Effect of poly(vinyl pyrrolidone) on the morphology and physical properties of poly(vinyl alcohol)/sodium montmorillonite nanocomposite films

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Abstract Nanocomposites of poly(vinyl alcohol) (PVA), poly(vinyl pyrrolidone) (PVP) and sodium montmorillonite (Na⁺MMT) were prepared by solution mixing and then cast into films. X-ray diffraction analysis and images of transmission electron microscopy establish the formation of PVA/Na⁺MMT intercalated nanocomposite. Exfoliated and highly intercalated PVA/PVP/Na⁺MMT nanocomposite formed in the presence of PVP. Inclusion of PVP in PVA/Na⁺MMT matrix enhances the hydrogen bonding interactions between PVA and Na⁺MMT and thus increases the mechanical properties and thermal stability of PVA/PVP/Na⁺MMT nanocomposites compared to PVA/Na⁺MMT nanocomposite. The interactions between PVA, PVP and Na⁺MMT were established by the Fourier transform infrared spectroscopy. The moisture absorption tendency of both the PVA and PVA/PVP films reduced after the incorporation of Na⁺MMT at 75% constant relative humidity. Differential scanning calorimetry studies show that the presence of PVP and Na⁺MMT both are responsible for reducing the heat of fusion, and
crystallinity of PVA. The flow behavior of the PVA, PVA/PVP and its nanocomposite solutions has been also studied. Water vapor permeability of PVA/PVP/Na⁺-MMT composite films decreased in the presence of nanoclay due to increasing tortuous paths for diffusion.

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1. Introduction

In recent years, biodegradable polymers, which are environmentally friendly and obtained from renewable resources, have been used in packaging to reduce solid waste from petroleum-based packaging materials [1]. In general, biodegradable polymers such as methylcellulose, hydroxypropyl cellulose, starch, lignin, cellulose acetate, poly(vinyl alcohol) (PVA), polyester, etc. have shown poor mechanical, thermal, gas barrier and water resistance properties compared to synthetic polymers. Therefore, in order to replace synthetic polymers with biodegradable polymers, the properties of biodegradable polymers have to be improved. There are various existing routes to improve the properties of biodegradable polymers such as blending with synthetic polymers [2,3] or natural polymers [4,5] or by adding nano-fillers such as various types of clays [6] and also by crosslinking [7].

Polymer-layer silicate nanocomposites have attracted much attention due to their improved properties, for example, increased mechanical strength and heat resistance, decreased gas permeability and flammability [8,9] compared to the base polymer. Nylon-layered silicate nanocomposites have already been applied in the automotive industry by Toyota Motor Company. The layer silicate clay is a sandwich type of structure with one octahedral aluminum sheet and two tetrahedral silicon sheets [10]. Various types of layered silicates are hectorite, kaolinite, montmorillonite (MMT), saponite, synthetic mica, etc. An improvement in the Young modulus and tensile stress of starch is observed by Cyras et al. [11] with the addition of clay. The synthesized starch/montmorillonite composite films with enhanced physical properties have shown poor water vapor transmission rates and moisture absorption [12]. Singh et al. [13] derived poly(ε-caprolactone) (PCL)/layered silicate nanohybrids with considerable enhancement in thermal and mechanical properties which showed significant biodegradability under controlled conditions in enzyme, pure microorganism (fungi), compost, Ganges water, and alkaline buffer solutions. Kuraoka et al. [14] investigated the effects of clay content on the oxygen barrier properties and surface hardness of the poly(methyl methacrylate) films.

PVA, a colorless, water-soluble synthetic resin is used principally in the treating of textiles, paper coating, flexible water soluble packaging films [15], drug delivery systems [16] and also for preparing membranes [17]. The nanocomposites of PVA/clay have been studied by several research groups. Strawhecker et al. [18] developed exfoliated and intercalated PVA/Na⁺-montmorillonite nanocomposite by solution intercalation process. Yeun et al. [19] reported lower gas permeability in PVA/clay nanocomposites. The enhancement in the thermal stability of PVA is studied by adding clay filler [20]. Sancha et al. [21] investigated the permeability behavior of PVA-graft acrylonitrile/clay nanocomposites towards vapor and liquid molecules.

