

## CALORIMETRIC CHARACTERIZATION OF MEMBRANE MATERIALS BASED ON POLYVINYL ALCOHOL

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There is ample scope for modification of polyvinyl alcohol (PVA) to derive diverse range of properties because of the presence of hydroxyl group in its chain. In the present work, PVA has been modified to carboxymethylated polyvinyl alcohol (CPVA) – a carboxy-functionalized membrane material. Generally the cohesive energy density has incremental influence on the melting point and mechanical strength of a material but in this case of CPVA even though theoretical cohesive energy density of CPVA is lower than that of PVA but paradoxically its mechanical strength was found to be higher than that of PVA (~202 vis-à-vis 207°C and ~174 vis-à-vis ~58 MPa, respectively). Calorimetric evaluation along with the energy balance concept have provided meaningful information to justify such paradoxical feature as a result of the dominating role of intermolecular hydrogen bonding in CPVA to compensate for its relatively lower cohesive energy density typically  $0.05 \text{ J m}^{-3/2}$ .

Thermal analysis has been made to examine the role of PVA and its carboxymethylated derivative (CPVA) towards moisture. It was observed that PVA membrane surface became sticky on exposure to water at 30°C for a period of 30 min, whereas under the same condition CPVA counterpart remained practically unaffected.

**Keywords:** cohesive energy density, hydrogen bonding, thermal analysis

### Introduction

Nanofiltration membrane is considered as an effective tool for water softening operation besides its application for filtration of dairy products. Recently, there have been few reports on the preparation of nanofiltration composite membranes through the application of coating technology using a combination of polyvinyl alcohol (PVA) and sodium alginate (SAZ) on microporous polysulfone (PSF) support system. But during application of such coating of PVA formulation, particularly when the coating is thin over the PSF supporting substrate, there often appear defects as a result of the differential hydrophilicity between PVA and PSF or similar substrates. Hence, it is not easy for the hydrophilic PVA layer to cover homogeneously across the surface of the hydrophobic substrates like PSF [1, 3–6].

Characteristically, PVA has a tendency to form film, thus providing scope for development of good membrane of appropriate texture, for which PVA based membranes are used for filtration purpose but their flux and rejection rate are rarely satisfactory. Many times such PVA based membranes often show low flux and low rejection [1, 3–5] efficiency. These drawbacks are believed to be due to the necessity of maintaining relatively higher thickness of PVA or their composite membrane to sustain against load during filtration operation. Therefore, in most such cases, it demands improvement of mechanical properties of PVA based products. In this investigation, PVA has been chemically modified by

carboxymethylation of PVA using monochloroacetic acid (MCAA) to improve the mechanical properties of PVA-based items. The investigation is particularly important in view of the fact, there is as yet practically no effort has been made to explore and characterize carboxymethylated polyvinyl alcohol (CPVA) based polymeric membrane.

### Experimental

#### Materials and methods

##### Preparation of membrane

At a given condition, membranes were prepared by pouring the aqueous solutions of the polymer (conc. 7.5 mass%) on a mould and slowly evaporating the solvent at room temperature (30°C) for 10 days. The samples of the membranes were found to be thermoplastic and were soluble in water.

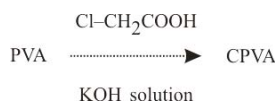
##### Chemical reaction

Conversion of PVA to CPVA was done by condensation reaction of PVA with MCAA in presence of aqueous KOH solution at 65°C. After the desired reaction was over, the product was isolated by neutralizing with hydrochloric acid solution. The product, CPVA was purified by usual reprecipitation method using methanol as nonsolvent and the

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process is repeated till the stock became free of chloride ions.

Following is the scheme of reaction for modification of PVA.



**Fig. 1** Schematic presentation of chemical reaction of PVA and MCAA

#### Acid number

It is taken as the mg of KOH required to neutralize 1 g of polymer sample where the volume of aqueous 0.01 N KOH titrant was noted in the experiment when the solution just turned to pink color in presence of phenolphthalein indicator and calculated from the standard expression. The acid number is the measure of amount of carboxyl acid group present in the polymer.

#### Tensile strength measurement

A tensile strength machine was used to test the membrane samples as per ASTM D 412 specification. The measurement was carried out with a constant velocity of load on the sample proceeded, and the maximum load was recorded.

