Physical Sciences Section

A STUDY OF ELECTRICAL PROPERTIES OF POLY(VINYL-ALCOHOL) CONTAINING METALS

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Films ($\cong 350$ µm) of poly (vinyl -alcohol) composites, containing copper (Cu), aluminium (Al), and iron (Fe), metallic powder very fine, were prepared by casting method. No drastic change in the maine transition temperature was observed by differential thermal analysis (DTA). The electrical resistivity, dielectric constant and dielectric loss (tanδ) were measured at temperature range from room temperature up to 260°. The values of activation energy which estimated from the resistivity curves tell us that the hoping conduction is the predominant for these samples at that temperature region. The result of the dielectric constant does not obeys Debye's theory, this behaviour attributed to space charge polarization due to lattice defect. The result of dielectric loss (tanδ) against temperature shows that there are two relaxation processes, α-relaxation at T=T$_g$ and β-relaxation at T below T$_g$ and the addition of metals as a dopant reduce the glass transition temperature.

Key words: Poly(vinyl-alcohol), Metals, Differential thermal analysis.

Introduction

In order to develop polymers having unique mechanical and electrical properties, doping of polymers with electropositive metal salts and metal complexes has been reported by several workers in the last few years [1-2]. The metal cation is reduced to metal during the cure cycle to obtain metal doped polymer. The electrical resistivity is significantly reduced by the incorporation of metal salts and metal complexes. Attention has been focussed on poly (vinyl-alcohol) (PVA) for more than 30 years, because of its unique chemical and physical properties as well as its industrial application [3]. The possibility of replacing metals of semi-conductor inorganic materials with recent discovered conducting polymer has lead to intensive interest in such materials [4-5]. However, no definitive theory has been proposed to explain the transport properties of materials such as conductor - insulator composites and disordered semi-conductor. Valuable information on transport mechanism in solid can be gained by studying the temperature dependence of resistivity, dielectric constant and dielectric loss.

The present work deals with the effect of Al, Cu and Fe metallic additives on the electrical properties of PVA composites films.

Experimental

The poly (vinyl-alcohol) (PVA) used in this study was obtained from Osaka, Hayashi, Chemical Industries Limited Japan. It had a molecular weight of 1700 $(CH_2\text{-}CHOH)_n$. Copper was 98.5% very fine powder, atomic weight 63.54, obtained from Proluba Paris, France. Aluminium (Al) metal powder 80 mesh, atomic weight 26.98, obtained from El-Nasr Pharma Chemical Co., U.A.R. Iron powder 99.5% from Fluka, AG, Chemical, Buchs, Germany.

The polymer was dissolved in distilled water and then heated gently, using water path for complete dissolution. After the solution attained a suitable viscosity, the desired metallic powder was added 2.5% by weight and the mixture was cast into a glass dish, and kept in a dry atmosphere for two weeks. Several thickness were available ($\cong 350$ µm).

The resistance, capacitance and dielectric loss of the samples were measured by using R.L.C. bridge type Tesla (BM 591 CSSR). The resistivity of the samples were calculated from the geometry of the samples and the measured value of the resistance. Also the values of the dielectric constant were determined using standard geometrical technique in which the capacitance is assumed to be given by the usual expression for the parallel plate capacitor.

$$C = \varepsilon \, \varepsilon_o \, (S / d)$$

where S is the area of the sample, d is its thickness and ε_o is the permitivity of free space.

Sample holder was specially designed to fit the present electrical measurements. Temperature variation was controlled by connecting the heater to a contact thermometer and relay. Measurement of the sample temperature was performed using a thermocouple type (NiCr - NiAl), attached to the upper surface of the sample. The temperature of the sample was raised from room temperature to 260° with constant rate of heating equal 10 degree/30 mins.

Results and Discussion

Thermal analysis. D.T.A. measurements for the samples

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was carried out in order to check the transition temperatures and ambient with the results of electrical measurements studies.

Figure 1 shows the D.T.A. plots for PVA as pure and as loaded with Cu, Fe and Al. It is noticed that all the plots mentioned exhibit approx. the same characteristic transition temperature. This implies that the present additives do not change the main structure of PVA.