Poly(vinyl pyrrolidone) (PVP) is a biodegradable water soluble polymer. The PVP is miscible into PVA matrix and vice-versa due to strong H-bonding interactions between –OH groups of PVA and C=O groups of PVP [22]. Nanocomposites of PVP and clay are prepared by the solution-intercalation method in aqueous medium [23]. So, introduction of PVP in the PVA/clay nanocomposite may improve the properties due to the presence of strong H-bonding interactions between PVP, PVA and layered silicates.

Herein, we have reported the effect of PVP on the properties of PVA/Na⁺-MMT nanocomposites. PVA/Na⁺-MMT and PVA/PVP/Na⁺-MMT nanocomposites are prepared by solution mixing process and cast into films. The nanocomposite films are characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared (FTIR) spectroscopy, thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC). Percent crystallinity of all nanocomposites is calculated from DSC studies and compared with XRD analysis. The mechanical, rheological and moisture absorption properties are also measured. This study aims to improve the properties of PVA/Na⁺-MMT nanocomposite by the incorporation of PVP so that films from these nanocomposites can be used for biodegradable food packaging and agricultural applications.

2. Experimental

2.1. Materials

Fully hydrolyzed (98%) poly(vinyl alcohol) (PVA) of average molecular weight 1.4 × 10⁴ Da was purchased from S.D. Fine Chem. Ltd., Mumbai, India. Unmodified montmorillonite clay (Na⁺-MMT) was obtained from Nanocor, USA with a cation-exchange capacity of 100 meq/100 g. The theoretical formula of the montmorillonite is M₂⁺[(Al₂–yMgₓ)y(Si₄–yAlₓ)O₁₀(OH)₂]·nH₂O and its chemical structure is shown in Fig. 1. Poly(vinyl pyrrolidone) (PVP, K-30 powder) of average molecular weight 4 × 10⁴ Da was obtained from Sisco Research Laboratories Pvt. Ltd., Mumbai, India.

2.2. Preparation of PVA/Na⁺-MMT and PVA/PVP/Na⁺-MMT nanocomposite by the solution mixing process

PVA/Na⁺-MMT and PVA/PVP/Na⁺-MMT nanocomposites were prepared by the solution mixing process. Various percentages of Na⁺-MMT suspensions were prepared by dispersing Na⁺-MMT in distilled water. PVA and PVP with a weight ratio of 3:1 was added in Na⁺-MMT suspension at 80 °C with continuous stirring for 3 h, followed by sonication for 30 min. The solutions were then transferred into a petri plate at room temperature. Thin films of average thickness were obtained after evaporation of water.

2.3. X-ray diffraction analysis

X-ray diffraction (XRD) analysis of the nanocomposite samples was performed at room temperature by an X-PERT-PRO Panalytical diffractometer using Cu Kα (λ = 1.5406) as X-ray source at a generator voltage of 40 kV and current of 30 mA. The scanning rate was 1 deg/min. From XRD data, the interlayer spacing of clay
platelets was calculated using Bragg's law as follows:

\[ d = \frac{\lambda}{2 \sin \theta} \]  

where \( d \) is spacing (nm) between two lattice plane, \( \lambda \) is wavelength of X-ray beam (nm), and \( \theta \) is the angle of incidence.

2.4. Transmission electron microscopy

The nanoscale morphology of the PVA/4 wt% Na\(^+\)MMT and PVA/PVP/4 wt% Na\(^+\)MMT nanocomposites was observed by using a transmission electron microscope (TEM). TEM was performed on a high resolution TEM (HRTEM) (model: JEM 2010 EM) at 120 kV accelerating voltage.

2.5. Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectroscopy experiments were performed with a Bruker-Optics Alpha-T spectrophotometer over the range 400–4000 cm\(^{-1}\).