#### Spectroscopy

FTIR (Nicolet) with a resolution of  $1 \text{ cm}^{-1}$  was scanned from  $400\text{--}4000 \text{ cm}^{-1}$  at room temperature to study the polymer samples.

#### Thermal analysis

A DuPont DSC instrument with 910 module was used for thermal analysis. An oxygen-free nitrogen stream of  $40 \text{ mL min}^{-1}$  was maintained through the cell during the measurement. The scan was performed at a rate of  $10^\circ\text{C min}^{-1}$ .

## Results and discussion

In the present work, attention has been paid to ensure same conditions during the preparation of the samples of PVA and CPVA to effect a neat comparative picture in the analysis.

The evaluation of acid number of CPVA showed 97.1% conversion of PVA 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 carboxymethylation. Recently it is reported that the thickness of PVA layers causes a problem due to low flux dur-

ing filtration because filtration is inverse function of thickness [7]. 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.

FTIR has been used to understand the features of hydrogen bonding in PVA as well as CPVA. FTIR spectra for OH stretching corresponding to CPVA and PVA occur at  $3391$  and  $3405 \text{ cm}^{-1}$  (Figs 2 and 3), respectively. It is clearly evident from the figures that the absorption of OH stretching for CPVA occurred at a lower vibrational frequency in comparison to that of PVA, thus revealing a more stable structure for CPVA as a result of the formation of associative structure (Fig. 4) through intermolecular hydrogen bonding [8, 9]. Interestingly, there are few kinks in the region of OH absorption for PVA sample but more importantly, such kinks are not evident in CPVA counterpart. Such kinks for PVA samples are indicative of the presence of different types of hydrogen bonding due to the presence of sorbed water entity [10] (which has also been implicitly understood from the DSC analysis as discussed later). The presence of methylene group ( $-\text{CH}_2-$ ) in PVA can be seen from the absorption at  $2926$  and  $2868 \text{ cm}^{-1}$ , whereas corresponding absorption for CPVA is manifested at  $2940$ ,  $2897$  and  $2854 \text{ cm}^{-1}$ . It is also of interest to note that because of the presence of additional methylene group ( $-\text{CH}_2-$  of  $-\text{O}-\text{CH}_2-\text{COOH}$ ) in CPVA, there was an extra peak at  $2897 \text{ cm}^{-1}$  in this region (Fig. 2).

Actually, the chemical structure of PVA rather favours the formation of intramolecular [1, 2] hydrogen bonding (hereafter <sup>intra</sup>HB) preferably because of favourable disposition of relatively small OH groups attached to alternate carbon atoms of PVA [1, 2]. It is reported that C–C bond length [10] is ca. 0.15 nm. Logically, within this 0.15 nm longitudinal space, a large and long group like carboxymethylated (CM) group ( $-\text{CH}_2\text{COOH}$ ) cannot exist but takes turn preferably along the latitudinal direction of the chain. Moreover, the ether group ( $-\text{O}-$ ) is known to allow easy rotation movement [11, 12]. So the CM-moiety attached to ether group ( $-\text{CH}-\text{O}-\text{CH}_2\text{COOH}$ ) is facile to take latitudinal rather than longitudinal disposition in forming intermolecular-HB (hereafter <sup>inter</sup>HB).

As a matter of fact, the bulky CM group is endowed with more effective polarity towards forming intermolecular-HB like many organic acids and acid-polymers [8, 9, 13–15]. Contribution of function of cohesive energy density parameter ( $\delta$ ) for  $-\text{OH}$  and  $-\text{OCH}_2\text{COOH}$  group was estimated [16] and found to be 0.05 and  $0.03 \text{ J}^{1/2} \text{ m}^{3/2}$ , respectively. Generally, mechanical strength is proportional to cohesive energy density [17–19] and according to Lindemann's criterion, the melting temperature of a material is propor-

