a.c. electrical conductivity with concentration:* Figure 1 shows dependence of the electrical conductivity of SrCl_2/PVA composites on the filler content. It can be seen that at around 20 wt% of filler, a sharp increase of electrical conductivity is observed. This concentration is called generally the percolation

Table 1. Polyvinyl-alcohol (PVA) mixed with granular strontium chloride ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$) with different concentration ratios.

Material	Sample code	Ratio (wt%)
PVA/ $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$	Sr1	95 : 5 PVA : $\text{Sr}_2 \cdot 6\text{H}_2\text{O}$
	Sr3	85 : 15 PVA : $\text{Sr}_2 \cdot 6\text{H}_2\text{O}$
	Sr5	75 : 25 PVA : $\text{Sr}_2 \cdot 6\text{H}_2\text{O}$
	Sr7	65 : 35 PVA : $\text{Sr}_2 \cdot 6\text{H}_2\text{O}$
	Sr9	55 : 45 PVA : $\text{Sr}_2 \cdot 6\text{H}_2\text{O}$
	Sr11	45 : 55 PVA : $\text{Sr}_2 \cdot 6\text{H}_2\text{O}$

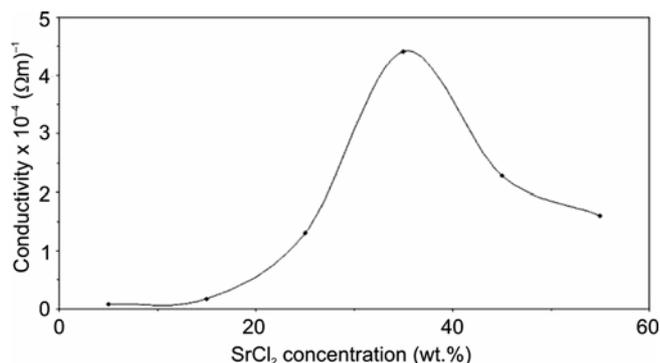


Figure 1. Electrical conductivity vs SrCl₂ concentration (wt.%).

concentration. In this case an infinite cluster of particles is formed within the polymeric matrix. This cluster penetrates throughout the sample and represents a conductive way for movement of the electrons throughout the sample. At this concentration the conductivity increases till it reaches an optimum point at 35 wt%; then the conductivity decreases. Since in the real situation only a limited number of experimental points is available, we arbitrarily identified a percolation threshold as an inflection point in an empirical fitting curve. The concentration of the doping required for the insulator–conductor transition is referred to as (threshold concentration) or (percolation limit). The electrical response described by percolation theory is given by (Kanchana *et al* 2003)

$$\sigma = C(f - f_c)^t \text{ or } \log \sigma = \log C + t \log(f - f_c), \quad (1)$$

where σ is the composite conductivity, f the weight percent of filler in the composite, f_c the percolation threshold, C is a constant and t the critical exponent. To determine the percolation threshold, we have fitted the experimental data using (1) and the resulting mathematical fit is drawn in figure 2. The percolation threshold and critical exponent were found to be 18 wt% and 2, respectively. The critical exponent depends solely on the dimensionality of the system and its universal value is close to 2 for a three-dimensional system as shown by Kanchana *et al* (2003).

The a.c. electrical conductivity as a function of temperature, $\sigma_{ac}(T)$, has been measured for all different samples at ten different temperatures, viz. 303 K, 313 K, 323 K, 333 K, 343 K, 353 K, 363 K, 373 K, 383 K and 393 K as shown in figure 3. From these figures, it can be seen that $\ln(\sigma_{ac})$ slowly decreases with reciprocal temperature for all samples. This decreasing relation indicates that the a.c. component of (σ_{ac}) has a temperature dependence of the following equation

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right) \text{ S m}^{-1}. \quad (2)$$

The increase in a.c. electrical conductivity values with temperature has been observed for all samples investi-

gated within all temperature ranges. In the lower temperature ranges, the conduction mechanism may be attributed to the electrons hopping under the effect of the electric field. By increasing temperature above 323 K, the thermal activation is more effective and a polarization conduction in addition to hopping over a barrier in the thermally assisted electric field can be expected.