2.6. Mechanical properties

The mechanical properties of the solution cast PVA, PVA/PVP and its nanocomposite films with Na\(^+\)MMT were determined using a Zwick Roell (ZO10) with film sample of 22 mm in length and 5 mm in width at a cross-head speed of 10 mm/min at 25 \(^\circ\)C (as per ASTM D882-95a) [24]. Tensile tests were performed on the samples in a normal relative humidity because completely dry PVA films are quite brittle [25].

2.7. Thermal analysis

Thermo-gravimetric analyses of PVA, PVA/PVP and its nanocomposite films with Na\(^+\)MMT were carried out with Mettler-Toledo at a heating rate of 10 \(^\circ\)C/min under N\(_2\) flow rate of 20 ml/min over a temperature range of 50–500 \(^\circ\)C.

Melting temperature (\( T_m \)) and the heat of fusion (\( \Delta H \)) of those samples were determined by differential scanning calorimetry (DSC) at a heating rate of 10 \(^\circ\)C/min under N\(_2\) flow rate of 150 ml/min. DSC was performed in Mettler-Toledo, model number DSC 822.

2.8. Moisture absorption of nanocomposites films

The moisture absorption of PVA, PVP and its nanocomposite films was determined by the following method. The film samples were cut in the dimension of 3 x 3 cm\(^2\). Then samples were dried until constant weight in an oven at 60 \(^\circ\)C to remove the moisture and immediately weighed as the initial weight (\( W_i \)). The samples were kept in a 75\% constant relative humidity environment generated in a hermetic glass container with aqueous saturated NaCl solutions (ASTM E 104-85) [11]. After 24 h, the film samples were weighed immediately to obtain their final weight (\( W_f \)). Then the moisture absorption of the film samples was calculated by the following equation:

\[ \text{Moisture absorption (\%) = } \left( \frac{W_i - W_f}{W_i} \right) \times 100 \]  

2.9. Water vapor transmission rate (WVTR)

Water vapor permeability of the layer silicate nanocomposite films was calculated in accordance with the modified ASTM E96-00
method [26]. Film samples were sealed over a 60 mm circular opening of a permeation cell containing calcium chloride (0% RH inside the cell). Then the permeation cells were placed inside a desiccator containing the saturated sodium chloride solution (75% RH outside the cell), to create a 75% RH gradient across the film [27]. The water vapor transport was determined from the weight gain of the permeation cell every 24 h until constant rate of weight gain was attained. Water vapor transmission rate was calculated by using the following equation:

$$ Q = \frac{W}{L/S} $$

(3)

where $W$ is increased in the desiccant weight per 24 h, $L$ is the film thickness (cm), $S$ is the exposed surface area (cm$^2$) and $Q$ is the water vapor transmission rate (g/cm$^2$/24 h).

2.10. Rheological measurement

The flow behaviors of the PVA, PVA/PVP and its nanocomposite solutions (3.33 wt%) were measured in HAAKE Viscotester 550 at 25 °C. The rheological behavior of the solutions was obtained by shear stress ($\tau$)-shear rate ($\dot{\gamma}$) measurements within 10–500 s$^{-1}$ shear rates.

3. Results and discussion

3.1. Structure and morphological analysis

Fig. 2 represents the XRD analysis of Na$^+$MMT and different combinations of Na$^+$MMT, PVA and PVP nanocomposites. The diffraction peak observed at 6.7° for Na$^+$MMT corresponds to a basal spacing of 1.32 nm. PVA shows a peak at 19.6°. With loading of 4 and 8 wt% Na$^+$MMT into the PVA matrix the diffraction peak shifts to 4.225° and 4.715° corresponding to a basal spacing of 2.092 and 1.874 nm, respectively. So, the basal spacing of Na$^+$MMT clay increases from 1.32 to 2.092 and 1.874 nm in the case of 4 and 8 wt% Na$^+$MMT loading respectively, indicating the formation of intercalated nanocomposite, and it is also clear that the extent of intercalation is more in the case of 4 wt% loading of Na$^+$MMT. The reason behind the intercalation is the strong interactions present between the OH functional groups of PVA and the negative charges present on the clay surface. On the other hand, no diffraction peak of Na$^+$MMT is observed when 4 wt% Na$^+$MMT is mixed with pure PVP [23]. Therefore, 25 wt% PVP is mixed with a PVA/4 wt% Na$^+$MMT combination with the objective to get exfoliated nanocomposite with better properties.

