monium salt) 6 starting from poly(γ-aminoalcohol) 4a (4 g) in n-butanol solution (80 ml), and methyliodide (15 g). The product is a white powder, $\eta_{sp/c}=0.12$ ($c=1\%$) (in H_2O C_2H_5OH 1:1 at 30°C). Analysis: Calculated for 89% conversion: C, 50.32; H, 6.56; N, 4.22; I, 34.04%. Found: C, 50.3; H, 6.7; N, 4.2; I, 34.0%.

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Effect of crosslinking on the charge storage characteristics of poly(vinyl alcohol)

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The charge storage characteristics of poly(vinyl alcohol) films crosslinked by doping with potassium dichromate and heat treatment have been investigated by surface-charge decay measurement and thermally stimulated depolarization techniques. It has been shown that the mobility of charge carriers decreases with increasing density of crosslinks giving rise to increase in charge storage capacity.

Keywords Polymer; crosslinking; charging; carrier mobility; electrical properties

INTRODUCTION

Recently a number of investigations have been reported on the various properties of poly(vinyl alcohol) (PVA) doped with metallic salts such as $CuCl_2$, $FeCl_3$, $CrCl_3$ etc.[1,2] It is well known that these salts from metal complexes, especially after heat treatment giving rise to crosslinking between the polymeric chains of PVA[3]. The dichromate ion, especially, is responsible for heavy crosslinking in PVA and is used quite extensively in lithographic plates[4]. However, little is known regarding the effect of such complex formation and crosslinking on electrical and charge storage properties. The results of our investigations are reported here.

EXPERIMENTAL

Since the dichromate ion is a good crosslinking agent for PVA, $K_2Cr_2O_7$ (concentration 4% by weight) was used for doping the films. The films were prepared from aqueous solution of PVA (BDH, *MW* 14000) on smooth aluminium substrates or glass slides by solution evaporation technique[5] at 313K. The films were nominally exposed (15 min) to Hg fluorescent lamp (100 lux) and then cured for 30 min at elevated temperatures ranging from 313 to 373K. The surface charge decay characteristics (SCDC) were investigated for the films (50 μ thick) coated on aluminium substrates using a xerographic discharge technique in the same manner as reported earlier[6]. The thermally stimulated discharge currents (*TSD*) were also investigated for these films using samples coated on glass slides with vacuum-deposited silver electrodes on top, forming a surface cell configuration (2.0×0.1 cm^2) and the method for the *TSD* studies was as described elsewhere[7].

RESULTS AND DISCUSSION

Pure PVA films as such accepted very little charge on exposure to corona emission from a wire source held at a potential of 7.0 kV a distance of 2 cm away from the film and it was not possible to record the same. However, films doped with $K_2Cr_2O_7$ accepted a considerable amount of charge and the surface potential was about 200 volts. It was found that this could be further increased to a greater extent by thermal treatment of the samples at elevated temperatures. *Figure 1* shows the typical SCDC observed for doped films cured at various temperatures. Curves 1 to 4 are for the annealing temperatures of 313, 323, 353 and 373K, respectively. It is interesting to note that the surface potential, which is indicative of the amount of charge accepted by the film (V_a), increases by nearly four times when the curing temperature is increased from 313 to

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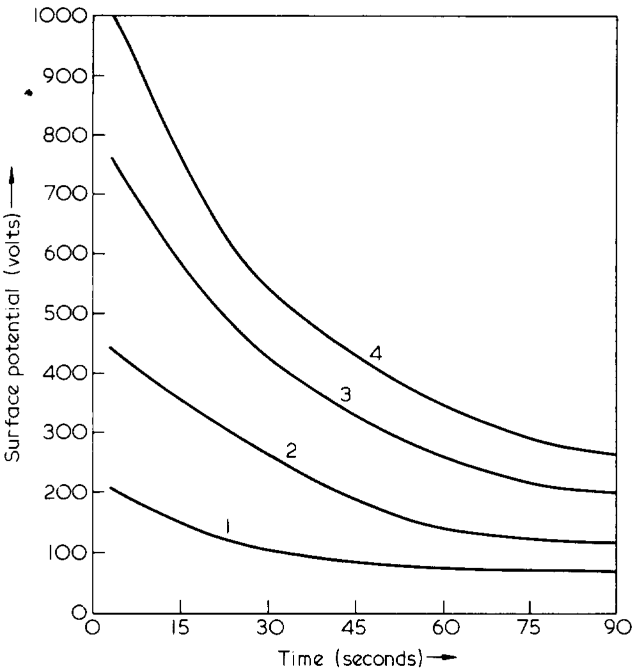

Figure 1 Surface-charge decay characteristics of PVA doped with $K_2Cr_2O_7$. Curves 1 to 4 are for samples cured at 313, 323, 353 and 373 K, respectively

373K. However, the surface potential decays fairly rapidly and saturates to much lower values (V_s). Nevertheless, V_s is 2.5 times higher in samples cured at 373K than those cured at 313K. The amount of charge the polymeric film accepts and retains depends on the electrical conductivity of the film and the mobility of charge in the bulk of the material. There are various models suggested for the SCDC, the most likely being based on space-charge formation[8]. In such a case the surface potential (V) decays as per the relation:

$$V = V_0 d/2(\alpha + E_0 \mu t) \qquad (1)$$

where V_0 is the initial potential, E_0 the initial field, μ the mobility of charge carriers, d the film thickness, t the time and α a constant related to space-charge distribution. Analysis of the SCDC, especially in the long time interval, as per equation (1) yields the value of carrier mobility. The values of mobility for these samples cured at various temperatures are given in *Table 1*. It can be seen that μ decreases from 8×10^{-10} to 1.6×10^{-10} cm^2 volt^{-1} s^{-1} when the curing temperature is increased from 313 to 373K.