The values of activation energies were derived from the calculation of the slopes in the plots in figure 3 after fitting procedures, which relates a.c. electrical conductivity with absolute temperature. In figure 4 which relates the activation energy, E_a (eV) for PVA/SrCl₂ samples as functions in its frequencies. The conduction mechanism in these composites in the high frequency region can be explained based on defect model suggested by Ingram (1987). The near linearity between the frequency and the activation energy (figure 4) suggests that the conductivity enhancement is directly related to the increasing mobility of the charge carriers. Since the PVA, ions are much less mobile than the SrCl₂ ions in the mixed PVA and SrCl₂. Therefore, the contribution to the conduction for the present composite in the high frequency region can be mainly considered due to SrCl₂ ions.

3.1b Variation of dielectric properties with temperatures and frequencies: The temperature dependence of the dielectric constant values, $\epsilon_r(T)$, were studied for all samples (figure 5). The measurement temperature range was from 293 K to 393 K, as mentioned before. For most samples the value of dielectric constant initially increases with temperature. It is possible that peaks present in the plots could not be detected because of the limitations imposed by our present experimental set-up. The dielectric dispersion appearing when the temperatures increase, attributed to the rotatory diffusional motion of the molecules from one quasi-stable position to another around skeletal bonds involving large-scale conformational rearrangement of main chains; it is generally known as the primary dispersion region. The low temperature dielectric response of side groups which are considered to be more mobile, or the small displacement of dipoles near the frozen position, and is generally known as the secondary dispersion region.

We can notice that the dielectric values increase with increasing concentration of SrCl₂ till 35% then it decreases again, this behaviour was expected from figure 1, because as a general trend, in many studies for the dependence of salt concentration on the ionic conductivity in polymers at low salt concentrations, there is a build-up of charge carriers which results in an increase of ionic conductivity and at high salt concentrations, build-up of charge carriers is offset by the retarding effect of ion cloud, thus, the ionic conductivity decreases as this latter effect begins to dominate.

The frequency dependence of the dielectric constant values ϵ_r , was studied for all samples and has been shown

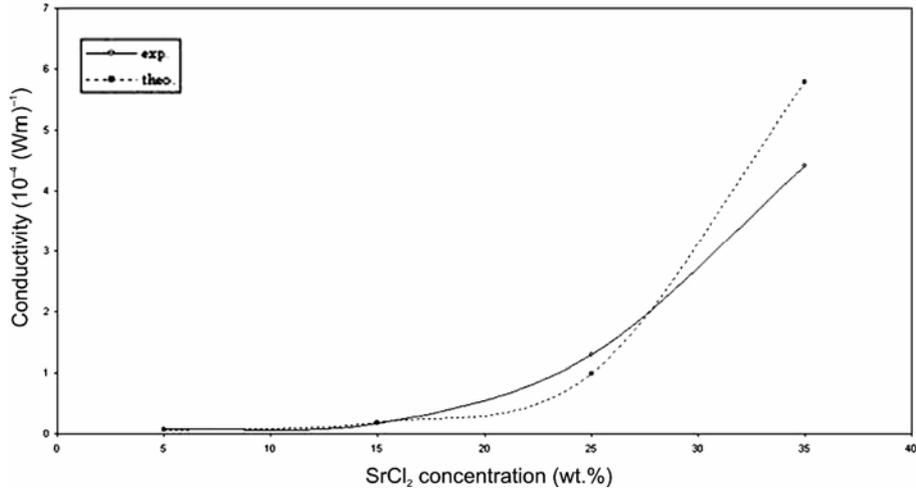


Figure 2. Theoretical and experimental data for the electrical conductivity as a function of filler loading.