The results indicate the presence of 25 wt% PVP in PVA/4 wt% Na$^+$MMT combination helps in the conversion from intercalated to exfoliated nanocomposite. When Na$^+$MMT concentration is increased from 4 to 8 wt% in the PVA/PVP matrix, the diffraction peak of Na$^+$MMT obtained at 2.56° corresponds to an interlayer distance of 3.445 nm. So, the interlayer distance is increased by 1.571 nm in the presence of PVP in the PVA/8 wt% Na$^+$MMT nanocomposite films. Therefore, PVP helps to better disperse the Na$^+$MMT layers in PVA due to the presence of strong H-bonding interactions between PVP, PVA molecules and clay layers.

Furthermore, the average number of clay layers forming tactoids has been calculated using the Scherrer equation as [28]

$$ L = \frac{K}{\beta_{(001)} \cos \theta} $$

Where $L$ is the average thickness clay stack, $\beta_{(001)}$ (radian) is the full width at half maximum for 001 reflection, and $k=0.9$.

The number of clay layers per stack ($N$) was calculated as

$$ N = \ln(L/d_{001}) + 1 $$

From Table 1, it is clear that the number of clay layers forming tactoids is found to be in-between 4.4 to 6.4 and decreases with the incorporation of PVP in PVA matrix. This indicates that 4–7 clay platelets are present in each tactoid.

Fig. 3a and b shows the TEM images of PVA/4 wt% Na$^+$MMT and PVA/PVP/4 wt% Na$^+$MMT nanocomposites, respectively. The dark lines represent Na$^+$MMT layers with 1 nm thickness, the space between two layers is interlayer spacing and the gray bases represent the polymer matrix. From Fig. 3a, it is clear that the intercalated nanostructure is formed in the case of PVA/4 wt% Na$^+$MMT nanocomposite and the interlayer distance is 2.14 nm, which is close to the interlayer distance of 2.092 nm obtained from XRD analysis.

Fig. 3b shows the partially exfoliated and partially intercalated nanostructure of PVA/PVP/4 wt% Na$^+$MMT. The interaction between polymer molecules and clay layers increases in the presence of PVP which causes the formation of exfoliated nanocomposite. From Fig. 3d and f, it is also noticeable that the dispersion in the case of PVA/PVP/4 wt% Na$^+$MMT (exfoliated) is more prominent than in the case of PVA/PVP/8 wt% Na$^+$MMT (intercalated) due to the presence of a higher percentage of Na$^+$MMT. Fig. 4 shows the schematic representation of the interactions present in PVA/Na$^+$MMT and PVA/PVP/Na$^+$MMT nanocomposites and how PVP helps in formation of exfoliated microstructure.

3.2. FTIR spectroscopy analysis

The FTIR spectra of PVA, PVP, Na$^+$MMT, PVA/PVP and its nanocomposites are shown in Fig. 5. The characteristic vibration bands of PVA are observed at 3386 cm$^{-1}$ (–OH stretching), 2944 cm$^{-1}$ (–CH stretching), 1098 cm$^{-1}$, (C–O stretching) and 1645 cm$^{-1}$ (C=O stretching) due to acetate groups which are still present in the partially hydrolyzed form of PVA. The characteristic vibration peaks of Na$^+$MMT appeared at 3450 cm$^{-1}$ (Si–O–H stretching), 1035 cm$^{-1}$ (Si–O stretching), and 521 cm$^{-1}$ (Al–O bending). The –OH stretching peaks of PVA at 3385 cm$^{-1}$ and SiO–H bond of Na$^+$MMT at
Table 1 Basal spacing and number of platelets present in each tactoid of PVA/Na\(^+\)MMT and PVA/PVP/Na\(^+\)MMT nanocomposite films.

