

On the crystallinity of PVA/palm leaf biocomposite using DSC and XRD techniques

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Abstract Biocomposites of polyvinyl alcohol (PVA) and palm leaf powder were prepared using solution casting method. The effect of addition of palm leaf into PVA matrix on thermal behaviour was studied by differential scanning calorimetry and on crystalline properties using X-ray diffraction (XRD) techniques. On the basis of differential scanning calorimetry (DSC) thermograms, the glass transition temperature, melting temperature, melting enthalpy of fusion and crystallinity were determined. It is found that the glass transition temperature initially decreases; however, it increases with further increase in amount of palm leaf powder in the biocomposite. The melting enthalpy of fusion and crystallinity is found to increase for samples with palm leaf up to 15 wt%. The crystallinity is observed to be 37.29 % for biocomposite with 15 wt% of palm leaf as compared to 27.45 % for pure PVA. On the basis of XRD studies, decrease in the interplanar distance and crystallite size is observed while the order of crystallinity is found to increase in similar manner as observed in DSC thermograms. Thus, the addition of palm leaf powder in the poly vinyl alcohol can be developed as a biocomposite with increased thermal stability and crystalline properties.

1 Introduction

The production and consumption of crude oil based plastics is increasing and about 150 million tons of plastic are produced annually around the world (Yun et al. 2006). These plastics are basically un-degradable polymers which cause serious environmental pollution. In recent years the environmental awareness and consciousness throughout the world has developed an increasing interest in biocomposites, biopolymers and natural polymers (Singha and Thakur 2008). Biocomposite materials are the materials composed of biodegradable matrix and reinforced with natural fiber (Kong and Hay 2003a).

The polymers are basically semicrystalline materials and fractional crystallinity of semicrystalline polymer reflects the morphology and determines mechanical properties. The Young modulus, yield stress, fatigue response and impact strength increase progressively with crystallinity (Kong and Hay 2003a). There are various analytical methods which we can be used to estimate the fractional crystallinity i.e. X-ray diffraction (XRD), density measurement, differential scanning calorimetry (DSC), infrared spectroscopy (IR) and nuclear magnetic spectroscopy (Runt 1986) etc. Mathot has reported that the degree of crystallinity is a temperature dependent physical property of polymer (Mathot 1994).

DSC is one of the important techniques widely used to determine the thermal parameter of the polymer. Most of the workers have utilized DSC as a tool for determining the glass transition temperature and melting temperature of the polymer (Rudnik 2007; Agrawal and Awadhia 2004; Dubey et al. 2008; Gaur et al. 2010; Hirankumar et al. 2005; Liu et al. 2007; Pereira et al. 1997; Tsukame et al. 1997). Apart from these workers some others have done good qualitative analysis by calculating the enthalpy of

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fusion and crystallinity of the polymer system (Kong and Hay 2003a; Asran et al. 2010; Averous and Digabel 2006; Cartledge and Baillie 1999; Goderis et al. 2005; Guo et al. 2010; Kim et al. 2008; Kong and Hay 2002a; Kong and Hay 2002b, 2003b; Li et al. 2005; Ma et al. 2009; Munaro and Akcelrud 2008; Schick 2009; Sudhamani et al. 2003; Verdonck et al. 1999; Wang et al. 2009; Wu et al. 2010). The degree of crystallinity can be calculated by estimating enthalpy of fusion from area under the curve in DSC endotherms by drawing a linear arbitrary baseline from the first onset of the melting to the last trace of crystallinity. The degree of crystallinity for polymer can be defined as-

$$X_c = \frac{\Delta H_f(T_m)}{\Delta H_f^0(T_m^0)} \quad (1)$$

where X_c is the weight fraction extent of crystallinity, $\Delta H_f(T_m)$ is the enthalpy of fusion measured at the melting point T_m , and $\Delta H_f^0(T_m^0)$ is the enthalpy of fusion of the totally crystalline polymer measured at the equilibrium melting point T_m^0 (Kong and Hay 2002b). In the case of composite the crystallinity can be determined using

$$X_c = \frac{\Delta H_f(T_m)}{\Delta H_f^0(T_m^0)(1 - m_f)} \quad (2)$$

where m_f is the mass fraction of filler in composite (Barone 2005).

