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Thermal Studies of the Starch and Polyvinyl Alcohol based Film and its Nano Composites

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Abstract

Starch is a naturally occurring biopolymer with sustainable resource. This biopolymer has lower tensile strength. To overcome this, it is blended with Poly-vinyl Alcohol (PVA), which is a synthetic polymer but biodegradable and biologically safe. Nanocomposite of this blend has been prepared with 1%, 2% and 3% nanoclay loading. The thermal properties of this polymer have been studied. In this paper, the thermal characterization using Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) of this blend and its nanocomposites has been done.

Keywords: Polyvinyl alcohol; Starch; Thermogravimetric analysis; Differential scanning calorimetry; X-ray diffraction technique

Introduction

Starch is a naturally occurring biopolymer which is available in abundance from various sources. One of the major such source is potato, which is readily available and can also be considered as one of the sustainable source of starch. But starch itself has certain limitations e.g., low strength, low elongation, high brittleness etc. Thus to enhance its properties it is mixed with Polyvinyl alcohol (PVA), which is synthetic but non toxic, biodegradable and food safe.

Increasing use of synthetic polymers and inadequate recycling of the same has increased the environment safety concerns. Thus replacement of the synthetic polymers with biopolymers as much as possible may be considered as one step ahead towards the green method. Biopolymers having sustainable resource may solve the environment related issues to a great extent. With this idea a lot of researchers worldwide are now working on biopolymers based blends for various polymeric applications and are trying to replace synthetic polymers with biopolymers as much as possible. In our earlier communication, the mechanical properties of the starch-PVA based nanocomposites have already been discussed [1].

In recent years many scientific groups are working on various renewable natural/ biopolymer based blends and composites [2,3]. Among different types of biopolymer like starch, cellulose, chitosan, polylactic acid [4-8] etc. starch is one of the most easily available, cheap and sustainable biopolymer. Moreover starch is available from various sources like potato starch, corn starch, wheat starch etc. Literature study reveals that addition of starch to various synthetic polymers not only improves the biodegradability of the end material but also reduces cost with better acceptability interns of properties.

Starch has been added to low density polyethylene, High density polyethylene, PVA [9-12] and many more synthetic polymers.

In this paper, the focus is on the thermal studies of the cross linked starch-PVA blend and its nanocomposites with different loadings. The starch and PVA have been mixed at equal ratios. Further the addition of nano clay, Cloisite 30B has modified the proper- ties of the blend. In this study of thermal properties, X-Ray diffraction results are also provided to support the data.

Experimental

Materials used

Starch: Soluble starch of Analytical Grade is used for the work. Starch comes in the form of white or almost white powder. The supplier of the starch is CDH$^{(R)}$.

Polyvinyl alcohol: Poly vinyl alcohol is purchased from Loba Chemie Pvt. Ltd., Mumbai, with a degree of polymerisation 1700-1800.

Citric acid: Citric acid is purchased from local Market.

Nanoclay: Cloisite 30B is generously supplied by Souther Clay Products, USA.

Instruments used

X-Ray diffraction: Polymer Film samples have been scanned through a speed of 2°C/min at ambient temperature using X-ray diffract meter. The data are collected from $2\theta° = 0°$ to $2\theta° = 40°$ interval using Rigaku Ultima X-Ray Diffraction Machine.

Differential Scanning Calorimetry (DSC): Differential Scanning Calorimetry has been done using Universal V4.5A TA Instruments, DSC Q200 V24.4 Build 116 in the tempera- ture range -50° to 150°C. The heating rate used is 10°s per minute in air.

Thermogravimetric Analysis (TGA): Thermogravimetric Analysis has been done using a Universal V4.5A TA Instruments, TGA Q500 V20.10 Build 36 instrument. The Experiments have been carried out from room temperature to 800°C at heating rate 10°s per minute in air.

Preparation of Starch-Polyvinyl Alcohol Film (Starch-PVA): Starch-PVA was taken in water in different composition, Like 30:70, 50:50, 70:30. The reaction mixture was heated at 70°C until uniformity appears, after cooling solution at 35°C, the solution is poured onto casting mold and dried under oven at 60°C to remove water contents. After complete drying, the films are stored in moisture free environment.