<table>
<thead>
<tr>
<th>Nanocomposites</th>
<th>(2\theta) (deg)</th>
<th>(d) (nm)</th>
<th>(\Delta d = d_2 - d_1) (nm)</th>
<th>Number of platelets/stack</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(^+)MMT</td>
<td>6.7</td>
<td>1.32</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>PVA/4 wt% Na(^+)MMT</td>
<td>4.225</td>
<td>2.092</td>
<td>0.772</td>
<td>4.9</td>
</tr>
<tr>
<td>PVA/PVP/4 wt% Na(^+)MMT</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>PVA/8 wt% Na(^+)MMT</td>
<td>4.715</td>
<td>1.874</td>
<td>0.554</td>
<td>6.4</td>
</tr>
<tr>
<td>PVA/PVP/8 wt% Na(^+)MMT</td>
<td>2.564</td>
<td>3.445</td>
<td>2.125</td>
<td>5.7</td>
</tr>
</tbody>
</table>

Fig. 3 TEM images of nanocomposites of (a and c) PVA/4 wt% Na\(^+\)MMT at high magnification and low magnification, (b and d) PVA/PVP/4 wt% Na\(^+\)MMT at high magnification and low magnification, and (e and f) PVA/8 wt% Na\(^+\)MMT and PVA/PVP/8 wt% Na\(^+\)MMT at low magnification respectively.
3450 cm\(^{-1}\) are merged and shifted to 3397 cm\(^{-1}\) in the case of PVA/4 wt% Na\(^+\)MMT [29]. The band of C==O of PVA at 1645 cm\(^{-1}\) is shifted to 1643 cm\(^{-1}\). This phenomenon reveals that the above shifting behavior occurs due to inter-molecular and intra-molecular H-bonding interactions [30]. In the case of PVP, the characteristic vibration bands appeared at 3423 cm\(^{-1}\) (-OH stretching), 1656 cm\(^{-1}\) (C==O stretching) and 1292 cm\(^{-1}\) (C–N stretching). With the addition of PVP in PVA, the shift of OH stretching of PVP from 3423 cm\(^{-1}\) to 3397 cm\(^{-1}\) arises from the strengthening the H-bonds due to hydrogen bonding between C==O of PVP and OH bonds of PVA. The conjugation of a lone pair of N with C==O increases the C–N single bond strength which causes the slight increase of the C–N bond stretching frequency from 1292 cm\(^{-1}\) to 1294 cm\(^{-1}\). The peaks of nanocomposites appeared at lower wave number 3396 cm\(^{-1}\) due to OH stretching. This can be correlated to the presence of extensive hydrogen bonding in PVA/PVP/Na\(^+\)MMT nanocomposite.

### 3.3. Mechanical properties

Fig. 6(A) shows the tensile strength of films of PVA, PVA/PVP and its nanocomposites with the loading of various percentages of Na\(^+\)MMT. The tensile strength of pure PVA increases from 52.25 MPa to 63.36 and 54.95 MPa with the addition of 4 and 8 wt% Na\(^+\)MMT, respectively. Therefore, the tensile strength of PVA increases by 21.26% and 5.17% with the addition of 4 and 8 wt% Na\(^+\)MMT respectively. On the other hand, the tensile strength of PVA/PVP combination increases by 14.97 and 23.19% with the addition of 4 and 8 wt% Na\(^+\)MMT, respectively.