The important properties of the polymer system are directly related to the structural feature called crystallinity (Statton 1967). X-ray diffraction technique can be used to study periodic arrangement and judge crystallinity of the polymer system. The estimation of the amount of crystalline content is usually based on comparison of the area under the XRD peaks. The degree of crystallinity can be written as-

$$C_r = \frac{\text{Area of Crystalline Fraction (under peak)}}{\text{Area of Crystalline Fraction} + \text{Area of Amorphous Fraction}} \quad (3)$$

Various analytical methods have been developed for measuring the area under various fractions (Statton 1967) and many workers have characterized the material by X-ray diffraction technique (Dubey et al. 2008; Pereira et al. 1997; Cartledge and Baillie 1999; Goderis et al. 2005; Guo et al. 2010; Kim et al. 2008; Ma et al. 2009; Munaro and Akcelrud 2008; Wu et al. 2010; Patel et al. 2011a; Ramrakhiani et al. 2005). Poly vinyl alcohol (PVA) selected for present work is one of the important polymeric material with good physical properties with many industrial applications (Yun et al. 2006; Agrawal and Awadhia 2004; Liu et al. 2007; Guo et al. 2010; Kim et al. 2008; Wu et al. 2010).

2 Experimental details

2.1 Materials

The 98 % acetalized PVA with molecular weight of 14,000 was procured from Research Lab Chemical Industries, Mumbai, India and used without further purification. The Alexander palm leaf has been obtained from Jawaharlal Nehru Agriculture University, Jabalpur, MP, India.

2.2 Preparation of specimen

The solution casting technique was adopted for the preparation of pure PVA films and palm leaf incorporated PVA composite films (Patel et al. 2011a, b). Palm leaf was grinded and mixed in PVA in required wt% concentration and the specimens were designated as of 5 % PL + PVA, 10 % PL + PVA, 15 % PL + PVA and 20 % PL + PVA respectively for 5, 10, 15 and 20 wt% concentration in the presence of deionized water as a solvent. The solution was constantly stirred with the help of electronic motor operating at 200 rpm for 4 h at room temperature to obtain homogeneous gel. The gel so obtained was poured on glass plate floating over mercury pool, so as to yield films with uniform thickness. The films were thereafter heated or cured for 24 h at 70 °C, The films were then removed from the glass plate and stored in air-tight polyethylene bags for further characterization.

2.3 Differential scanning calorimetry

The DSC is one of the effective techniques for determining the thermal parameters and crystallization mechanism in polymer system (Schick 2009). DSC enables the determination of melting, crystallization and mesomorphic transition temperatures and corresponding enthalpy and entropy changes, characterization of glass transition and other effect which show either changes in heat capacity or latent heat (Kong and Hay 2002a, b; 2003a, b). For universality and simplicity the energy characterization (heat capacity C_p and its integral over temperature T- enthalpy H), measured via calorimetry has a clear physical significance. The calorimetry is the study of heat transfer during physical and chemical process. The enthalpy of the substance increases with increasing temperature and depends on the conditions like constant pressure or constant volume. The most commonly used condition is constant pressure, and the heat capacity at the constant pressure is given as

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p \quad (4)$$

The heat capacity at constant pressure is then used to relate the change in enthalpy to change in temperature. For infinitesimal changes in temperature

$$dH = C_p dT \tag{5}$$

If the heat capacity is constant over the range of temperature of interest, then for a measurable increase in temperature

$$\Delta H = C_p \Delta T \tag{6}$$

In DSC, we basically measure heat flow and heat capacity as a function of time and temperature. If we plot the DSC thermogram consisting of a plot of C_p against T and if ΔH_f is the enthalpy of fusion, then change in enthalpy is written as

$$\Delta H_f = \int_{T_o}^{T_f} C_p dT \tag{7}$$

The temperatures T_o and T_f are known as onset melting temperature and final melting temperature of the specimen, respectively. Now the weight fraction crystallinity for composite can be measured by dividing the enthalpy of fusion at different temperature (i.e.)

$$X_c(T) = \frac{\Delta H_f(T_o - T_f)}{\Delta H_f^o(T_m) \times (1 - m_f)} \times 100 \% \tag{8}$$

where $X_c(T)$ is the weight fraction crystallinity, $\Delta H_f(T_o - T_f)$ is enthalpy of fusion of the sample between temperature T_o and T_f as shown in Fig. 1 and $\Delta H_f^o(T_m)$ is the enthalpy of fusion of the totally crystalline (100 % crystalline) specimen or sample, m_f is the mass fraction of filler in composite. In the case of PVA the enthalpy of fusion of 100 % crystalline PVA was taken ($\Delta H_f^o(T_m)$) = 138.6 Jg^{-1} from literature (Peppas and Merrill 1976). The method adopted for the calculation of crystallinity is known as first law method. The DSC studies on prepared pure PVA polymer and palm leaf reinforced PVA composite were carried out with TA instruments DSC 2910 for temperature range 55–220 °C with linear heating rate of 10 °C/min.

