Studies on the properties of carboxymethylated polyvinyl alcohol

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Polyvinyl alcohol (PVA) has been chemically modified to its carboxymethylated form and the product, designated as CPVA are cast into transparent films. It was observed that the mechanical strength of CPVA film was much higher than that of PVA. The wide angle X-ray diffraction (WAXD) pattern showed a higher molecular order in CPVA compared to that in PVA. Influence of water towards CPVA was found to be quite different as revealed from the studies based on DSC, FTIR, WAXD and mechanical strength evaluation. Because of higher molecular order, water sorption of CPVA membrane was found to be lower than that of PVA. The interplaner distance for PVA was found to be higher than that of CPVA. Interestingly, DSC profile of PVA and CPVA showed different features; PVA underwent an exothermic change at a peak exothermic temperature of $T_p=76.7^\circ$ followed by two distinct endothermic changes. Interestingly, CPVA neither showed any such initial exothermic nor any initial endothermic change unlike showed by PVA but it did exhibit only one distinct endothermic change at trough melting temperature of $T_{t2}=207.3^\circ$. The value of entropy of melting for PVA and CPVA corroborates with their respective WAXD pattern.

Keywords: Polyvinyl alcohol, Carboxymethylation, Thermal analysis, Mechanical strength

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Introduction

Polyvinyl alcohol (PVA) is a polymer of major and diverse industrial importance. It has wide scope for applications in various civil and defense sectors. They may be used for making different kinds of articles such as, laundry bags, packaging items, and for various purposes including, of course, for the preparation of gels and the like. Gel is particularly important to explore many possible applications. For example, PVA-material based ferro-gel is an important item for possible use in the field of actuators. Moreover, because of the nontoxic nature of PVA, they are particularly suitable for biomedical applications like, artificial tissue.

Of late, nanofiltration membrane is considered as an effective tool for water treatments. Such nanofiltration membranes have wide applications like, water softening, instantaneous concentration, and desalting of cheese whey. Recently, Jegal et al. have reported the preparation of nanofiltration composite membranes by coating a combination of PVA and sodium alginate (SAZ) on microporous polysulphone (PSF) supports. But it may be noted that the defects commonly occurred during such coating of thin PVA formulation over the supports were usually a result of the different 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 PSF or similar supports.

Moreover, PVA is a known polymeric material having good chemical stability and hydrophilicity for which there have been many experiments using PVA for the fabrication of reverse osmosis (RO) or nanofiltration membranes but their flux and rejection are rarely satisfactory. Mostly, such PVA based membranes show low flux and low rejection. These drawbacks are believed to be due to the relatively higher membrane thickness of PVA as such or their composite membrane needed to ensure adequate mechanical strength. Therefore, in most such cases, it demands improvement of mechanical properties of various forms of PVA based materials. In this investigation, PVA has been chemically modified by carboxymethylation of PVA, using monochloroacetic acid (MCAA) to improve the mechanical properties of PVA-based plastics items. The investigation is particularly important in view of the fact that there is practically, as yet, no exploration for the characteristics of CPVA.

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Experimental Procedure
Condensation of Polyvinyl Alcohol (PVA) with Monochloro-acetic Acid (MCAA)

PVA was dissolved in the desired amount of aqueous potassium hydroxide solution of desired concentration and heated in a water bath. The calculated amount of the MCAA was then added (1:2::OH:MCAA) and the reaction mixture was stirred at 65°C for 3 h. At the end of the reaction the mixture was acidified with 0.1 N hydrochloric acid. The product was precipitated with methanol. It was then dissolved in distilled water and reprecipitated from the solution using methanol as non-solvent. The process was repeated till the polymer became free of chloride ions.

Preparation of Membranes
At a given condition, membranes were prepared by pouring the solutions (conc. 7.5 wt per cent) of the polymers on a mould and slowly evaporating water at room temperature for 10 d. The samples of the membranes were found to be soluble in water.

Determination of Tensile Strength
A tensile strength machine was used for studying the mechanical properties of the membranes. The sample was tested as per ASTM D 412 specification. The measurements were carried out with a constant velocity of load on the sample proceeded, and the maximum load reached was recorded.

Thermal Analysis
A Du Pont DSC instrument with 910 module was used for thermal analysis. An oxygen-free nitrogen stream of 40 mL/min was maintained through the cell during the measurement. The scan was performed at a rate of 10°C/min.