Fig. 6(B) shows the initial tensile modulus at 0.01% strain of hybrid films. The tensile modulus of pure PVA increases from 1.47 GPa to 2.16 GPa and 2.69 GPa with the addition of 4 and 8 wt% Na\(^+\)MMT, respectively. Therefore, the initial tensile modulus increases by 46.94% and 82.99% from the incorporation of 4 and 8 wt% Na\(^+\)MMT in PVA matrix, respectively. It is reported that the initial tensile modulus of pure PVA increases linearly with the addition of Na\(^+\)MMT [31]. It is observed that initial tensile modulus increases from 1.47 to 1.78 GPa by inclusion of PVP in the PVA matrix. On further loading of 4 and 8 wt% Na\(^+\)MMT in the PVA/PVP matrix, the initial tensile modulus increased from 1.78 to 2.65 and 4.58 GPa, respectively. Therefore, the initial tensile modulus increased by 48.88% and 157.30% with the addition of 4 and 8 wt% Na\(^+\)MMT respectively compared to pure PVA/PVP film.

Fig. 6(C) shows the elongation at the break of hybrid films made of PVA, PVP and Na\(^+\)MMT. The elongation at the break of pure PVA is marginally improved with the incorporation of 4 wt% Na\(^+\)MMT and then decreases up to 8 wt% Na\(^+\)MMT. But, there is a gradual decrease in elongation at the break of PVA/PVP blend with the inclusion of different percentages of Na\(^+\)MMT.

### 3.4. Thermal properties

Fig. 7 shows the thermo-gravimetric analyses of hybrid film samples. It is observed that the weight loss of PVA/Na\(^+\)MMT nanocomposites
film increases initially and then decreases compared to pure PVA. It is also observed that the addition of PVP in PVA increases the thermal stability of PVA. At 400 °C, weight loss of PVA/PVP blend is 64.12% which is much less compared to 73.33% in the case of PVA and 88.31% in the case of PVP. That means PVP/PVA blend shows improved thermal stability compared to both pure polymers, this is due to the strong interactions existing between PVA and PVP molecules through hydrogen bonding. Table 2 shows the weight loss (%) of PVA, PVP, PVA/PVP blend and its nanocomposite at different temperatures. It is observed that with a loading of 4 wt% Na⁺ MMT in PVP matrix [32], the temperature of the half-way degradation process (the temperature at which 50% of the sample weight is lost) increases from 361 to 431 °C along with the overall thermal stability. It is also observed that with the addition of PVP in the PVA/Na⁺ MMT nanocomposite, improved thermal stability occurs, due to the PVP which helps in the creation of exfoliated and highly intercalated nanocomposites of Na⁺ MMT and clay layers which act as barriers to maximize the heat insulation [23]. The temperature of the half-way degradation PVA/4 wt% Na⁺ MMT and PVA/8 wt% Na⁺ MMT nanocomposites increases from 332 to 351 °C and 325 to 383.9 °C, respectively, with the addition of PVP. So, it can be concluded that the thermal stability of PVA/PVP/Na⁺ MMT nanocomposite is better than PVA/Na⁺ MMT nanocomposite films as PVP helps to create strong H-bonding interactions between PVA and Na⁺ MMT which results in the formation of exfoliated and highly intercalated polymer/clay nanocomposites that are also cleared from XRD and TEM results.

The melting points of PVA, PVA/PVP blend and its nanocomposites are measured by DSC analysis. From Table 3, it is clear that the melting point of PVA and PVA/PVP blend is virtually unchanged with the addition of Na⁺ MMT. The heat of fusion (ΔH) of PVA [33] decreases from 47.85 J/gm to 41.07 and 32.83 J/gm in the presence of 4 and 8 wt% Na⁺ MMT because of interactions between PVA and Na⁺ MMT. It is also observed that with the addition of PVP in PVA/4 wt% Na⁺ MMT and PVA/8 wt% Na⁺ MMT, the heat of fusion (ΔH) decreases to 22.55 and 20.81 J/gm respectively. From Table 3, it is clear that the crystallinity of PVA decreases in the presence of PVP and Na⁺ MMT and the extent of the interaction is more in the case of PVA/PVP/Na⁺ MMT nanocomposite as revealed from the lowest heat of fusion and lowering of crystallinity. Similar decreasing trends in crystallinity are also observed in the case of XRD analysis which is clear from Fig. 8. XRD peak of PVA is obtained at 19.6°. Peak intensity of PVA decreases with the addition of Na⁺ MMT and PVP exhibiting less crystallinity because of the interactions between PVA, PVP and Na⁺ MMT [33].