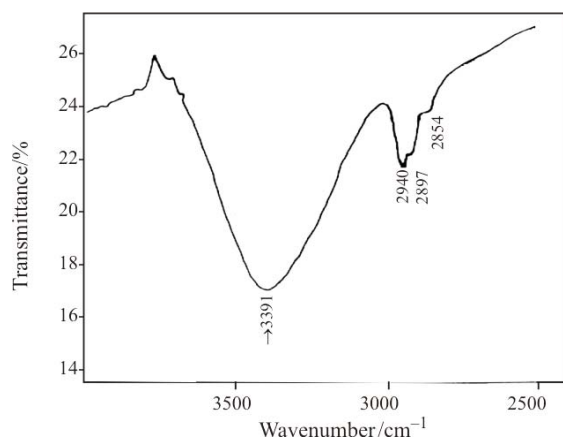


Fig. 2 FTIR spectral data of CPVA sample

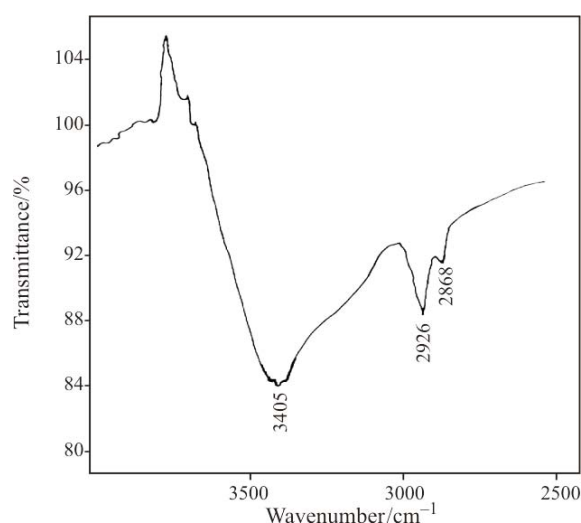


Fig. 3 FTIR spectral data of PVA sample

tional to its cohesive energy,  $a_v$  ( $T_m = Ca_v$ ) [18]. Therefore, theoretically, PVA should show higher mechanical strength than CPVA. But paradoxically, experimental mechanical strength of CPVA is found to be higher than that of PVA as a result of predominance in the chain association through intermolecular HB to effect enhancement in the mechanical strength as well as melting point (207 vis-à-vis 202°C as obtained from DSC diagram, Figs 5 and 6) besides improving moisture resistance characteristics. In fact, higher value of  $\delta$  for OH in PVA led to forming intramolecular-HB preferably over intermolecular-HB.

In the thermal evaluation through DSC analysis, PVA exhibited two endothermic events – first at  $T_{t_1} = 126^\circ\text{C}$  and second at  $T_{t_2} = 202^\circ\text{C}$  (Fig. 5), where suffices  $t_1$  and  $t_2$  represent 1<sup>st</sup> and 2<sup>nd</sup> trough temperatures respectively.

It should be noted that the final melting phenomenon in PVA, occurring at  $T_{t_2} = 202^\circ\text{C}$ , where the dismantling of some molecular packing is quite different from the features corresponding to the texture responsible for the endothermic transition at  $T_{t_1} = 126^\circ\text{C}$  for