FTIR (Nicholet) was run at room temperature to study the samples of PVA and CPVA.

WAXD—The x-ray diffraction patterns were obtained with CuKα radiation from Rich Seifert X-ray generator fitted with graphite monochromator, using ISO Debyflex-2002 counter diffractometer. The generator voltage of 30 kV and current of 20 mA were maintained during the operation.

Results and Discussion
The chemical modification of PVA occurs in accordance with the following reaction scheme:

\[ (-\text{CH}_2\text{CH}_2\text{OH})_n \xrightarrow{\text{OH}} (-\text{CH}_2\text{C=O})_n \xrightarrow{\text{OH}} \]

Acid number (mg of KOH for neutralization of 1 g of sample) of CPVA was determined titrimetrically as 548 which showed >99 per cent conversion of PVA into CPVA. The tensile strengths of PVA and CPVA films were found to 600 and 2100 kg/cm², respectively, under comparable conditions. The results show that there is substantial increase in the tensile strength after modification of PVA. It may be mentioned here that thickness of PVA layer often becomes a problem for low flux while using for filtration. In this situation, CPVA based membranes may be more suitable in the perspective of obtaining a membrane with same mechanical strength but at a lower thickness. It may be mentioned here that in the field of filtration technology the permeation rate or flux Qi is inversely proportional to the thickness (l) of the membrane. In fact, thickness has a major role to play; and breakthrough by Loeb and Sourirajan resulted in the formation of ultrathin membranes. In fact, an ultrathin membrane should have higher mechanical strength to thickness ratio to help achieve higher filter efficiency. A thin film ensures a high flux even if the intrinsic permeability of the polymer is low. In fact the film thickness becomes an important economic consideration. For example, it is understood from the reports that a reduction in the membrane thickness from 50 µm to 3 µm leads to 150 per cent increase in carbon dioxide permeability which further causes 93 per cent reduction in capital investment.

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. In the DSC study, PVA showed two endothermic phenomena—one at T1 =126°C and other at T2 =202°C; where suffices ‘t1’ and ‘t2’ of T represent the 1st and 2nd endothermic trough temperatures, respectively.
It should be noted that the final melting phenomena in PVA, occurring at $T_{t2} = 202^\circ C$, in which the dismantling of some molecular packing is quite different from the features corresponding to the texture responsible for the endothermic transition at $T_{t1} = 126^\circ C$ for PVA. The change in entropy at $T_{t1}$ and $T_{t2}$ for PVA is calculated as 13.18 and 1.289 cal/deg/mole, respectively. Thus, from the studies of the thermal properties it is indicated that the change of entropy for the endothermic transition at $T_{t1} = 126^\circ C$ is much higher than that occurring at $T_{t2} = 202^\circ C$. Because of the relatively easy detachment of small molecules of bound water from the PVA texture, there is, as a whole, more disorder due to easy mobility of the molecules after completion of the transition at $T_{t1}$, leading to a higher change in the value of entropy.

The DSC profile, shown in Figure 1, indicates that PVA initially undergoes exothermic transformation, starting at 70$^\circ C$ with a $\Delta H_{ex}$ of 233 J/g before undergoing a major endothermic transformation at a trough temperature $T_{t1} = 126^\circ C$. Many hydroxy compounds are reported to produce exotherm when they are mixed. Mukherjee et al. have also observed similar exotherm when hydroxyl containing thermoplastic epoxy resin was mixed with excess of polyethylene glycols. Only recently, Zhang et al. have reported one pertinent very interesting observation on the water of crystallization in polyvinyl methyl ether, detected from the exotherm in DSC scanning at low temperature. There are few reports on the heat of solution of PVA in water as well. Studies on the interaction among the distinct water-polymer complex reveals the mechanism of anomalous crystallization of water during heating. When PVA sample was heated during DSC scanning, it seemed that the system 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. In fact, when PVA was heated, it first underwent rearrangement followed by establishment of some kind of linkages through hydrogen bonding with water molecules. Intuitively, this rearrangement also took place through intercalation of water molecules with the PVA. The evidence of such intercalation is implicitly understood from the WAXD pattern discussed subsequently. It may be recalled that the entrapped water including intercalated water in the PVA matrix is nothing but a gel kind of material. It may observed from Figure 1 that the scanning follows a quite distinct and appreciably sharp endothermic transition at $T_{t1} = 126^\circ C$; 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 water intercalated ordered texture such PVA sample showed some phantom melting at relatively lower temperature at $T_{t1} = 126^\circ C$, where detachment of such loosely bound water from the gel textures takes place. Such transition at $T_{t1} = 126^\circ C$, involving PVA and water is neither a glass transition nor a pure melting transition but some kind of gel-sol transition. In fact, gel structure depends on the involuted state of PVA (ref. 24) chain in conjunction with water and accordingly such transition temperature varies. And for this special characteristic, the authors coined the term phantom melting. In fact, only very 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. Interestingly, in contrast to PVA, there is hardly any formation of such textures in CPVA with water of the kind as observed in PVA from the transition at $T_{t1} = 126^\circ C$ (Figure 2).