It is well known that PVA doped with $K_2Cr_2O_7$ is crosslinked on exposure to light and is made insoluble due to the formation of complexes with Cr(III)$^+$ which link mostly the hydroxyl groups[9]. The process of crosslinking is further enhanced on heat treatment and is used in the 'burning in' step during lithography or photoengraving process[10]. In the present case it may then be expected that as the curing temperature is increased the polymer becomes more crosslinked. This apparently causes a reduction in the mobility of charge carriers and a decrease in the electrical conductivity giving rise to an increase in the charge acceptance of PVA.

To investigate the charge-storage mechanism, the *TSD* current was studied in pure, doped and cured samples. In all cases the same polarizing field (1.0×10^4 V cm^{-1}) polarizing time (1 hour) and temperature (293K) were used. The heating rate was also kept constant, viz. 0.1K s^{-1} during the depolarization studies. *Figure 2* shows the *TSD* current traced for the three cases. Curves 1, 2 and 3 are for pure, $K_2Cr_2O_7$-doped and films cured after doping (373K), respectively. It can be seen that for pure films, two relaxation peaks were observed with broad maxima at 338 and 365K. The lower temperature peak may be assigned to the motion of ionic carriers or due to the absorbed water which is known to be inherent in PVA. This latter explanation may be especially true in view of the data reported for dielectric relaxation for this polymer[11]. The high temperature peak (365K) can easily be assigned to the segmental motion of the polymeric chain which is especially enhanced at the glass transition temperature, which for PVA lies[12] around 363K. Thus the high temperature peak is strongly linked with T_g. It is interesting to note that for the doped films, the low temperature peak almost disappears (curve 2) while the high temperature peak becomes sharp with a slight shift in the peak temperature (T_{max}) towards the higher side (376K). It may be noted that this shift is further enhanced ($T_{max} = 387$K) in cured samples (curve 3). Since the high temperature peak has been associated with T_g, it can easily be understood that the shift in T_{max} is essentially due to the shift in T_g caused by crosslinking of the PVA. The relation

Table 1 Electrical properties of crosslinked PVA

Film type	μ (cm^2 volt^{-1} s^{-1})	ΔE (eV)
Pure (A)	–	0.9
Doped (B)	8.1×10^{-10}	1.1
(B) Cured at 333K	4.8×10^{-10}	1.15
(B) Cured at 353K	2.25×10^{-10}	1.2
(B) Cured at 373K	1.58×10^{-10}	1.24

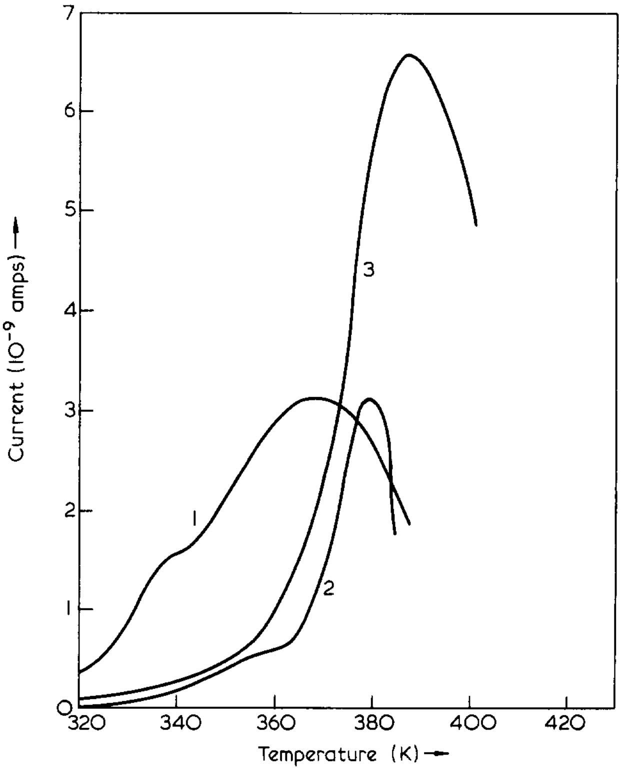

Figure 2 Thermally stimulated depolarization current spectra for PVA films. Curves 1 to 3 are for pure, doped with $K_2Cr_2O_7$ and after-curing of doped films, respectively

between T_g and density of crosslinking is usually given as[13]:

$$\Delta T_g = K_x \cdot \rho \qquad (2)$$

where K_x is a constant and ρ is the density of crosslinks in moles g^{-1}. The value of K_x is found to be in the range of $0.5–1.0 \times 10^5$ depending on the polymeric material. If one takes the average value of K_x (7.5×10^4) and the shift in *TSD* peak as the shift in T_g then it is found that the crosslink density rises by nearly 10^{20}/g (expressed now in number/g) in doped PVA and by twice as much when the doped films are cured at high temperature. It may be interesting to note that the activation energy (ΔE) for discharge current, as estimated from the initial rise method[14], also increases with crosslinking. For pure PVA it is 0.9 eV, for doped PVA 1.1 eV and for cured PVA it is 1.24 eV. This is mainly due to the formation of strong crosslinking bonds *via* $Cr(III)^+$ between the polymeric chains giving rise to stiffness in the segmental motion.

Clearly then crosslinking in PVA leads to a lowering of the charge carrier mobility and the electrical conductivity and hence an increase in the charge-storage capacity of the films. This may be occurring due to the arresting of the segmental motion of the polymeric chain.

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