The observed transition can be assigned as: the T_{gg} exothermic at about (125°) may arise from the wagging motion of the vinyl ring [6-7]. The T_g endothermic change at about (220°) can be assigned to the glass-rubber transition due to the motion of the main chain segments. As shown in Fig. 1. The addition of impurities changed the glass - rubber transition temperature [8].

Temperature dependence of A.C. resistivity. Figure 2 shows the temperature dependence of the resistivity for pure PVA, PVA-Al, PVA-Cu and PVA-Fe composites, at fixed applied voltage 1 volt and fluency 1 KHz. For all samples we can see that the resistivity decreased with temperature, then increased after certain temperature 220°, we can see that the general tendency of curves are similar, sometimes overlapped and intersected. The behaviour of these curves can be explained as the conductivity in metal-PVA composites occur along particles contact each other or separated by small gaps. These interaggregate gaps may be considered as potential barriers for charges to hop by tunnelling. Reduction in the interaggregate gaps enhances the flow of charge and decrease the resistivity. The average interaggregate distance is affected by means of parameters including concentration, structure, size, shape of the molecules and temperature.

Conductor - insulator composites become conductive only after a certain concentration (ρ_c) of the conductive filler has been added. This critical percolation represents a system where continuous conductive chain have been first formed. The conducting element of these chains either make contacts between themselves or separated by a very small distance across which charge can hop by tunnelling. Also system consisting of the critical concentration become insulating if their interaggregate distance increased by external means, such as thermal expansion or mechanical stress. The resistivity ρ characteristics is given by

$$\rho = \rho_o \, e^{E/KT}$$

where E represent the activation energy, T is the absolute temperature and K is Boltzman constant.

The activation energies calculated from the slopes of $\ln \rho$ against 1/T for our samples before and after the glass-rubber transition (region I and II) are given in Table 1.
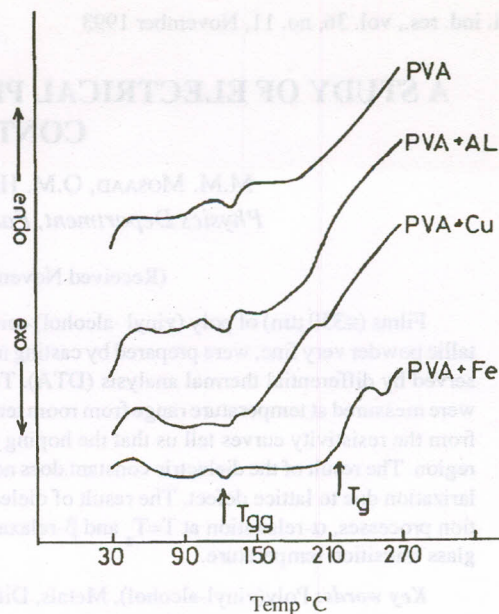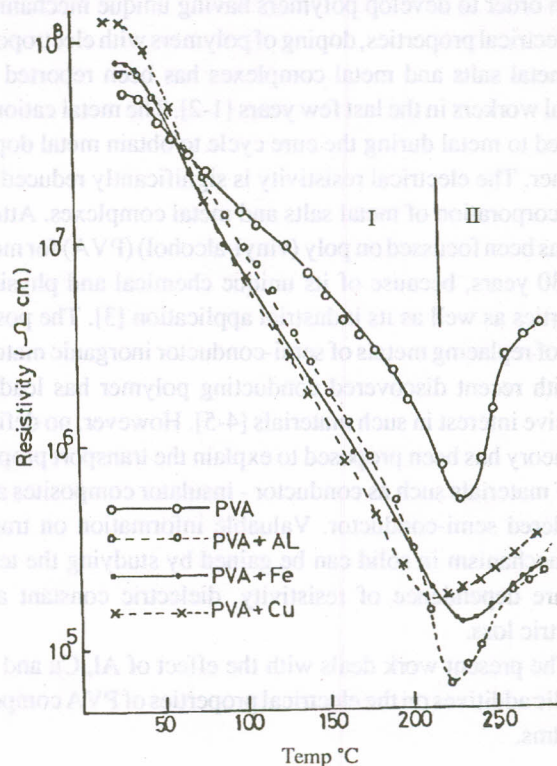

Fig. 1. DTA curves for the samples.