3.5. Moisture absorption

Table 4 shows the moisture absorption of PVA, PVA/PVP and its nanocomposite hybrid films. The moisture absorption of PVA and PVA/PVP films decreases with the loading of Na⁺ MMT due to the formation of strong hydrogen bonding between polymer molecules and Na⁺ MMT. For this reason, free water molecules cannot interact as strongly as with nanocomposite films as with polymer film alone.
The moisture absorption of pure PVA increases with the addition of PVP as PVP is more hydrophilic in nature. The moisture absorption of pure PVA is 14.02% at 73% relative humidity. With loading 4 and 8 wt% MMT in the PVA film matrix the moisture absorption decreases to 12.09% and 11.66%, respectively. The moisture absorption of pure PVA/PVP decreases from 17.73% to 16.55% and 15.64% with loading 4 and 8 wt% MMT respectively.

3.6. Water vapor transmission rate (WVTR) of nanocomposite films

Water vapor permeability of PVA, PVA/PVP and its nanocomposite hybrid films are shown in Table 4. It is observed that water vapor permeability of PVA/PVP blend films are greater than PVA film because in the presence of PVP, the degree of crystallinity of PVA decreases which is clear from DSC results and lower degree of crystallinity yields greater permeability [36]. The water vapor permeability of PVA and PVA/PVP blend films decreases in the presence of Na⁺MMT due to the increase in path of diffusion for water vapor diffusion. The water vapor permeability of PVA and PVA/PVP blend films decreases from 12.86 × 10⁻⁵ to 11.4 × 10⁻⁵ and 29.49 × 10⁻⁵ to 24.06 × 10⁻⁵ g/cm²/day with addition of 4 wt% Na⁺MMT. The increase in water vapor barrier property of polymer/clay composite films is mainly attributed to the tortuous paths for water vapor diffusion due to the impermeable clay layers distributed in the polymer matrix which increases the effective diffusion path length [37].

3.7. Rheological properties

Table 4 shows viscosity of those compositions at constant shear rate 150 S⁻¹ at 25 °C. Viscosity of PVA is reduced with the addition of PVP [38]. Therefore the dispersion clay layer is better in the PVA/PVP matrix than PVA matrix which causes the formation of exfoliated nanocomposites. It is observed that viscosity increases with loading Na⁺MMT in the PVA, PVP and PVA/PVP blend solutions. This enhancement arises due to the interaction and dispersion of clay in the

| Table 2 | Weight loss (%) at different temperatures of all samples. |
|-----------------------------------------------|
| Nanoocomposites | 200 °C | 300 °C | 350 °C | 400 °C | 450 °C | 500 °C |
| PVA | 7.32 | 30.58 | 58.95 | 73.33 | 86.66 | 96.17 |
| PVA/PVP | 11.53 | 28.63 | 50.48 | 64.12 | 84.94 | 93.13 |
| PVA/4 wt% Na⁺MMT | 8.09 | 33.81 | 59.93 | 71.05 | 81.52 | 87.74 |
| PVA/PVP/4 wt% Na⁺MMT | 11.43 | 33.26 | 50.6 | 60.19 | 79.61 | 92.3 |
| PVA/8 wt% Na⁺MMT | 9.4 | 36.74 | 63 | 69.98 | 79.41 | 84.83 |
| PVA/PVP/8 wt% Na⁺MMT | 7.78 | 23.56 | 42.92 | 54.12 | 75.68 | 85.46 |
| PVP | 18.6 | 21.22 | 37 | 88.31 | 92 | 97.88 |
| PVP/4 wt% Na⁺MMT | 19.06 | 21.02 | 22.47 | 27.75 | 72.31 | 87.24 |