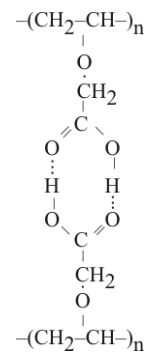


Fig. 4 Schematic presentation of intermolecular hydrogen bonding in CPVA

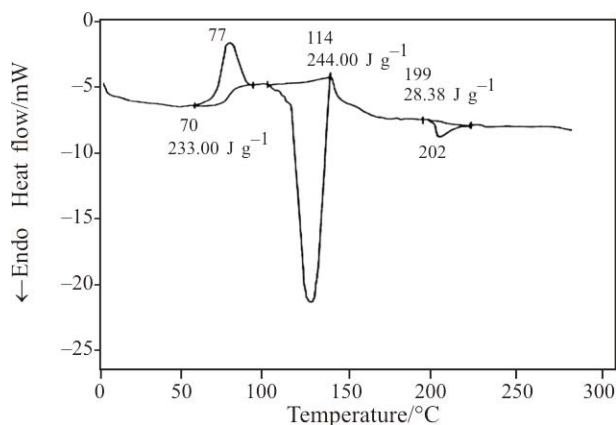


Fig. 5 DSC curve of PVA sample

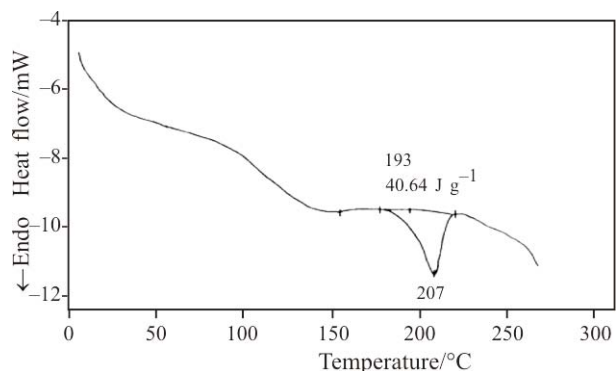


Fig. 6 DSC curve of CPVA sample

PVA. The change in entropy at  $T_{t_1}$  and  $T_{t_2}$  for PVA is calculated as 13.18 and 1.289 cal  $^\circ\text{C}^{-1}$  mol $^{-1}$ , respectively. Clearly, the change of entropy for the endothermic transition at  $T_{t_1} = 126^\circ\text{C}$  is much higher than that occurring at  $T_{t_2} = 202^\circ\text{C}$ . Because of the relatively easy detachment of small molecules of bound water from the PVA texture, there is, as a whole (overall), more disorder due to easy mobility of the molecules after completion of transition at  $T_{t_1}$ , leading to a higher change in the value of entropy.

The DSC feature in figure indicates that PVA initially undergoes exothermic transformation, starting at  $70^\circ\text{C}$  with a  $\Delta H_+$  of 233 J  $\text{g}^{-1}$  before undergoing

a major endothermic transformation at a trough temperature  $T_{t_1}=126^\circ\text{C}$ . It is reported that many hydroxyl compounds can produce exotherm when they are mixed [20–22]. Mukherjee *et al.* [21] have also observed similar exotherm when hydroxyl containing thermoplastic epoxy resin is mixed with excess of polyethylene glycols. Zhang *et al.* also have observed an interesting exotherm in DSC scanning at low temperature to detect water of crystallization in polyvinyl methyl ether [22]. There are quite a few reports on the heat of solution of PVA in water as well. Studies on the interaction among the distinct water–polymer complex also reveal the mechanism of anomalous crystallization of water during heating [22–24]. Studies on the interaction among the distinct water–polymer complex reveal the mechanism of anomalous crystallization of water during heating [22]. When PVA sample was heated during DSC scanning, it is presumed that the system involving PVA in conjunction with water within its vicinity got activated to overcome the activation energy barrier required for the entrapped absorbed water molecules to get adsorbed through hydrogen bonding with the liberation of heat. It is reported that properties of PVA depends on the involuted state of the polymer chain, which is a function of temperature [26]. In fact, when PVA was heated, it first underwent rearrangement followed by establishment of some kind of linkages through hydrogen bonding with water molecules [23–25, 27]. Intuitively, this rearrangement also took place through intercalation of water molecules with the PVA. It may be noted that the entrapped water in the PVA matrix is nothing but a gel [28] kind of material. It may be observed from Fig. 5 that the scanning follows a quite distinct and appreciably sharp endothermic transition at  $T_{t_1}=126^\circ\text{C}$ ; and such typical reasonably sharp endothermic profile is indicative of the existence of some kind of loose but reasonably ordered gel texture. Because of such loosely bound ordered water texture such PVA sample shows some phantom melting at relatively lower temperature at  $T_{t_1}=126^\circ\text{C}$ , where detachment of such loosely bound water occurred from the gel textures [29]. Understandably, such transition at  $T_{t_1}=126^\circ\text{C}$ , involving PVA and water is neither a pure glass transition nor a pure melting transition of PVA but some kind of gel–sol transition [29]. In fact, gel structure depends on the involuted state of PVA [19, 28–30] chain in conjunction with water and accordingly such transition temperature varies. And for this special characteristic, the author coined the term phantom melting. In fact, only recently, it is reported that for certain systems physical states or different states of water in a polymer system are responsible for different types of ordered water molecules [2, 31]. Interestingly, in contrast to PVA, there is

hardly any formation of such textures in CPVA with water (Figs 2 and 6) of the kind as observed in PVA from the transition at  $T_{t_1}=126^\circ\text{C}$  (Figs 3 and 5).

