

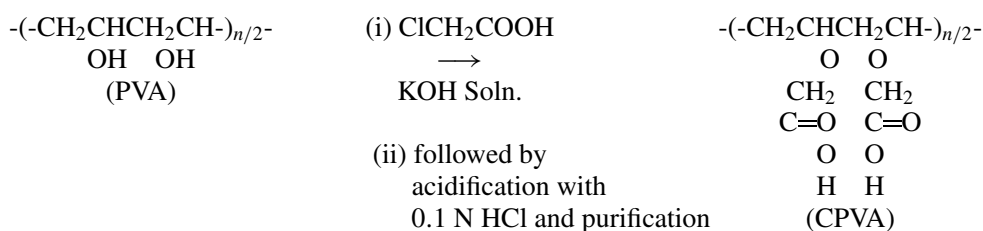
Modification of poly(vinyl alcohol) for improvement of mechanical strength and moisture resistance

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Although there is ample scope for modification of poly(vinyl alcohol) (PVA) [1] through carboxymethylation to derive a diverse range of properties, very little information is available in literature. In this backdrop PVA has been chemically modified to carboxymethylated-PVA (CPVA) to develop membranes and their properties studied because there is as yet practically no exploration in this direction.

Modification of PVA to CPVA is achieved by condensation reaction of PVA with monochloroacetic acid in the presence of KOH at 65 °C as per the following scheme. CPVA was isolated and purified by the usual method of reprecipitation and washing.



Membranes of PVA and CPVA were prepared by pouring respective aqueous solutions (7.5 wt%) on a mould and allowing water to evaporate slowly at 30 °C for 20 days. The same conditions were applied during preparation of each of the samples.

Measurement details: (i) Tensile Strength (ASTM D 412) (ii) DSC analysis (Du Pont, 910 module, $N_2 = 40 \times 10^{-6} \text{ m}^3/\text{min}$, 10 °C/min) (iii) WAXD (Rich Seifert, Cu K_α , graphite monochromator, 30 kV, 20 mA).

The evaluation of Acid Number of CPVA showed 97.1% conversion to CPVA. The tensile strength of PVA and CPVA films were found to be 58.8 and 174.3 MPa respectively, thus showing substantial increase in tensile strength after modification. Recently it is reported that the thickness of PVA layers causes a problem due to low flux during filtration [2, 3] because filtration is inverse function of thickness. In this perspective CPVA membrane is a better choice as it can provide lower specific thickness (i.e., thickness to mechanical strength ratio) to ensure faster filtration.

The DSC profile of PVA showed two endothermic phenomena—one at $T_{t1} = 126^\circ\text{C}$ and other at $T_{t2} =$

202 °C (Fig. 1), where suffices 't1' and 't2' represent 1st and 2nd trough temperatures respectively. It also indicates that PVA initially undergoes exothermic transformation before undergoing a major endothermic transformation ($\Delta H_{en} = 244 \text{ J/g}$) at a trough temperature $T_{t1} = 126^\circ\text{C}$. Many hydroxy compounds are reported to produce similar exotherms [4–6]. During DSC scanning, it seemed the system involving PVA in conjunction with water within its vicinity got activated to overcome the activation energy barrier required for the entrapped water molecules to get adsorbed through H-bonding with the liberation of heat [4–8] ($\Delta H_{ex} = 233 \text{ J/g}$). Moreover, a quite distinct and appreciably

sharp endothermic transition at $T_{t1} = 126^\circ\text{C}$ (Fig. 1) clearly shows the existence of some kind of ordered texture. Because of such bound water texture [7, 8], PVA sample showed some *phantom melting* at relatively lower temperature at $T_{t1} = 126^\circ\text{C}$ where such adsorbed water molecules got detached from their gel-sol kind of texture [8]. Such transition at $T_{t1} = 126^\circ\text{C}$ involving PVA and water is neither a glass nor a pure melting transition [7, 8] as it is very much a function of *in-situ* composition of the gel texture. And for this special manifestation, the term *phantom melting* is coined. In fact only very recently, it is reported that for certain polymer-water systems, there exists different types of ordered water molecules [7]. But in contrast to PVA, such sol-gel kind of textures was virtually not visible in CPVA.