2.4 X-ray diffraction

The degree of crystallinity of polymer is very important. It defines the physical and mechanical properties of the polymer system. The chemical resistance, moisture absorption and mechanical properties like tensile properties and stiffness are directly proportional to the crystallinity. The X-ray diffraction technique is the most reliable technique for determining the crystallinity of the semi crystalline polymer system (Mathot 1994; Goderis et al. 2005;

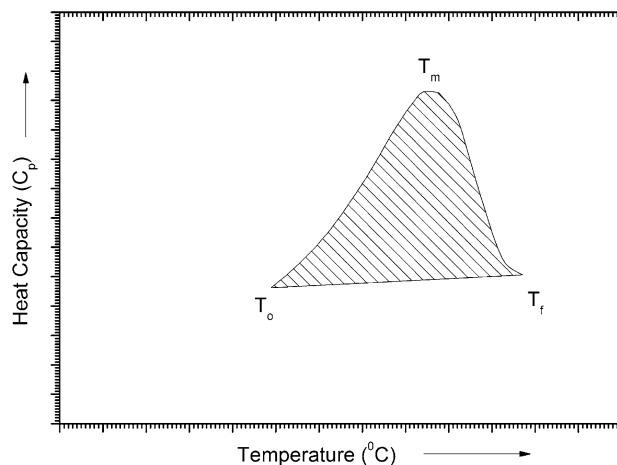


Fig. 1 A schematic representation of the enthalpy of fusion $\Delta H_f(T_o - T_f)$ between temperature T_o and T_f in DSC endotherms. A linear arbitrary baseline drawn from temperature T_o to T_f for calculating area under the curve

Patel et al. 2011a). The X-ray diffraction studies of prepared pure PVA polymer and palm leaf powder reinforced PVA composites were carried out with Bruker D8 Advance X-ray diffractometer with $\text{CuK}\alpha$ radiation. The X-ray powder diffraction pattern was recorded in the 2θ range from 10° to 50° with scanning speed of 0.2° per min.

The height (C_rH) of the main peak above its adjacent minimum represents the crystallinity of the sample and the width (A_mW) of the peak at this adjacent minimum is considered as the amorphousness of the sample. The crystallinity C_rI , is calculated from the Eq. (9):

$$C_rI = \left[1 - t \times \frac{A_mW}{C_rH} \right] \tag{9}$$

where t is the scale factor relating the height of C_rH to full scale (total blackness) (Statton 1967). From the diffraction patterns of the various samples, the interplanar distance d was computed for different peaks. Bragg’s Eq. (10) was used to determine the distance between two successive planes from which the X-rays were diffracted:

$$2d \sin \theta = n\lambda \tag{10}$$

where λ is the X-ray wavelength, θ is Bragg’s angle and n is the order of diffraction. The interplanar distance d was calculated from the first order ($n = 1$) for various peaks obtained in the diffraction patterns (Eq. (11)):

$$d = \frac{\lambda}{2 \sin \theta} \tag{11}$$

The relationship between the crystallite size and X-ray line broadening was determined from Scherrer’s equation:

$$D = \frac{k\lambda}{\beta \cos \theta} \tag{12}$$

Here, D is the crystallite size, λ is the wavelength, β is the angular line width of half maximum intensity, and is the Bragg's diffraction angle, while k is the constant with a value of 0.89 (Dubey et al. 2008).

3 Result and discussion

3.1 Differential scanning calorimetry

The interaction between the palm leaf powder and the attached polymer i.e. the effect of the palm leaf powder on the thermal properties of pure PVA and palm leaf powder reinforced PVA was investigated using DSC.

The first heating and cooling run of the DSC at the rate of 10 °C/min and a nitrogen flow of 10 ccpm was used to characterize the thermal properties of all samples. The heating run was used to obtain the melting temperature and melting enthalpy. The result of DSC run of pure PVA and palm leaf reinforced samples (5 %PL + PVA, 10 %PL + PVA, 15 %PL + PVA, and 20 %PL + PVA) are presented in Figs. 2, 3, 4, 5 and 6 and summarized in Table 1.