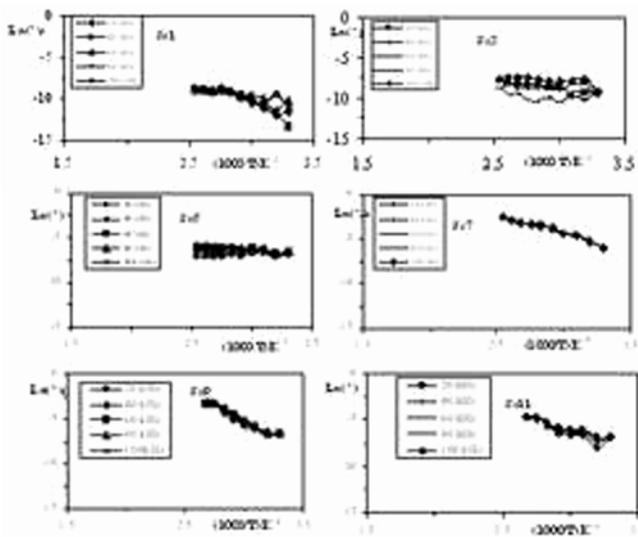


Figure 3. Variation of Ln conductivity with temperature for PVA/SrCl₂ samples.

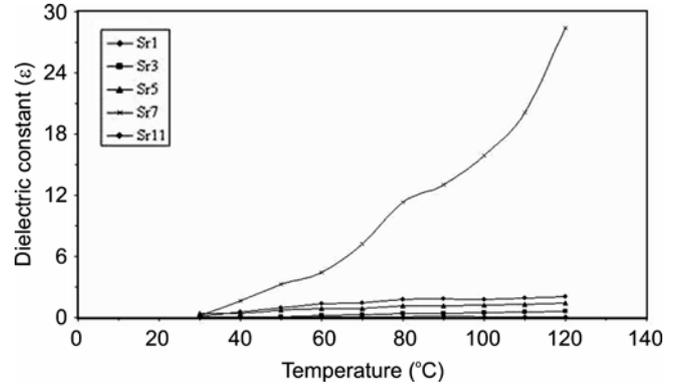


Figure 5. Temperature dependence of dielectric constant $\epsilon(T)$, for all samples of PVA/SrCl₂ composites at different frequencies.

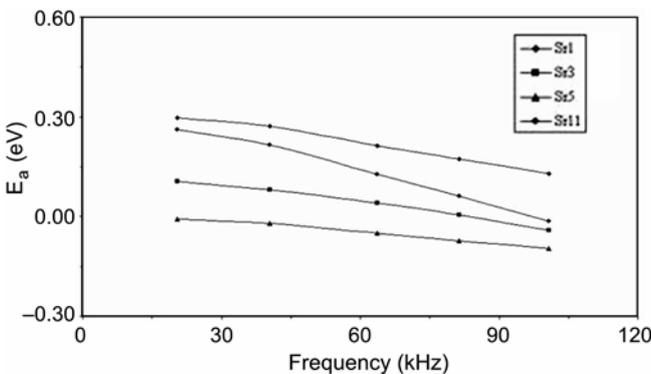


Figure 4. The activation energy, E_a (eV), for PVA/SrCl₂ samples as functions of frequencies.

in figure 6. This may be attributed to the interfacial polarization, which dominates in the low frequencies, and/or qualitatively as due to the fact that electronic exchange between the ions for the two types of PVA and SrCl₂ cannot follow the frequency change of the externally applied alternating field beyond the critical frequency value (Kamel and Georgy 1979). Figure 7 shows the frequency dependence of the dielectric loss for different concentrations at different temperatures. It should also be noted from this figure and others that ϵ follows the expected behaviour of a Debye relaxation. The ϵ value increases in a sigmoidal fashion from the unrelaxed value at low temperature to the relaxed value at increased temperatures. The point of inflection for the curve of ϵ should occur at approximately the same temperature of the maximum peak height in ϵ .