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Preparation of starch-PVA based nano composites: A specified amount of Nano Clay (1%, 2%, 3% by wt. of starch-PVA used) was dissolved in the starch-PVA solution. The starch solution containing the clay was heated to 70°C, held at that temperature for 20 min, then cooled to 50°C and poured onto petridish and kept in an oven at 60°C for drying and peeled off.

Discussion

X-Ray Diffraction Studies (XRD)

The X-ray Diffraction studies have been conducted on the starch-PVA blend based nano composite samples where the Cloisite 30 B clay loading has been varied. The XRD spectra of the starch-PVA blend with 1%, 2% and 3% nanoclay loading have been shown in the Figures 1-3 respectively. The comparison of these XRD results shows that there are no peaks at the lower angle from 0 to 10°s. XRD peaks in this range are generally known to be indicative of the presence nano clay layered structure. At around 29°s there is a sharp peak in all the three clay filled nano composite XRD figures which appears because of the polymer crystallinity. There is a small hump around 15° in 1%, 2% and 3% clay loaded samples. The peaks around 20°s and 29°s are present in all the three compositions. Literature search results have shown a peak at around 20°s for Polyvinyl Alcohol [2] and at around 15° and 28° for the starch [3]. Pure Cloisite 30 B shows a peak at 5° [4]. Hence, the absence of any peak between 0° to 10° confirms the exfoliation of the nano clays in all the compositions. The appearance of the other three peaks at 15°s; 20° and 29°s contribute to the presence of PVA and starch. The positions of all the three peaks remains unchanged in all the three clay loaded compositions, which indicates that there is no change in the crystalline structure or pattern of the component materials. However the intensities of the peaks have varied in all the three cases. The variations of intensities of the above mentioned three peaks in the three compositions refer to the interference of nano clay at 1% and 2% loading with the crystalline phases of both PVA and starch. That is why the peak at 15° and at 20° (due to starch) is not so prominent. At 3% clay loading, probably the nanoclay starts to form agglomerates and hence does not interfere with the crystalline structure of the constituent polymers leading to sharper peaks. The variations in the XRD peak intensities are observed mainly with the peak at 29° which appears due to PVA. This also indicates towards the interaction of the nano fillers (Figure 1) with the PVA phase in preference to the starch phase. Whenever the nano clay interacts with the PVA phase, the corresponding peak intensities are affected. That is why; the peaks in Figure 3 are much more sharp and distinct. This explanation of the variation of peak intensities may further be confirmed by DSC results (Figures 2 and 3).

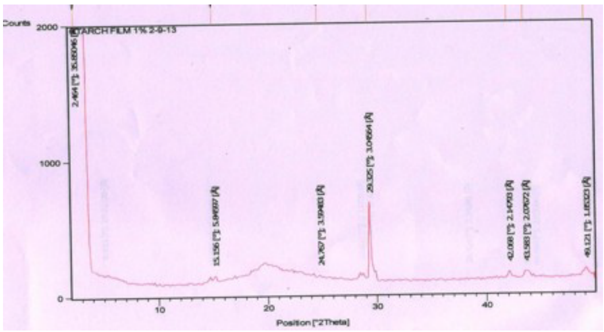

Figure 1: XRD spectra of strach-PVA blend with 1% clay loading.

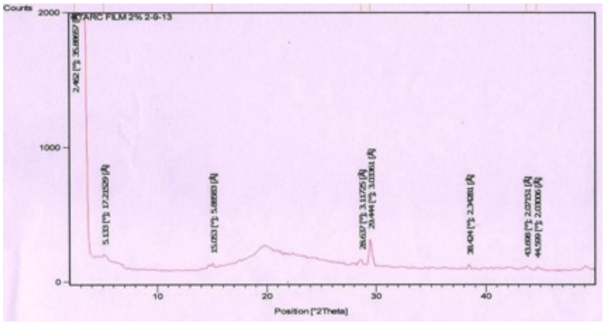

Figure 2: XRD spectra of starch-PVA blend with 2% clay loading.

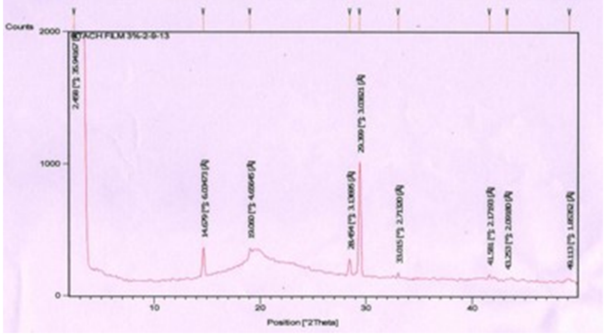

Figure 3: XRD spectra of starch-PVA blend with 3% clay loading.