3.1.1 Thermal analysis of pure PVA

The Fig. 2 shows DSC thermogram of pure PVA recorded with the heating run from 55 to 220 °C.

Fig. 2 DSC thermogram of the pure PVA

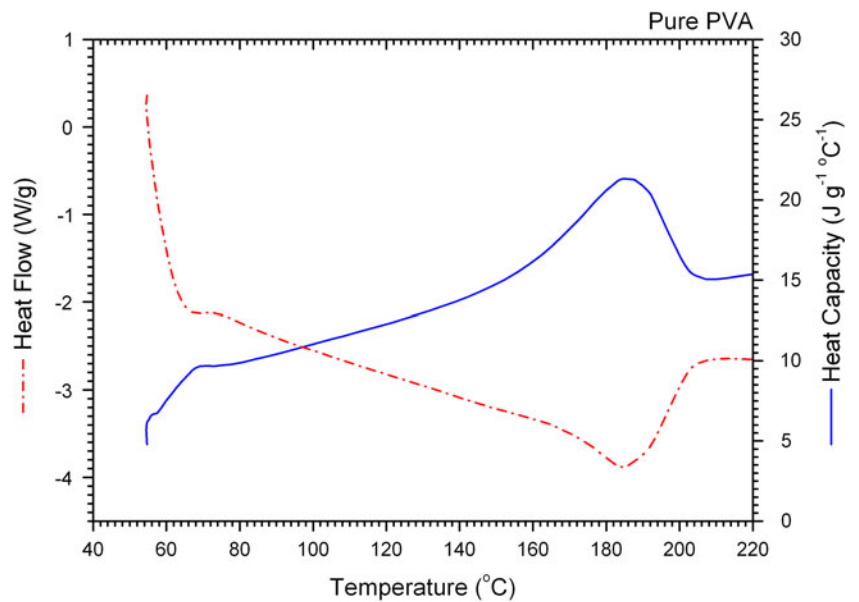


Fig. 3 DSC thermogram of the 5 %PL + PVA

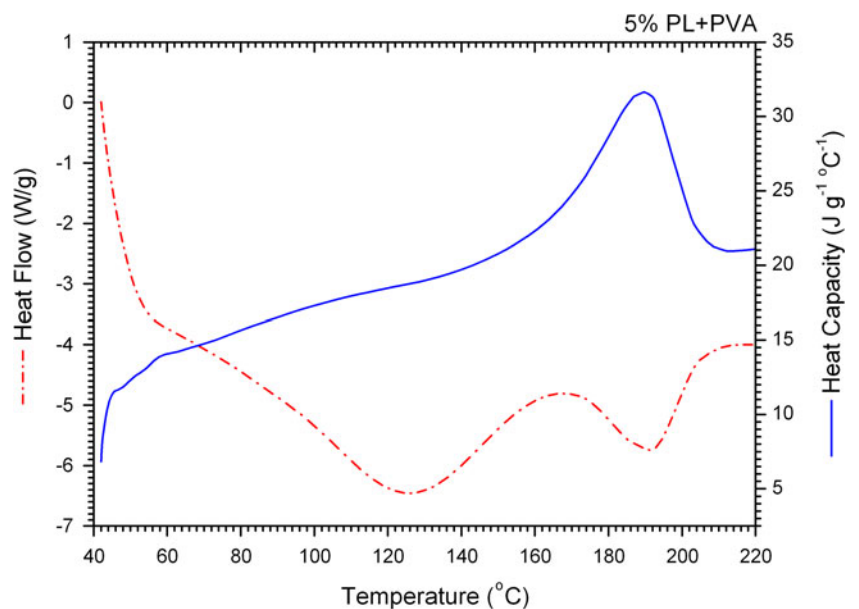


Fig. 4 DSC thermogram of the 10 %PL + PVA

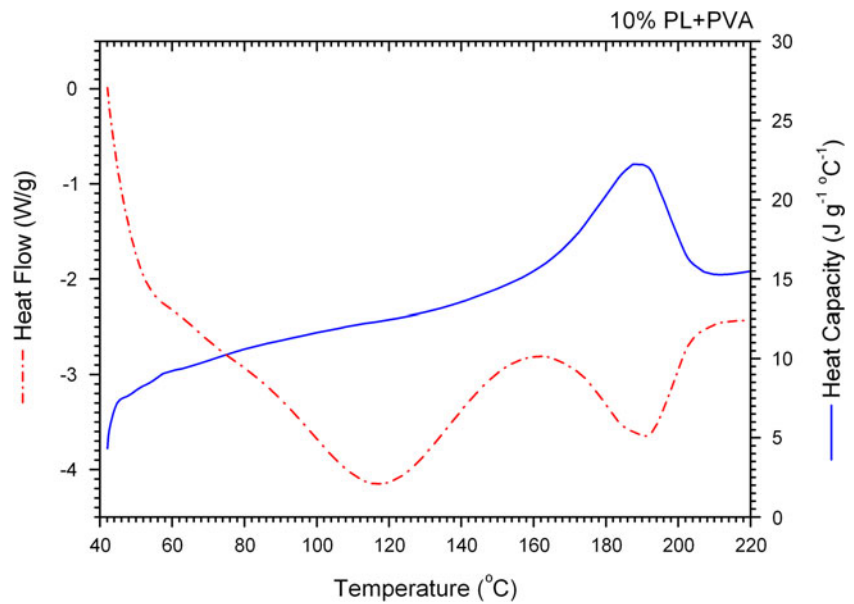
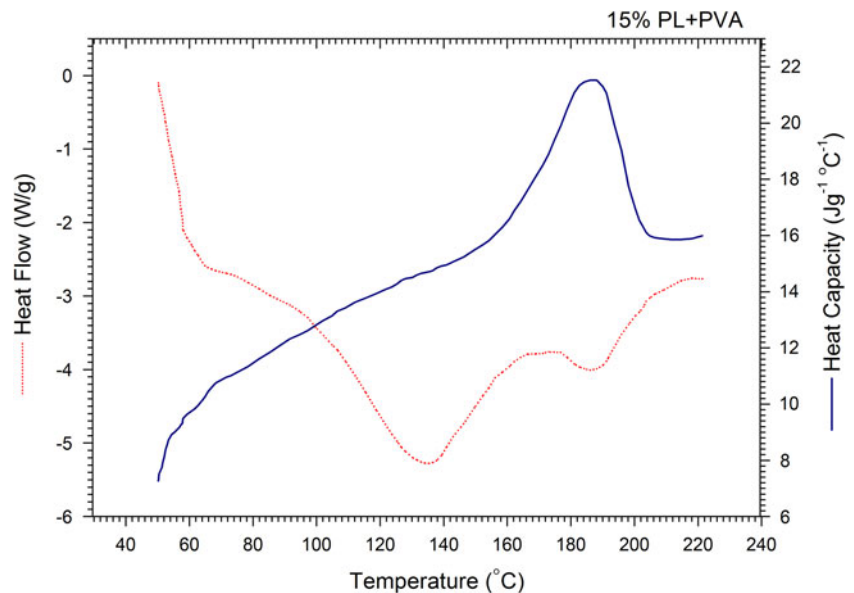


Fig. 5 DSC thermogram of the 15 %PL + PVA



The glass transition temperature of the pure PVA is found to be 66 °C, which is less than the reported value, and this reduction of glass transition temperature is due to the plasticization of PVA by water (Hirankumar et al. 2005). For pure PVA the onset melting temperature raises from 148.9 °C, the peak melting temperature is obtained at 185.0 °C and the final melting temperature at 207.1 °C. The enthalpy of fusion for pure PVA is found to be 38.05 J/g. The crystallinity calculated on the basis of first law principle is found to be $X_c = 27.45\%$ with respect to the reported value of the enthalpy of fusion for 100 % crystalline PVA polymer (Peppas and Merrill 1976).

3.1.2 Thermal analysis of palm leaf powder reinforced PVA

The DSC thermograms of various palm leaf powder reinforced PVA biocomposites are shown in Figs. 3, 4, 5 and 6. The glass transition temperature of palm leaf powder reinforced PVA biocomposite initially decreases from 66 to 58.2 °C for sample with 5 wt% (5 %PL + PVA). However, when we increase the concentration of palm leaf powder to 10 wt% (10 %PL + PVA), the glass transition temperature increases to 61 °C. On further increasing the concentration of palm leaf powder, the glass transition temperature increases and glass transition occurs at 66 °C

for 15 %PL + PVA and 68.2 °C for 20 %PL + PVA biocomposite film samples, respectively.