Actually, the chemical structure of PVA rather favors the formation of intramolecular [1] hydrogen bonding (HB) because of favorable disposition of relatively small OH groups attached to alternate carbon atoms of PVA. It is reported that C–C bond length [9] is ca. 0.15 nm. Logically, within this 0.15 nm longitudinal space, a large and long group like carboxymethyl (CM)

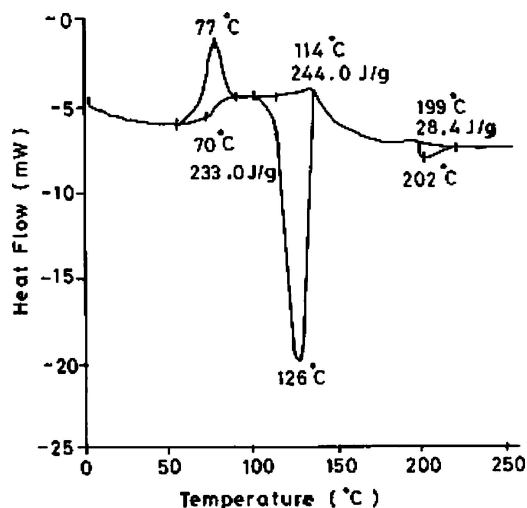


Figure 1 DSC profile of PVA membrane sample.

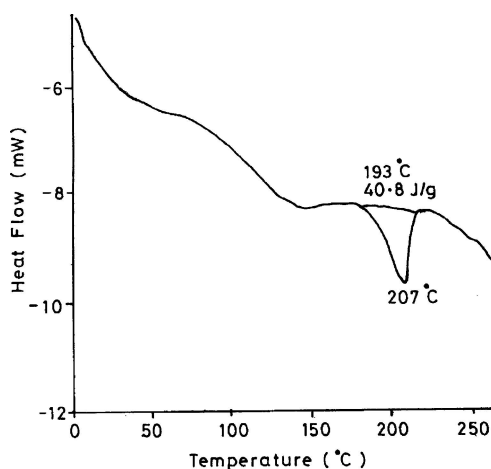


Figure 2 DSC profile of CPVA membrane sample.

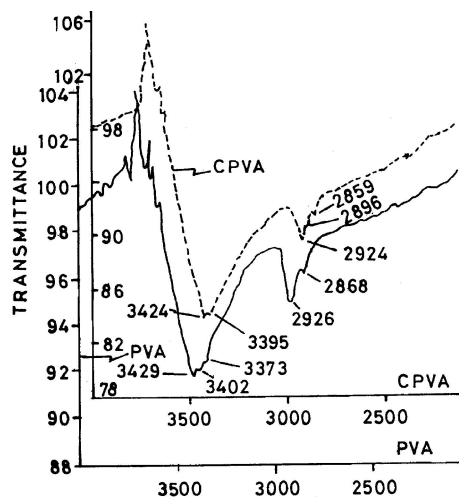


Figure 3 FTIR spectroscopic profile of PVA and CPVA.

(-CH₂COOH) group cannot exist but must turn along the latitudinal direction of the chain. Moreover, the ether group (-O-) is known to allow easy rotational movement [10]. So the CM-moiety attached to ether group (-CH-O-CH₂COOH) is facile to take latitudinal rather than longitudinal disposition in forming intermolecular-HB. In fact, the bulky CM group is endowed with more effective polarity towards form-

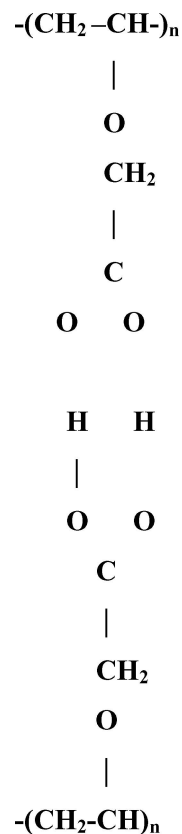


Figure 4 Structure of CPVA.

ing intermolecular-HB like many organic acids and acid-polymers [11, 12]. Contribution of cohesive energy density parameter (δ) for -OH and -OCH₂COOH group was estimated [13] and found to be 0.05 J^{1/2}m^{3/2} and 0.03 J^{1/2}m^{3/2}, respectively. Generally, mechanical strength is proportional to cohesive energy density [14]. Therefore, theoretically, PVA should show higher mechanical strength than CPVA. But paradoxically, experimental mechanical strength of CPVA is found to be higher. This can only be possible if there exists intermolecular-HB through CM groups to cause chain association in enhancing mechanical strength and melting point (207 °C vis-à-vis 202 °C) besides improving moisture resistance characteristics (Fig. 2). In fact, higher value of δ for OH in PVA led to forming intramolecular-HB preferably over intermolecular-HB.