Fig. 2. Temperature dependence of A.C. resistivity.

TABLE 1. ACTIVATION ENERGY (EV).

Composite	Region I	Region II
PVA pure	0.89	0.15
PVA + Cu	0.09	0.23
PVA + Fe	0.16	0.20
PVA + Al	0.27	0.19

The electrical conduction in polymers can be attributed to ions due to impurity incorporation and the electrons which migrate along the polymer chain. The distinction between electronic and ionic conduction may be very difficult problem and in some cases it may not possible to give a conclusive answer to this question. But it is assumed as a general rule that values for activation energies less than 0.2eV should be considered as indicating undoubtedly electronic mechanism and values more than 0.6eV would normally associated with ionic transport [9]. The low values of the activation energies in the Table are an indication that the hopping conduction is still predominant at that temperature region for these samples.

Temperature dependence of dielectric constant (ε). Temperature dependence of dielectric constant at fixed fluency of 1 KHz is shown in Fig. 3, from room temperature to 120° the dielectric constant of pure PVA has the highest values and above 120° the sample contains Al metal has the highest values of dielectric constant, the dielectric constant for all samples increases with increasing temperature and have maximum value at temperature 220° which is the T_g transition temperature. Above 220° the dielectric constant decrease with temperature.

In general the dielectric constant of material is composed of four contribution, electronic, ionic, orientational and space charge polarization. The space charge contribution will depend on the purity and perfection of the material.

We know from Debye's theory that ε is inversely proportional to temperature, but in the present study we notice a considerable increase of ε with temperature up to T_g. This behaviour can be attributed to space charge polarization due to lattice defects [10].

Temperature dependence of dielectric loss (tan δ). One of the main method of investigating molecular motion in polymers is the study of the temperature dependence of the parameters characterizing the dynamic mechanical properties. The most important in this respect is to study the dependence of the loss factor on temperature.

Figure 4 represents the behaviour of dielectric loss against temperature for pure and doped PVA samples. It is clear from the Figure that (tan δ) for all samples are dependent to a considerable degree on temperature and nearly all the curves are similar in shape but with different positions for the peaks. At temperature range 120°–150° a first peak was observed and other peak was observed at temperature range 210°–240°. These two peaks are consider due to a two relaxation processes and symboled β and α. The secondary relaxation β is observed experimentally at temperature below the major glass transition temperature (T_g) and is termed β-process to differentiate secondary relaxation from primary α-relaxation occurring at T_g [11]. Most theories of relaxation phenomena in polymer rest on the fundamental assumption of the possibility of internal rotation of the individual elements of macromolecules about certain chemical bonds. Process of this type are thermal activation processes and invo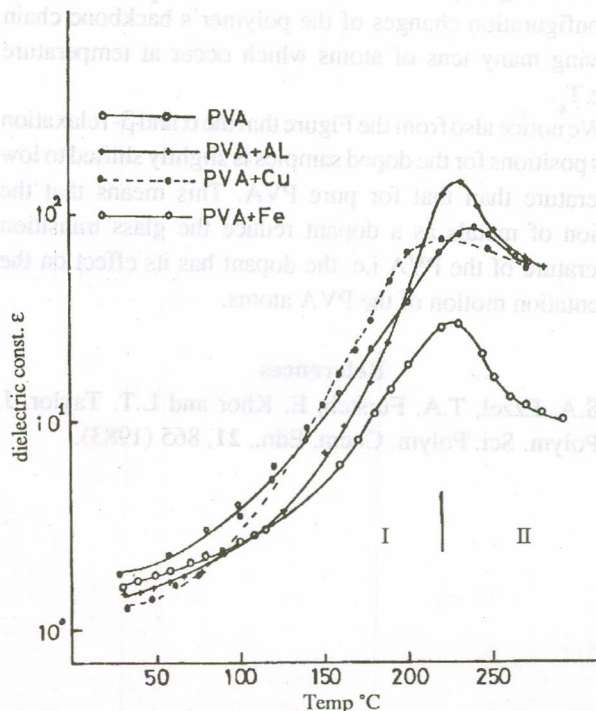lve the jump of atoms (or groups of small side groups which can occur at $T < T_g$. In contrast to the configuration changes of the polymer's backbone chain involving many ions of atoms which occur at temperature above T_g.