Sample	1st peak	2nd peak	3rd peak	Residue Left (%)
PVA	150	350	435	
PVA-starch blend	70.66	303.58	437.43	14.92
PVA-starch 1% nano	94.86	284.67	441.97	23.34
PVA-starch 2% nano	109.23	277.87	443.48	22.06
PVA-starch 3% nano	100.91	278.62	439.7	23.57

Table 1: TGA results of starch-PVA based samples.

Thermogravimetric Analysis (TGA)

TGA has been done for all the samples with and without nanoclay to understand the thermal stability and its behavior at high temperature. The TGA data of the PVA without any starch has also been done for reference. The PVA and all the PVA starch blends and their nano composites undergo three step degradation and the results are tabulated in the Table 1. The thermogravimetric analysis of PVA and it is blend and composites are given below (Figures 4a and 4b) in 100°C but the 1st peak maxima appears around 1500 C. The 2nd and 3rd peak maxima of the PVA appear at 350°C and 435°C. Maximum amount of weight loss has occurred in the 2nd step of degradation (Table 1).

When starch is added to the PVA at 50:50 ratios, the stability of the blend lowered down compared to pure PVA. The 1st and the 2nd degradation peak appeared at 70.66°C and 303.58°C respectively for starch-PVA 50/50 blend. The 3rd degradation peak also remained almost unchanged when compared to pure PVA. As nano clay is added to the blend at 1% and 2% loadings, the 1st degradation peak shifted towards higher temperature from 70.66°C in pure starch-PVA blend to 94.86°C in 1% clay loaded sample to 109.23°C in 2% clay loaded sample. In 3% clay loaded sample the 1st degradation peak moved slightly towards lower temperature i.e., 100.91°C. The 2nd degradation peak continuously moves towards lower temperature as the clay loading is increased from 0% to 1%, 2% and 3% loading. The 3rd degradation peak does not shift drastically. Rather it shows very slow and steady increase in the degradation peak temperature from 437.43°C at 0% clay loading to 441.97°C in 1% clay loading to 443.48°C in 2% clay loading to finally 439.70°C at 3% clay loading. The TGA curves of the PVA, starch- PVA blend at 50:50 ratio and the nano clay filled starch-PVA composites are given in Figure 4.

The results may be explained with the help of the XRD results where 1% and 2% clay loadings show good dispersion of the clay particles whereas the 3% loading shows some agglomeration. As the dispersion improves the nano clay enhances the thermal stabilities of the blends. At 3% loading due to improper dispersion and mixing in the starch-PVA matrix, the stabilizing effect of the clays are somewhat less effective.

With loading of clay the residue increases from 14.92% in case of unfilled starch-PVA blend to 23.57% in case of 3% clay loaded starch-PVA blend. The residue left in all the three clay filled samples is almost same (Figures 4c-4e).

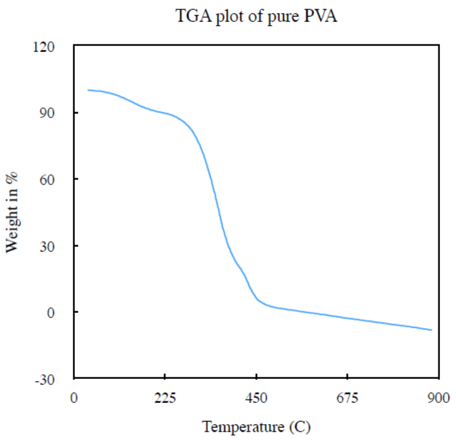

Figure 4a: TGA curves of various blends and nanocomposites.
a: TGA plot of pure PVA.

