

## Thermal and IR studies on copper doped polyvinyl alcohol

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**Abstract.** 5 mol% PVA :  $x$  mol% Cu<sup>2+</sup> polymer films were prepared by casting process. Thermal transitions and thermal degradation of samples with respect to copper concentration were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), respectively. Increase in glass transition temperature as a function of copper concentration shows a strong branching and steric effects in copper doped PVA complexes. Thermal degradation of films to an extent of 4–5% was found with an increase in copper content. FTIR spectrum of PVA doped Cu<sup>2+</sup> ions indicate the presence of O–H, C–H, C=C and C–O groups.

**Keywords.** Polyvinyl alcohol; differential scanning calorimetry; thermogravimetric analysis; Fourier transform infrared spectroscopy (FTIR).

### 1. Introduction

Photoconductivity and non-linear optical properties of organic materials have attracted the scientific community due to their multidimensional applications in holography, optics and mechanically flexible systems (Ducharme *et al* 1991; Moerner and Silence 1994; Mithilesh Kumar *et al* 2002). Polymers have potential applications as permanent and transient data storage materials or as a basic material for the fabrication of active and passive light guides. Ion doped organic polymers are highly efficient in holographic recording (Filoti *et al* 1995). Availability of polymers in solid and liquid states and the methods of building polymeric structures from simple molecules are often required for studies in physical, chemical and biological sciences (Tomita *et al* 1994; De Queiroz *et al* 1995; Chanda and Dekker 2000). Polyvinyl alcohol (PVA) is recognized as one of the very few vinyl polymers soluble in water. PVA is environmental-sensitive and used in textile wrap sizing, adhesive, paper sizing agent, ceramic binder and also used in cosmetics, pharmacy and electronic industry. Cr(VI) and Fe(III) doped PVA films are excellent in real time holographic recording materials (Changkakoti *et al* 1993; Kuroda *et al* 1995). The ion exchange is based on the distribution of soluble ions between an aqueous solution and a reactive polymer containing selective ligands (Kolarz *et al* 2002). EPR spectroscopy appeared to be an especially valuable method to investigate the functionalized polymer properties by introducing Cu(II) ions into polymer matrix as a spin probe (Boudakgi *et al* 1992; Kolarz *et al* 1994). The Cu(II) ion introduces more packing efficiency

to the host, which in turn influences the thermal properties of the polymer. The aim of the present work was to study the thermal properties and infrared studies of PVA doped Cu<sup>2+</sup> by using differential scanning calorimetry, thermogravimetric analysis and Fourier transform infrared techniques.

### 2. Preparation and characterization of samples

Freshly prepared 5 mol% PVA and CuSO<sub>4</sub>·5H<sub>2</sub>O solutions (AR) were taken in proportion ( $x = 1, 2, 3, 4$  and 5 mol% of copper content) for the preparation of 5 mol% PVA :  $x$  mol% Cu<sup>2+</sup> polymer films. These solutions were stirred well for about 10–20 min and uniformly spread over a glass plate. After drying for 48 h, the films were removed from the glass plate. DSC studies were carried out (TA Instruments, USA) in the range 30–350°C and the thermograms were recorded for all the films at a heating rate of 5°C/min. Variation of melting point and glass transition temperature with change of copper content was studied. TGA analysis (TA Instruments, USA) of the films was carried out between 30 and 500°C and thermograms were recorded in the presence of nitrogen atmosphere at a rate of heating, 5°C/min. Variation in thermal degradation of films with copper content was studied. For stretching and bending modes analysis, Fourier transform infrared (FTIR) spectrum was recorded from 500–4000 cm<sup>-1</sup> by using a JASCO spectrometer.