Careful observation on the data of exotherm ( $\Delta H_+$ ) and endotherm ( $\Delta H_-$ ) of the DSC profile implies that the differential heat of  $11\text{ J g}^{-1}$  (i.e.,  $244\text{--}233\text{ J g}^{-1}=11\text{ J g}^{-1}$ ) is possibly responsible for the texture corresponding mainly to the transformation of intramolecular hydrogen bonding. This fact is understood implicitly from the fact that if this  $11.0\text{ J g}^{-1}$  is added with the second melting endotherm  $\Delta H_{-1}=28.38\text{ J g}^{-1}$  associated with PVA, the total becomes  $39.38\text{ J g}^{-1}$  which is close to the endotherm associated with the melting of CPVA at the trough melting temperature  $T_{t_2}=207^\circ\text{C}$ . Thus, from energy balance viewpoint, it implies that the endothermic profile starting at  $114^\circ\text{C}$  comprises two components of heat-absorption processes such as one may be contributing towards the dismantling and/or rearrangement of intramolecularly hydrogen-bonded partially ordered texture in the original PVA sample and the other contributing towards dismantling of the ordered texture having been originated in conjunction with the water molecules as revealed during DSC scanning.

The endothermic profile at  $T_{t_2}=202^\circ\text{C}$  for PVA is the final melting point of PVA, whereas  $T_{t_2}=207.34^\circ\text{C}$  is the final melting point of CPVA. Logically, structure involving intermolecular hydrogen bonding enhances the melting point more than the corresponding intramolecularly hydrogen bonded structure. Therefore, the melting point of CPVA was found to be higher than that of PVA.

The first order transition temperature can be characterized by the ratio of heat of final melting to the melting entropy of the repeating unit [2, 31]. From this relation, the changes in entropies of melting at  $T_{t_2}$  ( $\Delta S_{mi}$ ) for PVA and CPVA were found to be  $\Delta S_{mPVA}=1.289\text{ cal }^\circ\text{C}^{-1}\text{ mol}^{-1}$  and  $\Delta S_{mCPVA}=4.25\text{ cal }^\circ\text{C}^{-1}\text{ mol}^{-1}$  of repeating unit, respectively. Thus,  $\Delta S_{mCPVA}>\Delta S_{mPVA}$ . Evidently, the higher value of change of entropy of melting for CPVA compared to that for PVA suggests that CPVA should have more ordered texture compared to that exists in PVA.

The surface wettability of the membranes has been assessed by immersing both PVA and CPVA film samples separately in water at ambient temperature of  $30^\circ\text{C}$  for half-an-hour at room temperature under a given set of experimental condition for both the membrane samples. It was observed that the PVA membrane got affected easily and the surface became sticky, whereas CPVA membrane remained unaffected. The gain in water sorption in PVA membrane was found to be much higher than that of CPVA. The higher gain in water sorption in PVA membrane clearly indicates its greater apparent affinity towards water molecules. On the other hand, because of the

formation of more intermolecular associative texture in CPVA, its affinity for water is reduced drastically. This is in conformity with the fact that the molar water-content of polymers per –OH group is considerably higher than the –COOH group [32]. In fact, the molar water content per –OH and –COOH groups at relative humidity of 1.0 are 2.0 and 1.3, respectively [32]. It is of interest to note that once the film of CPVA is formed, it takes more time to make a solution out of CPVA unlike PVA sample.

Recently it is reported that nanofiltration (NF) composite 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 [1]. That is to say (in other words), it is not easy for the hydrophilic PVA to homogeneously cover across the surface of hydrophobic PSF supporting substrate [1, 3–6]. In this context, DSC features reveal that CPVA membrane is less inclined to sorption of water molecules compared to PVA (Figs 5 and 6). As CPVA membrane showed less affinity for hydration than PVA, therefore advantageously, CPVA expected to be a more suitable coating material for fabrication of nanofiltration (NF) composite membrane for intended application in industry.

## Conclusions

PVA can be carboxymethylated to CPVA to improve mechanical property of the membrane which in fact enhances the strength to thickness ratio intended for faster filtration. Analytical information reveals that PVA membrane undergoes thermal transition in a more complex manner than CPVA does. Thermal analysis has provided useful complementary information to implicate the prevalence of intermolecular chain association in CPVA to make it more resistant to water.

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