The variation in melting temperature is also observed to change due to addition of palm leaf powder. The peak melting temperature occurs at the temperature of 189.7, 187.4, 188.0 and 189.0 °C for 5 %PL + PVA, 10 %PL + PVA, 15 %PL + PVA and 20 %PL + PVA respectively. The onset melting temperature also increases for palm leaf powder reinforced films as compared to pure PVA film.

Further, the melting enthalpy of the samples also increases with increasing concentration of palm leaf powder within the Poly vinyl alcohol up to 15 % concentration. The crystallinity also increases by increasing the concentration of palm leaf powder in the biocomposite. The melting enthalpy of the samples is found to be 38.94, 43.44, 46.77 and 41.26 J/g for 5 %PL + PVA, 10 %PL + PVA, 15 %PL + PVA and 20 %PL + PVA samples respectively. The crystallinity has been calculated by applying the

Fig. 6 DSC thermogram of the 20 %PL + PVA

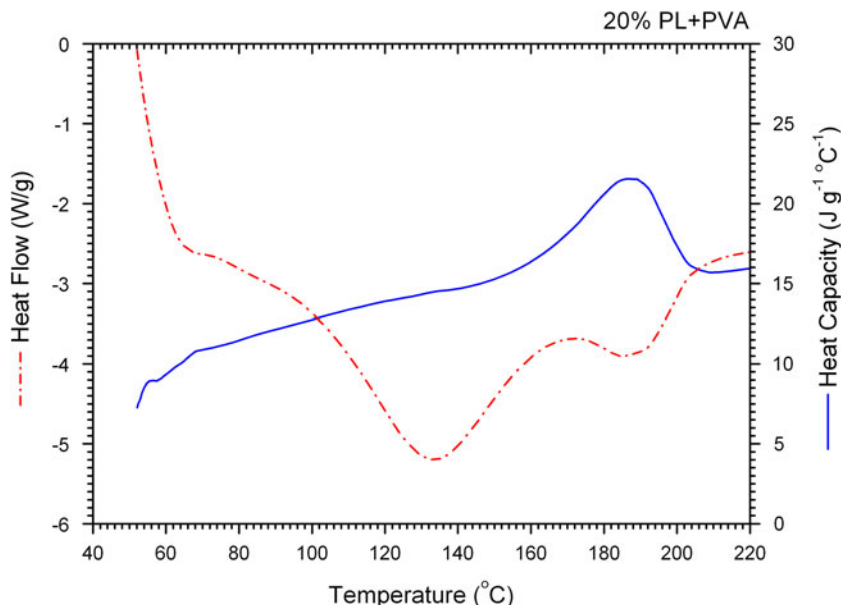


Table 1 DSC melting results of pure PVA and palm leaf powder based biocomposite

| Samples | Mass taken for DSC (in mg) | T_g (in °C) | T_m^{on} (in °C) | T_m^p (in °C) | T_m^f (in °C) | $\Delta T_m = T_m^{on} - T_m^p$ (in °C) | ΔH_m (in J/g) | X_c (in %) |
|---------------|----------------------------|---------------|--------------------|-----------------|-----------------|---|-----------------------|--------------|
| Pure PVA | 4.5 | 66 | 148.9 | 185.0 | 207.1 | 58.26 | 38.05 | 27.45 |
| 5 % PL + PVA | 7.0 | 58.2 | 149.7 | 189.7 | 210.8 | 61.05 | 38.94 | 29.57 |
| 10 % PL + PVA | 3.8 | 61 | 159.3 | 187.4 | 211.8 | 52.49 | 43.44 | 34.82 |
| 15 % PL + PVA | 3.3 | 66 | 156.5 | 188.0 | 210.0 | 53.5 | 43.93 | 37.29 |
| 20 % PL + PVA | 4.0 | 68.2 | 152.2 | 189.0 | 211.5 | 59.3 | 41.26 | 37.20 |

T_m^{on} onset melting temperature of sample, T_m^p peak melting temperature of sample, T_m^f final melting temperature of sample, $\Delta T_m = T_m^{on} - T_m^p$, ΔH_m melting enthalpy of sample, X_c is the crystallinity, $X_c(T) = \frac{\Delta H_f(T_o - T_f)}{\Delta H_f^p(T_m) \times (1 - m_f)} \times 100$ %, $\Delta H_f^p(T_m)$ is the enthalpy of fusion of the totally crystalline (100 % crystalline) specimen, $\Delta H_f^p(T_m) = 138.6 \text{ Jg}^{-1}$ for PVA (36), m_f is the mass fraction of filler in composite