Careful observation on the data of exotherm and endotherm ($\Delta H_{ex}$, and $\Delta H_{en}$) of the DSC profile implies that the differential heat of 11 J/g (i.e. 244 -- 233 J/g = 11.0 J/g ) is possibly responsible for the texture corresponding mainly to the transformation of
intramolecular hydrogen bonding to intermolecular hydrogen bonding. This fact is understood implicitly from the fact that, if this 11.0 J/g is added with the second melting endotherm $\Delta H_{enm}=28.38$ J/g associated with PVA, the total becomes 39.38 J/g which is close to the endotherm associated with the melting of CPVA at the trough melting temperature $T_{t2}=207^\circ C$. Thus, considering from energy balance point of view, it implies that the endothermic profile starting at 114$^\circ C$, in fact, comprises two components of heat-absorption processes, i.e., one may be contributing to the dismantling and/or rearrangement of already existing intramolecularly hydrogen-bonded partially ordered texture in the original PVA sample and the other contributing towards dismantling of the ordered texture that originated in the dynamic in situ process, occurring during DSC scanning.

The endothermic profile at $T_{t2}=202^\circ C$ for PVA is the melting point of PVA, whereas $T_{t2}=207.34^\circ C$ is the melting point of CPVA. Logically, structure involving intramolecular 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.

It is reported that the approximate C-C bond length is ca. 1.5 Å and after every alternate carbon atom one OH group is attached to PVA. The OH size of group in PVA is smaller, compared to carboxymethyl (CM) group of CPVA. OH group in PVA is small and close enough to form intramolecular H-bonding. It is logical to assume that within this 1.5 Å longitudinal space, a large and long group like carboxymethyl (-CH$_2$COOH) group in CPVA cannot exist but moves along the latitudinal direction of the chain. Moreover, because of the existence of ether group (CH—O--CH$_2$COOH), known to allow easy rotational movement of the CM-group, it leads the bulky CM-group to take latitudinal disposition rather than the longitudinal, thus preferably allowed formation of intermolecular hydrogen bonding in CPVA. In fact, carboxylic acid has flair for intermolecular association. Thus, CPVA forms intermolecular association through CM groups like many organic acids and acid-polymers. Evidence of such association through CM can be understood from a very recent report by Chen and Du on the behaviour of carboxymethylated chitin in aqueous solutions.

FTIR spectroscopy was used to understand the aspect of hydrogen bonding in PVA vis-a-vis CPVA samples. In fact, FTIR spectral data supports the phenomenon of stabilization of the associative structure through intermolecular H-bonding (Figure 3) in CPVA. FTIR spectra for CPVA and PVA show absorption due to OH stretching at 3391 cm$^{-1}$ (Figure 4) and 3405 cm$^{-1}$ (Figure 5), respectively. Evidently, absorption of OH stretching for CPVA occurred at lower IR frequency compared to that of PVA, thus revealing a more stable structure for CPVA as a result of formation of associative structure (Figure 3).
through intermolecular hydrogen bonding. Interestingly, there are few kinks in the region of OH absorption for PVA sample; whereas such kinks are not apparent 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. The presence of methylene group in PVA can be seen from the absorption at 2926 cm⁻¹ and 2868 cm⁻¹, whereas corresponding absorption for CPVA is represented at 2940 cm⁻¹, 2897 cm⁻¹ and 2854 cm⁻¹. It is interesting to note that because of additional methylene groups (i.e., -CH₂ - or –O-CH₂-COOH ) in CPVA, there was an extra absorption at 2897 cm⁻¹ in this region (Figure 4).