3.2 Mechanical measurements

Our experiments of stress–strain relations for the different samples were run at room temperature to avoid any

transformation by heat resulting from the access loads. Also, because the real materials always yield to some

extent under the influence of the applied forces; due to the microstructural features such as pores and grains which act as stress raisers, we used an apparatus which directly give the relation between tensile strain and tensile stress. Stress-strain curves are shown in figure 8; from it we show that Young's modulus (stretch modulus) values of all samples has been calculated. Figure 9 shows Young's modulus values as functions of SrCl₂ contents in PVA/SrCl₂ specimens. This figure shows the increase in SrCl₂ additives from 0 to 15 wt%, which may cause decrease in the elasticity of the samples leading to a decrease in average Young's modulus reaching a minimum value of 0.5×10^7 N/m². A further increase in SrCl₂ addition above 25 wt% causes increase in Young's modulus values to a level just over 0.5×10^7 N/m². The forementioned behaviour for these samples may be attributed to the existence of two competing processes taking place in the samples with increasing SrCl₂ content. Figure 10 shows the energy of these samples as functions of their length elongation; which has been calculated using (6) above. Also, other several runs were conducted in order to choose the most suitable conditions of the creep experiments. The creep curves for these samples at 5.9 and 2.9 MPa as constant loads at room temperature are presented in both figures 11 and 12. From the curves we note that the sample Sr₃ which contains 15 wt% SrCl₂ has

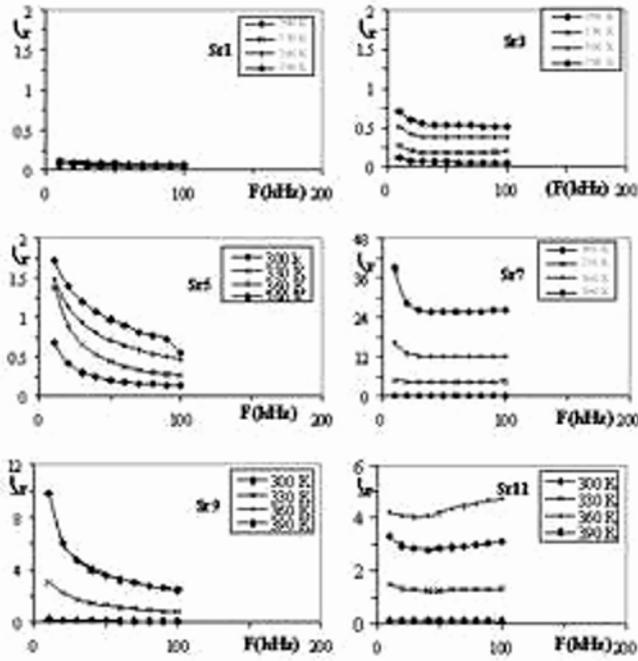


Figure 6. Dielectric constants as functions of frequency for all samples of PVA/SrCl₂ composites at different temperatures.

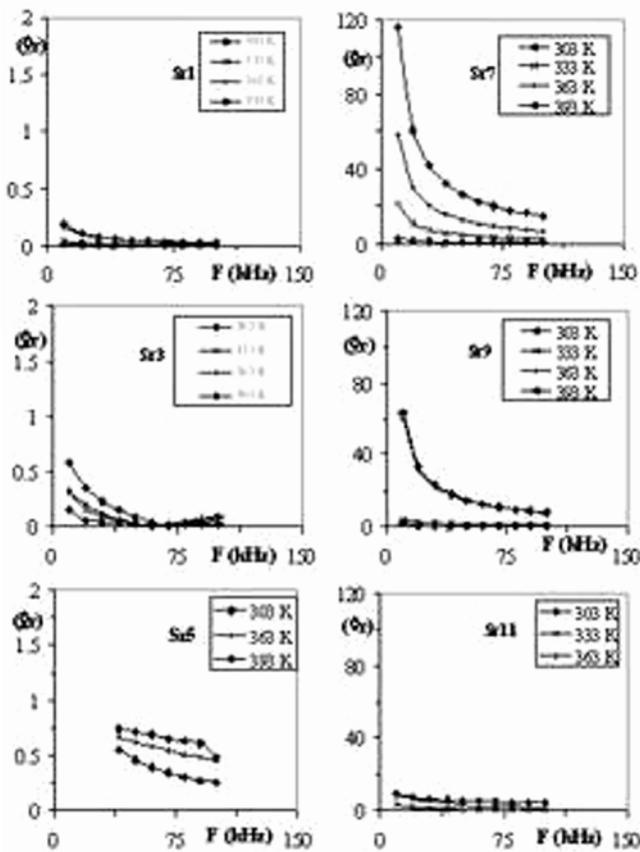


Figure 7. Dielectric loss as a function of frequency for all samples of PVA/SrCl₂ composites at different temperatures.