Table 2 Crystallinity, peaks at 2 θ (°), interplanar distance ‘d’ and crystallite size ‘D’ (Å)

| S. no | Sample with wt% of palm leaf powder(PL) | Crystallinity index or order of crystallinity $C_r I$ (%) | Peaks at 2 θ (°) | Interplanar distance ‘d’ (Å) | Crystallite size ‘D’ (Å) |
|-------|---|---|-------------------------|------------------------------|--------------------------|
| 1 | Pure PVA | 28.1 | 19.50 | 4.551 | 42.665 |
| 2 | 5 %PL + PVA | 30.5 | 19.55 | 4.540 | 31.792 |
| 3 | 10 %PL + PVA | 33.3 | 19.84 | 4.473 | 27.968 |
| 4 | 15 %PL + PVA | 33.9 | 19.94 | 3.578 | 32.447 |
| 5 | 20 % PL + PVA | 30.7 | 19.64 | 3.495 | 27.485 |

Eq. (8), and using the reported value of the enthalpy of fusion = 138.6 J/g for 100 % crystalline PVA polymer (Peppas and Merrill 1976). The crystallinity is observed to be 29.57, 34.82, 37.29 and 37.20 % for 5 %PL +

PVA, 10 %PL + PVA, 15 %PL + PVA and 20 %PL + PVA samples, respectively. The variation profile of crystallinity has been shown in Fig. 8 and it is clear from the crystallinity variation profile that the crystallinity increases by up to the 15 wt% concentration of palm leaf powder.

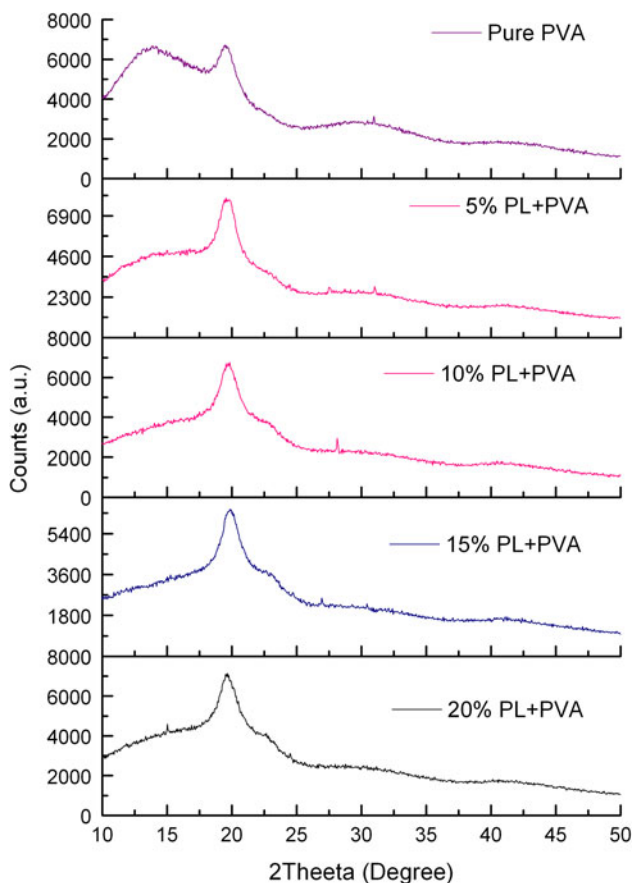
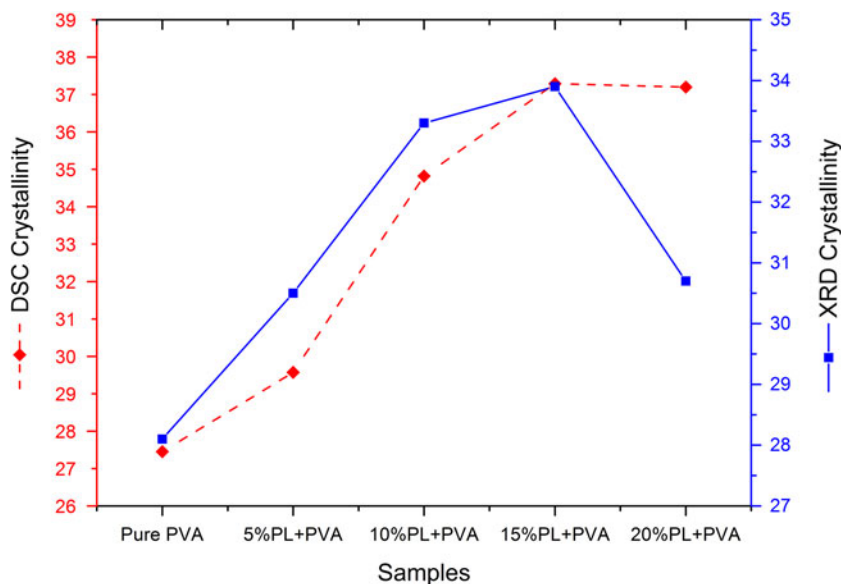