CPVA absorbed as doublet at 3424 cm⁻¹, 3395 cm⁻¹ (FTIR) due to intra and inter molecular hydrogen bonded OH stretchings, respectively (Fig. 3). Whereas PVA absorbed in the form of a triplet at 3429, 3402 and 3373 cm⁻¹ due to different OH stretching (Fig. 3) associated with intra and intermolecular-HB besides association of bound water (as observed in DSC analysis). Clearly, OH stretching for CPVA was observed at lower IR frequency compared to that of PVA because of the formation of a more stabilized structure [11] through intermolecular-HB (Fig. 4) in CPVA.

When PVA and CPVA membranes were immersed in water at 30 °C for 30 min, it was observed that the PVA membrane got affected more easily and the surface became sticky whereas the CPVA membrane remained unaffected. The gain in water sorption in the

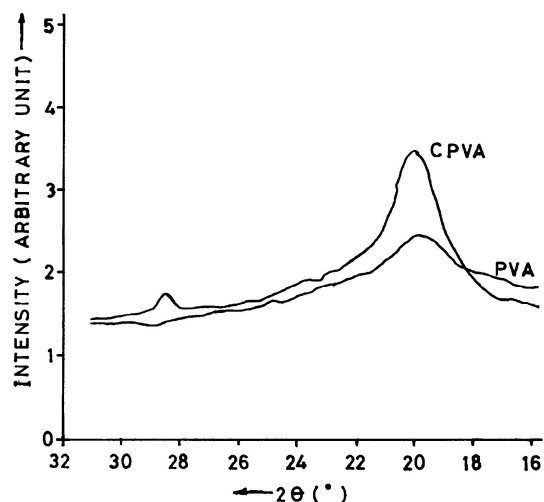


Figure 5 WAXD pattern of PVA and CPVA.

PVA membrane was found to be much higher than that of CPVA thus indicating PVA's greater affinity towards water molecules. Because of the formation of more ordered texture in CPVA, its affinity for water is much reduced. This observation conforms with the fact that the relative molar water content per $-OH$ group is considerably higher than that of $-COOH$ group (e.g., the relative molar water content per $-OH$ and $-COOH$ group is 1.3 cf. 2.0, respectively) [15].

Recently it is reported that nanofiltration (NF) composites membrane based on the combination of PVA and microporous polysulfone (PSF) often suffer from defects due to different degrees of hydrophilicity between PVA and the support polymer like PSF [2]. In fact, it was not easy for hydrophilic PVA to homogeneously cover the surface of hydrophobic PSF substrate. Clearly, CPVA membrane showed less affinity for hydration than PVA. Therefore, advantageously, CPVA will be a more suitable coating material for fabrication of nanofiltration (NF) composite membrane [2].

From the WAXD pattern, the Bragg angle for PVA is found to be 9.8° but those for CPVA are found to be at 9.95° and 14.15° . Therefore a shift of 0.15° in the Bragg angle in respect of first diffraction for PVA vis-a-vis CPVA was observed. Interplaner distance (d_{100}) in PVA was found to be 0.4524 nm. But in case of CPVA there were two different planes—one with an interplaner distance (d_1) of 0.4456 nm and other with an interplaner distance (d_2) of 0.3142 nm. Thus, the ratio

of d_2 to d_1 is $1/\sqrt{2}$ showing the crystal is simple cubic in nature [16]. WAXD profile for CPVA indicates higher molecular order existing in CPVA samples compared to PVA for which the tensile strength of CPVA was found to be higher (Fig. 5). But for the same reason, CPVA showed lower moisture sorption characteristics and higher melting point.

Changes in entropies of melting at $T_{12}(\Delta S_{mi})$ for PVA and CPVA were calculated from DSC data [1, 9] and were found to be respectively $\Delta S_{mPVA} = 5.4 \text{ J-deg}^{-1}\text{mole}^{-1}$ and $\Delta S_{mCPVA} = 17.8 \text{ J-deg}^{-1}\text{mole}^{-1}$. Clearly, $\Delta S_{mCPVA} > \Delta S_{mPVA}$ which suggests that CPVA has a more ordered texture compared to that existing in PVA.

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