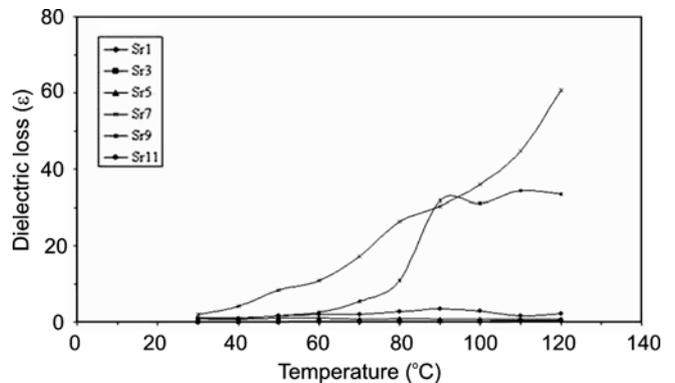


Figure 8. Dielectric loss vs temperature.

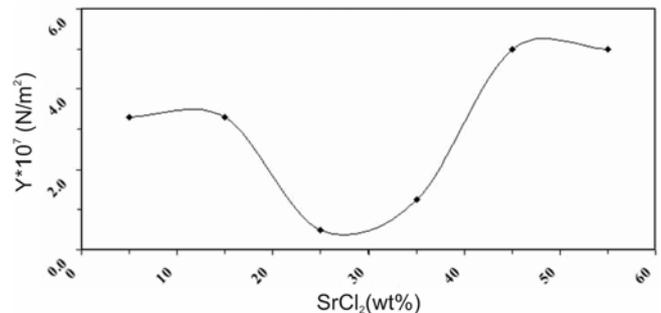


Figure 9. Young's modulus as a function of SrCl₂ content in PVA/SrCl₂ specimens.

the most higher strain. This may be explained, by increasing the elasticity values by increasing with further increase of SrCl₂ content. Using the Maxwell model for viscoelasticity (Klompfen 2005), the generalized linear Maxwell model could be expressed by

$$E_t = \sum_1^{n_i} E_i \exp(t / \tau_i), \tag{3}$$

where $\tau_i = \eta_i/E_i$; η is the sample viscosity, E the Young's modulus and the index i refers to the i th Maxwell element, while n_i the number of elements (Klompfen 2005).

Viscosity is very dependent on temperature. The viscosity of SrCl₂ at room temperature decreased and then

increased. We calculated the viscosity of the samples at different concentrations, and the obtained results are shown in figure 13. It is clear that with increase of SrCl₂ concentration the viscosity of the samples decreases till 35% and then increases with higher concentrations.

4. Conclusions

We have investigated the electric, dielectric, and mechanical properties of polyvinyl-alcohol (PVA) mixed with different concentration ratios of granular strontium chloride (SrCl₂·6H₂O) which were prepared by casting technique method at room temperature. It can be concluded that doping of PVA with SrCl₂ increases the conductivity of the system till 35 wt% of SrCl₂ concentration, which is mainly due to the introduction of conducting paths in the polymer matrix. The percolation threshold is estimated to be 18 wt%. The values of a.c. conductivity, σ_{ac} , dielectric constant, ϵ_r , dielectric loss, ϵ_r'' , and activation energy, E_a , at different temperatures and frequencies were investigated using RLC bridge. Then we measured the relationships between the a.c. electric conductivity values and SrCl₂ contents in SrCl₂/PVA samples and from it we note that by increasing strontium chloride content by more than 35 wt%, the conductivity decreases. Mechanical properties such as Young's modulus, and creep curves have been done for the samples as a function in SrCl₂ concentration at room temperature. We used Maxwell model to calculate the viscosity of the samples with different concentrations. The stress-strain curves show the increase in SrCl₂ additives from 0 to 15 wt%, may cause decrease in the elasticity of the samples leading to a decrease in average Young's modulus reaching minimum value of 0.5×10^7 N/m². Also a further increase in SrCl₂ addition above 25 wt% causes the increase in Young's modulus values to a level just over 0.5×10^7 N/m². The fore mentioned behaviour for these samples may be attributed to the existence of two competing processes taking place in the samples with increasing