Fig. 7 X-ray diffraction pattern of pure PVA, 5 %PL + PVA, 10 % PL + PVA, 15 %PL + PVA, 20 % PL + PVA

3.2 X-ray diffraction

X-ray diffraction patterns of pure PVA and palm leaf reinforced PVA samples have been recorded. The X-ray diffractograms of pure PVA and palm leaf reinforced PVA samples are shown in Fig. 7 and summarized in Table 2. In all the samples, the crystalline peak is observed between $2\theta = 19.50^\circ$ to 19.94° . For pure PVA film, the crystalline peak is observed at 19.50° , which yields crystallinity of 28.1 %, interplanar distance, $d = 4.551 \text{ \AA}$ and crystallite size $D = 42.66 \text{ \AA}$. As a result of the addition of palm leaf powder in PVA shifts in crystalline peak are observed toward the higher glancing angle side and observed peaks are also sharp. For 5 %PL + PVA biocomposite film, crystalline peak is observed at $2\theta = 19.55^\circ$, which yields the crystallinity of 30.5 % with interplanar distance, $d = 4.540 \text{ \AA}$, and crystallite size $D = 31.79 \text{ \AA}$. For 10 and 15 wt% biocomposite films (i.e. 10 %PL + PVA and 15 %PL + PVA) similar increases in various properties have been observed. The crystallinity observed for 10 and 15 wt% films are 33.3 and 33.9 %, respectively. In the case of 20 wt% biocomposite film, the decrease in various properties has been observed, the crystalline peak has been observed at $2\theta = 19.64^\circ$, i.e. there is a shift towards lower glancing angle, the calculated crystallinity value is 30.7 %, interplanar distance, $d = 3.495 \text{ \AA}$ and crystallite size $D = 27.48 \text{ \AA}$. The variation in profile of crystallinity for

Fig. 8 Crystallinity variation profile of various samples as calculated from DSC and XRD studies



various weight proportion calculated by XRD can be seen in Fig. 8.

4 Conclusion

In the present work biodegradable biocomposites of PVA and palm leaf powder has been synthesized. The prepared samples were characterized by DSC and XRD techniques. The first law principle on DSC thermograms has been utilized for calculation of glass transition temperature, melting point, enthalpy of fusion and crystallinity. The DSC study shows that for pure PVA the enthalpy of fusion is 38.05 J/g and the crystallinity of pure PVA comes out to be 27.45 %. By adding Palm Leaf powder into PVA, the glass transition temperature (T_g) of biocomposites increases except for 5 wt% film. The melting temperature (T_m), melting enthalpy and crystallinity of biocomposites increases with respect to pure PVA sample. However, these properties are found to be maximum for 15 wt% concentration of Palm Leaf powder samples.

The XRD measurements indicate that the lamellae thickness (Crystalline Size, D) decreases with increase in concentration of palm leaf powder except for that of 15 wt% concentration sample. The order of crystallinity measured by XRD also increases with increasing concentration of palm leaf powder except for maximum concentration of palm leaf powder (i.e. 20 wt%).

The results show that the method and procedure adopted for the calculation of crystallinity of the samples from the first law method is valid and it measures a fractional crystallinity which compares fairly well with the value determined by X-ray diffraction method. Both the studies indicate that the crystalline properties of synthesized biocomposite change synergistically up to the level of 15 wt% of the palm leaf powder content in the film. Thus, it can be concluded that the addition of palm leaf powder in the PVA, increases the thermal stability and crystalline properties, yielding environmental friendly biocomposite material.

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