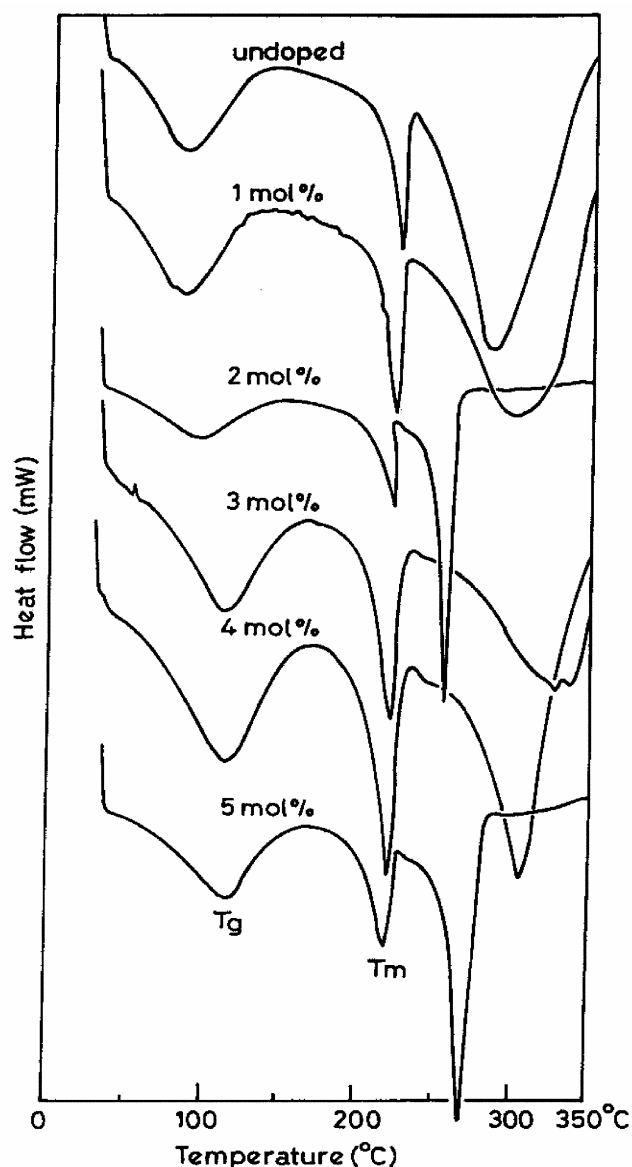
### 3. Results and discussion

The DSC thermograms of PVA :  $x$  mol% Cu<sup>2+</sup> (for  $x = 1$ –5 mol%) polymer films in the temperature range 30–350°C

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are shown in figure 1. Three major thermal transitions corresponding to glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ) and vapourization temperature were observed in the thermograms for different copper concentrations ( $x$ ). In the present study, we have not focused our attention on vapourization. In fact, almost all the polymers will thermally degrade before they vapourize. 5 mol% PVA reveals relatively a large and sharp melting endothermic peak at 226°C and a broad peak at 85°C corresponds to melting temperature and glass transition temperature, respectively. The temperature corresponding to the two transitions for pure PVA is in good agreement with the reported values (Kim *et al* 2002; Prakash *et al* 2003). For different concentrations of copper ions, the endothermic peaks of thermograms of PVA segments related to the

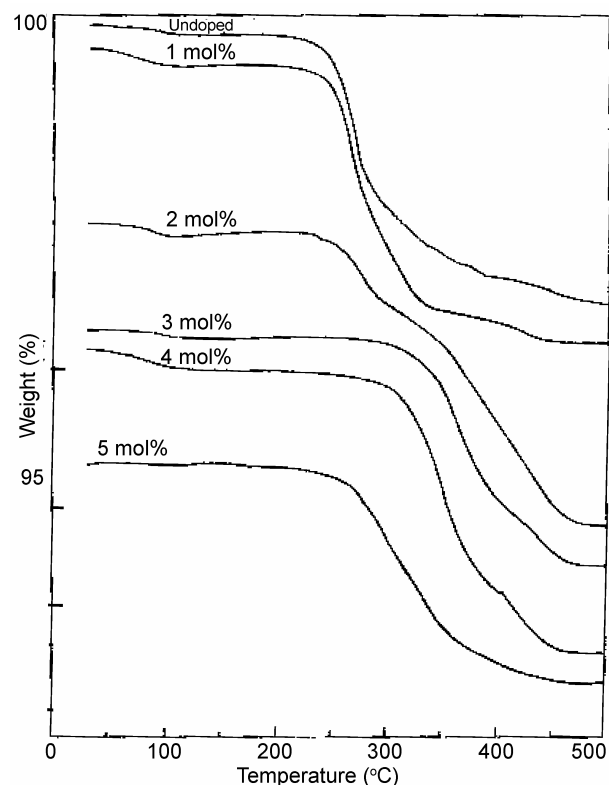
melting point became sharper and the corresponding melting temperatures are in the range 218–226°C. Therefore, the influence of  $\text{Cu}^{2+}$  ions is negligible on the melting temperature of PVA: ( $x$  mol%  $\text{Cu}^{2+}$ ) complexes. As the copper concentration ( $x$ ) is increased from 0–5%, the  $T_g$  value shifted from 85–118°C. With increase in copper concentration, the  $\text{Cu}^{2+}$  groups were substantially branched out with the chain of PVA molecules and packing efficiency increased and also the steric effect of –OH groups is restricted by the branching effect of copper content, as a result the lateral forces in the bulk state is more which leads to a shift in  $T_g$  value towards high temperature region. Table 1 shows the values of glass transition temperature and the value of melting temperature with respect to copper



**Figure 1.** DSC thermograms of pure PVA and 5 mol% PVA doped with different (1–5 mol%)  $\text{Cu}^{2+}$  concentrations.