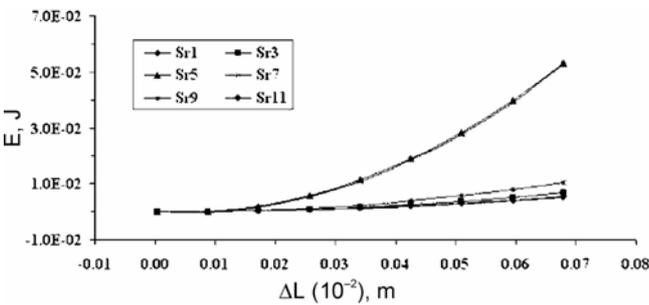


Figure 10. Energy as a function of PVA/SrCl₂ specimen length elongation.

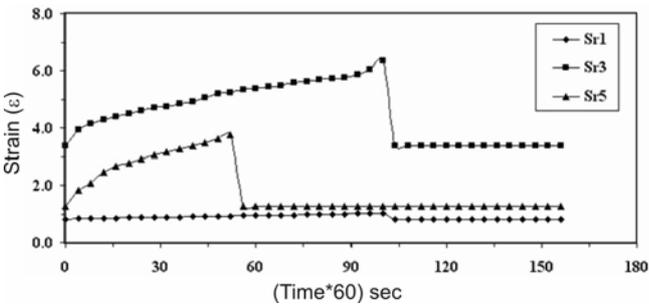


Figure 11. The forward and backward creep relations for each Sr1, Sr3, and Sr5 specimens at 5.9 MPa as a constant stress.

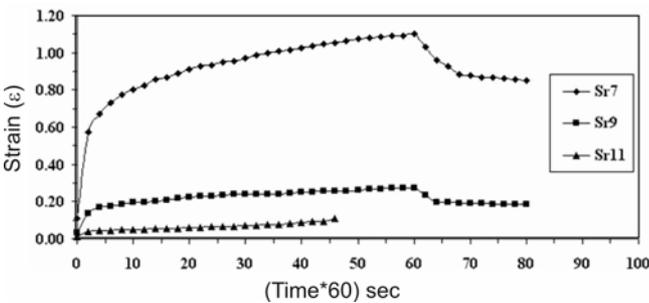


Figure 12. The forward and backward creep relations for each Sr7, Sr9 and Sr11 specimens at 2.9 MPa as a constant stress.

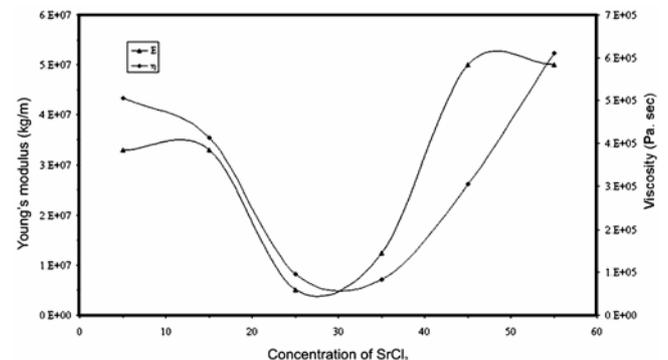


Figure 13. Young's modulus and viscosity vs SrCl₂ concentration.

SrCl₂ content other than PVA case only. We note from creep curves, that the sample Sr3 which contains 15 wt% SrCl₂ has the most higher strain.

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