| Table 3 | Melting temperature, the heat of fusion and crystallinity index of PVA, PVA/PVP blend and its nanocomposites with MMT. |
|-----------------------------------------------|
| Nanoocomposites | Melting point Tm (°C) | ΔH (J/g) | Crystallinity (%) |
| PVA | 225.7 | 47.85 | 29.72 |
| PVA/PVP | 226.7 | 21.49 | 13.35 |
| PVA/4 wt% Na⁺MMT | 224.8 | 41.07 | 25.51 |
| PVA/PVP/4 wt% Na⁺MMT | 227.6 | 22.55 | 14.01 |
| PVA/8 wt% Na⁺MMT | 222.5 | 32.83 | 20.39 |
| PVA/PVP/8 wt% Na⁺MMT | 226.8 | 20.81 | 12.92 |

Fig. 8 XRD patterns and DSC curves in melting region of (a) PVA, (b) PVA/4 wt% Na⁺MMT, (c) PVA/8 wt% Na⁺MMT, (d) PVA/PVP, (e) PVA/PVP/4 wt% Na⁺MMT and (f) PVA/PVP/8 wt% Na⁺MMT.
Established by FTIR analysis. DSC studies also show that the presence of strong H-bonding interactions in the presence of PVP improved compared to PVA/Na⁺ MMT. Interactions between PVA, PVP and Na⁺ polymer molecules [39].

Table 4  Moisture absorption, water vapor permeability and viscosity of PVA, PVA/PVP and its nanocomposite samples with MMT.

<table>
<thead>
<tr>
<th>Nanocomposites</th>
<th>Moisture absorption (wt%)</th>
<th>Water vapor transmission rate (g/cm²/day)</th>
<th>Viscosity at 25°C (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA</td>
<td>14.022</td>
<td>12.86 × 10⁻⁵</td>
<td>11.86</td>
</tr>
<tr>
<td>PVA/PVP</td>
<td>17.73</td>
<td>29.45 × 10⁻⁵</td>
<td>7.96</td>
</tr>
<tr>
<td>PVA/4 wt% Na⁺ MMT</td>
<td>12.09</td>
<td>11.40 × 10⁻⁵</td>
<td>13.29</td>
</tr>
<tr>
<td>PVA/PVP/4 wt% Na⁺ MMT</td>
<td>16.56</td>
<td>24.06 × 10⁻⁵</td>
<td>8.34</td>
</tr>
<tr>
<td>PVA/8 wt% Na⁺ MMT</td>
<td>11.66</td>
<td>7.18 × 10⁻⁵</td>
<td>15.04</td>
</tr>
<tr>
<td>PVA/PVP/8 wt% Na⁺ MMT</td>
<td>15.64</td>
<td>24.08 × 10⁻⁵</td>
<td>10.09</td>
</tr>
</tbody>
</table>

4. Conclusions

PVA/Na⁺ MMT and PVA/PVP/Na⁺ MMT nanocomposites have been successfully prepared by the solution mixing process. From XRD and TEM analysis, it is clear that with the addition of PVP in the PVA/Na⁺ MMT matrix, exfoliated and highly intercalated PVA/PVP/Na⁺ MMT nanocomposites formed. The tensile modulus of PVA and PVA/PVP blended films increased with loading 4 and 8 wt% Na⁺ MMT. Thermal stability of PVA/PVP/Na⁺ MMT nanocomposites improved compared to PVA/Na⁺ MMT nanocomposite films due to the presence of strong H-bonding interactions in the presence of PVP established by FTIR analysis. DSC studies also show that the presence of PVP and Na⁺ MMT are both responsible for reducing the heat of fusion and crystallinity of PVA, again indicating a presence of strong interactions between PVA, PVP and Na⁺ MMT. So, PVA/PVP/Na⁺ MMT nanocomposite has promising potential as a low cost, biodegradable alternative to conventional plastics in flexible packaging applications for food products. Enhanced modulus, higher thermal stability and improved moisture resistance properties may be advantageous for making biodegradable packaging films.

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