**Table 1.** The melting temperatures ( $T_m$ ) and glass transition temperatures ( $T_g$ ) of pure PVA and PVA doped with different copper concentrations.

Concentration ( $x$ )	$T_m$ (°C)	$T_g$ (°C)
Undoped PVA	226	85
1 mol% $\text{Cu}^{2+}$ : PVA	224	86
2 mol% $\text{Cu}^{2+}$ : PVA	223	96
3 mol% $\text{Cu}^{2+}$ : PVA	222	113
4 mol% $\text{Cu}^{2+}$ : PVA	220	115
5 mol% $\text{Cu}^{2+}$ : PVA	218	118



**Figure 2.** TGA thermograms of pure PVA and 5 mol% PVA doped with different (1–5 mol%)  $\text{Cu}^{2+}$  concentrations.

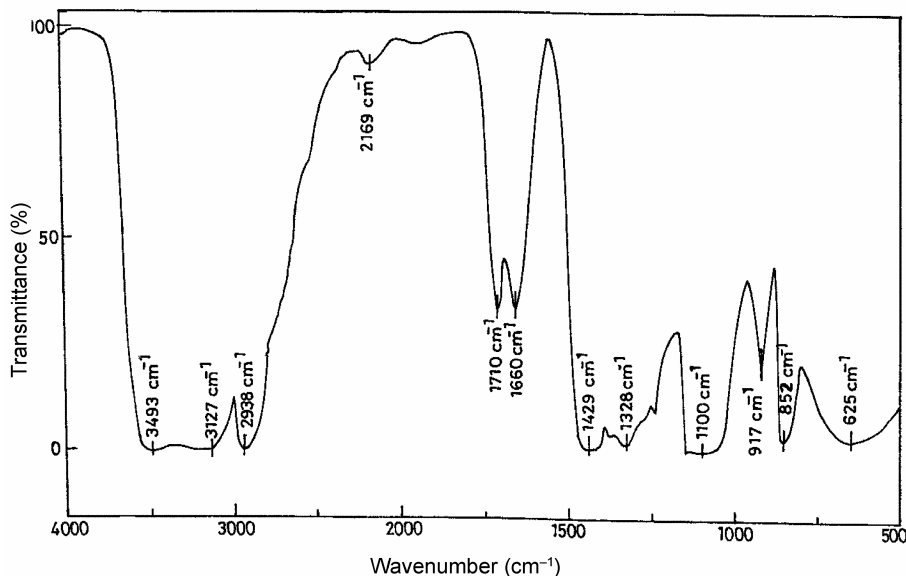


Figure 3. FTIR spectrum of  $\text{Cu}^{2+}$  ions doped PVA film.

Table 2. Assignment of peak positions and their corresponding frequencies in IR spectra of  $\text{Cu}^{2+}$  doped PVA.

Vibration frequency ( $\text{cm}^{-1}$ )	Band assignment (Nakamoto 1986)
625	OH (st)
852	$\text{CH}_2$ (st)
917	CC (st)
1100	CO (st)
1328	CH + OH
1429	$\text{CH}_2$ (b)
1660	C=C (st)
1710	–
2169	CH + CC
2938	$\text{CH}_2$ (st)
3127	OH (st)
3493	–

st. stretching; b. bending

( $x$  mol%) concentration. Figure 2 shows the thermal stability and thermal degradability of 5 mol% PVA and PVA: $x$  mol%  $\text{Cu}^{2+}$  complexes for different concentrations ( $x = 0$ –5 mol%) were investigated using TGA. 5% Weight loss in the samples is observed because of loss of water molecules at below  $100^\circ\text{C}$ . There is a considerable weight loss in the samples between  $100^\circ$  and  $250^\circ\text{C}$ , due to degradation of the large chain of molecules into small fragments. In all the thermograms, the major weight losses are observed in the range  $200$ – $400^\circ\text{C}$ . Hemantha Kumar *et al* (2004) reported FTIR spectrum and the corresponding transitions for pure PVA and  $\text{Mn}^{2+}$  doped PVA films. In the present study, we have concentrated on different