The accessibility of the polar groups and the degree of crystallinity of the polymer matrix are very important factors to influence the water-content in the polymer. The surface wettability of the membranes has been assessed by immersing both the PVA and CPVA films separately in water at room temperature 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 wettability towards water molecules. On the other hand, because of the formation of more ordered and 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. In fact the molar water content per –OH and –COOH groups at relative humidity of 1.0 are 1.3 and 2.0 respectively. 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 membrane.

Recently, it was reported that nanofiltration (NF) composites membrane based on the combination of PVA and microporous polysulfone (PSF) often suffer from defects due to the difference in hydrophilicity
between PVA and the support polymer like PSF. That is to say, it was not easy for the hydrophilic PVA to cover homogeneously across the surface of hydrophobic PSF support. In this context, DSC features reveal that CPVA membrane is less inclined to sorption of water molecules compared to PVA (Figure 1 vis-à-vis Figure 2). Thus, advantageously, CPVA may be a more suitable coating material during fabrication of nanofiltration (NF) composite membrane for intended application in industry.

The WAXD pattern for PVA and CPVA are shown in Figure 6. The glancing angle for PVA is found to be 9.8°. But for CPVA, such angles are found to be at 9.95° and 14.15°. There is some shift of 0.15° in the Bragg’s angle of diffraction while comparing the first diffraction for PVA vis-a-vis CPVA. The interplaner distance (d₁) in PVA was found to be 45.24 nm but in the case of CPVA there were two planes - one with an interplaner distance (d₁) of 44.56 nm and other with an interplaner distance (d₂) of 31.42 nm. Thus the ratio of the interplaner distances, d₁ to d₂ is 1/√2. Therefore the diffraction pattern of CPVA showed that the crystal is simple and cubic in nature. Evidently the interplaner distance for CPVA is smaller than that of PVA; and the difference between the two d₁ planes is 0.68 nm. Thus the gap per single d₁ plane is 0.34 nm. There are reports that the nature of adsorbent and experimental condition influences the area covered by the water molecule over the adsorbent. Also, this area varies within a definite range. For example the minimum area requirement of an adsorbed water molecule is reported to be 10.5 Å² (ref. 44) which corresponds to a water molecule of diam 0.39 nm. The apparent pore diam for sodium zeolite is 0.36-0.40 nm (i.e. molecular sieve 4A), whereas potassium zeolite with pore diam is 0.33 nm (i.e. molecular sieve 3A) and both are employed for removal of water molecules selectively because such pore diam correspond to the size of water molecules [p. 396 of refs. 37 and 49]. Thus, from the above the diam of water is variously considered in the range of ca. 0.3-0.4 nm (refs 44-48). Interestingly the evaluated gap per d₁ plane is 0.34 nm, which falls well within the range of the diam of water molecule. This suggests that the intercalation of water in PVA is monomolecular. Interestingly the DSC feature (Figure 1) revealing the existence of some kind of ordered texture through water molecules, as discussed in foregoing is also understood from the intercalation of water between the interplanes of PVA. The WAXD profile for CPVA indicates higher molecular order existing in CPVA samples compared to that in PVA. Because of the higher molecular order the mechanical strength of CPVA sample was found to be higher than that of PVA samples. Other interesting point is that because of the more ordered texture in CPVA, it did not practically sorb water molecules unlike PVA, as evident from DSC or wettability information.

The first order transition temperature can be characterized by the ratio of heat of final melting to the melting entropy of the repeating unit. From this relation, the changes in entropies of melting at T₂ (∆Sₘ₁) for PVA and CPVA were found to be ∆Sₘ₃PVA = 1.289 cal./deg/mole and ∆Sₘ₃CPVA = 4.25 cal./deg/mole of repeating unit, respectively. Thus, ∆Sₘ₃CPVA > ∆Sₘ₃PVA. 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 existing in PVA.

**Conclusion**

Chemical modification of PVA to CPVA can improve the mechanical strength substantially because of the formation of more ordered texture and molecular association through intermolecular hydrogen bonding in CPVA sample. PVA membrane is more prone towards moisture sorption compared to that of CPVA. Spectroscopic features in terms of DSC, FTIR, WAXD as well as assessment of mechanical strength and surface wettability information complement each other.

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