We notice also from the Figure that α and β relaxation peaks positions for the doped samples are may shifted to low temperature than that for pure PVA. This means that the addition of metal as a dopant reduce the glass transition temperature of the PVA i.e. the dopant has its effect on the reorientation motion of the PVA atoms.

References

1. S.A. Nouh, T.A. Fayek, E. Khor and L.T. Takon, Polym. Sci. Polym. Chem. Edn., 21, 865 (1983).

Fig. 3. Temperature dependence of dielectric constant ε.
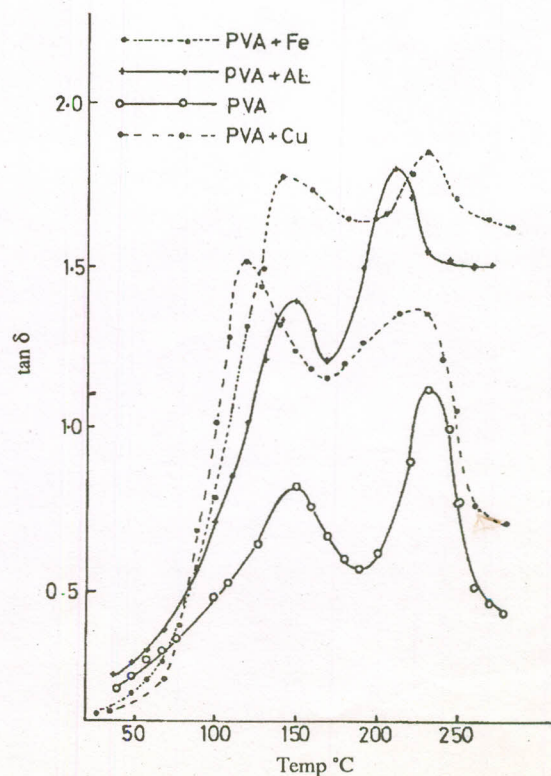

Fig. 4. Temperature dependence of dielectric loss, tan δ.

of atoms) over a potential energy barrier from one equilibrium position to another.

For the case of glassy polymer β-relaxation can be understood physically as the (rotational vibrational) rearrangement of small side groups which can occur at $T < T_g$ in contrast to the configuration changes of the polymer's backbone chain involving many tens of atoms which occur at temperature above T_g.

We notice also from the Figure that the α and β-relaxation peaks positions for the doped samples is slightly shifted to low temperature than that for pure PVA. This means that the addition of metals as a dopant reduce the glass transition temperature of the PVA i.e. the dopant has its effect on the reorientation motion of the PVA atoms.

References

1. S.A. Ezzel, T.A. Furstch, E. Khor and L.T. Taylor, J. Polym. Sci. Polym. Chem. Edn., **21**, 865 (1983).

2. T.A. Furstch, L.T. Taylor, T.W. Fritz, G. Fortner and E.J. Khor, Polym. Sci., Polym. Chem. Edn., **20**, 1287 (1982).

3. I. Sakuroda, *Polyvinyl Alcohol* (Marcel Dekker, New York, 1985).

4. V.E. DuBrov, M.E. Levinshtein and S. Shur, Soviet Phys. JETP, **43**, 1050 (1976).

5. D.T. Bergman and Y. Imry, Phys. Rev. Lett., **39**, 1222 (1977).

6. M. Kalnin and D.T. Turner, J. Mater. Sci. Lett., **4**, 1476 (1985).

7. P. Hedvig, *Dielectric Spectroscopy of Polymers* (Hilger, Bristal, 1977), pp. 76.

8. E.A. Dimarzio and J.H. Gibbs, J. Polym. Sci. A1, 1417, 9(1963).

9. A.K. Jonscher, Thin Solid Films, **1**, 213 (1967).

10. K.V. Rao and Smakula, J. Appl. Physics, **36**, 2031 (1965).

11. S.R. Elliott, *Physics of Amorphous Materials* (John Wiley, New York, 1990).