vibrational modes of PVA doped  $\text{Cu}^{2+}$  ions for 5 mol% and the spectrum is shown in figure 3. The IR spectrum exhibits several bands characteristic of stretching and bending vibrations of O–H, C–H, C=C and C–O groups. Three broad and strong bands are observed at 3493, 3127 and  $625\text{ cm}^{-1}$  corresponding to the O–H stretching frequency, which indicate the presence of hydroxyl groups (Sweeting 1968; Ege 1989). The band observed at  $2938\text{ cm}^{-1}$  indicates an asymmetry in stretching mode of  $\text{CH}_2$  group. A weak band is observed at  $2169\text{ cm}^{-1}$  and has been assigned to the combination frequency of (CH + CC). The twin bands observed at 1710 and  $1660\text{ cm}^{-1}$  have been assigned to C=C stretching mode. Two strong bands observed at 1429 and  $852\text{ cm}^{-1}$  have been attributed to bending and stretching modes of  $\text{CH}_2$  group, respectively. A weak band at  $1328\text{ cm}^{-1}$  has been assigned to the combination frequency of (CH + OH) group. The strong band at  $1100\text{ cm}^{-1}$  and sharp band at  $917\text{ cm}^{-1}$  have been attributed to the stretching mode of CO and CC groups, respectively. The IR band positions and their assignments are presented in table 2.

#### 4. Conclusions

A shift in glass transition temperature with increase in copper content was due to increase of branching and steric effects in the PVA molecules. The influence of  $\text{Cu}^{2+}$  ions on the melting point of the samples is negligible. From TGA analysis, 4–5% thermal degradation of the films was found at below  $100^\circ\text{C}$ . Absorption bands in the FTIR spectrum were assigned to stretching and bending vibration modes of O–H, C–H, C=C and C–O groups.

**References**

- Boudakgi A, Kplarz B N and Jezierska J 1992 *Macromol. Chem.* **59** 343
- Chanda M and Dekker M 2000 *Advanced polymer chemistry* (NY: New York Publishers)
- Changkakoti R, Manivannan G, Singh A and Lessard R A 1993 *Opt. Engg.* **32** 2240
- DeQueiroz A A A, Gallardo A, SanRoman J and Higa O Z 1995 *J. Polym. Sci.* **7** 523
- Ducharme S, Scoll J C, Twieg R J and Moerner W E 1991 *Phys. Rev. Lett.* **66** 1846
- Ege S N 1989 *Organic chemistry* (Michigan: The University of Michigan) p. 361
- Filoti G, Kuncser V, Franke H, Kardinahl T and Manivannan G 1995 *J. Radioanal. & Nucl. Chem.* **190** 315
- Hemantha Kumar G N, Lakshmana Rao J, Gopal N O, Narasimhulu K V, Chakradhar R P S and Varada Rajulu A 2004 *Polymer* **45** 5407
- Kim S J, Park S T, Kim I Y, Lee Y H and Kim S I 2002 *J. Appl. Polym. Sci.* **86** 1844
- Kolarz B N, Jezierska J, Bartkouriak D and Gontar Czyk A 1994 *React. Polym.* **23** 53
- Kolarz B N, Trochimc Zuk A W, Jermakowicz-Bartkowiak D and Jezierska J 2002 *Polymer* **43** 1061
- Kuroda S, Murata K, Noguchi T and Ohnishi T 1995 *J. Phys. Soc. Jpn.* **64** 1363
- Mithlesh Kumar K, Babu Y, Dhobala A R, Kadam R M and Sastry M D 2002 *Pramana-J. Phys.* **58** 101
- Moerner W E and Silence S M 1994 *Chem. Rev.* **94** 127
- Nakamoto K 1986 *Infrared and Raman spectra of inorganic and coordination compounds* (New York: Wiley Publishers) 10th ed.
- Prakash R, Somani R, Viswanath A K and Radhakrishnan S 2003 *Polym. Degrad. & Stability* **79** 77
- Sweeting O J 1968 *The science and technology of polymer films* (New York: Interscience Publishers)
- Tomita N, Tamai S, Okajima E, Hirao Y, Ikauchi K and Ikada Y 1994 *J. Appl. Biomater.* **5** 175