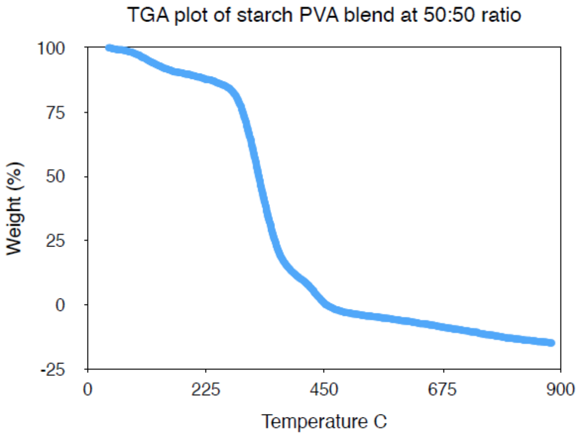

Figure 4b: TGA plot of PVA:Starch blend at 50:50 ratio.

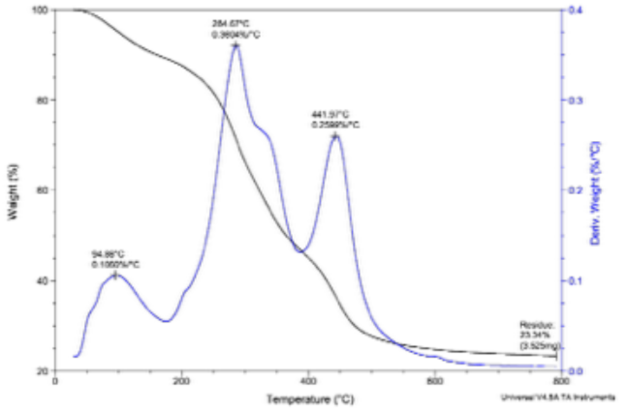

Figure 4c: TGA and DTG curve of 1% nano clay filled starch-PVA 50:50 blend.

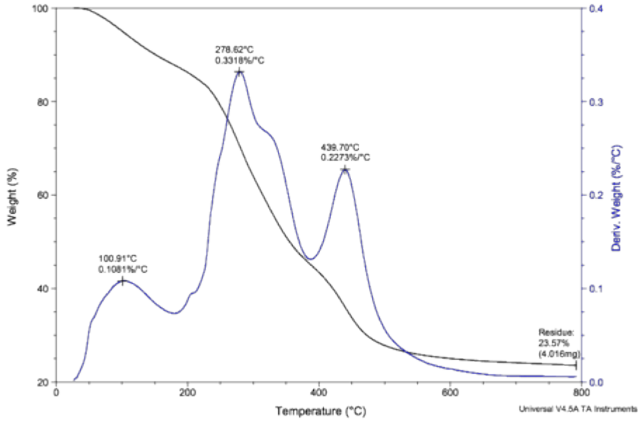

Figure 4d: TGA and DTG curve of 2% nano clay filled starch-PVA50:50 blend.

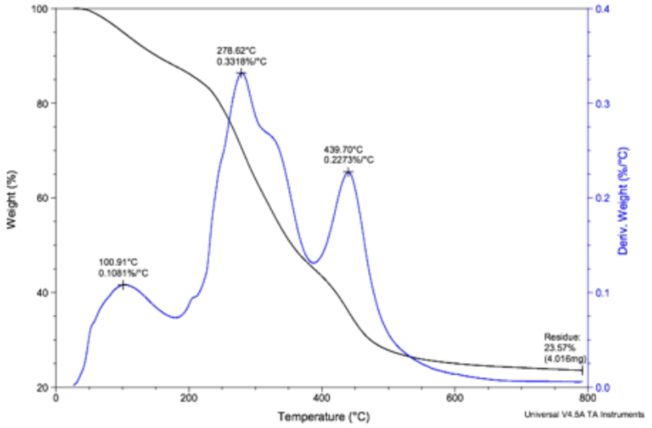

Figure 4e: TGA and DTG curve of 3% nano clay filled starch-PVA 50:50 blend.

Differential Scanning Calorimeter (DSC)

DSC has been done for two representative samples: a) starch-PVA

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blend b) 2% nano clay filled starch-PVA blend for understanding their thermal behaviour. The DSC studies have been carried out from -50°C to 150°C. The results show that the pure starch-PVA 50:50 blend gives one exothermic peak starting at 50.39°C and the peak temperature at 81.82°C (Figure 5a). Addition of 2% nano clay shifts the onset temperature by 6°C and peak temperature by 2°C towards higher temperature. A major change in the energy involved is also observed. The energy liberated in the pure blend without nano clay is 165.9 J/g while that of starch-PVA blend with 2% nano clay is 222.4 J/g (Figure 5b).

The XRD data of 2% nano clay filled starch-PVA blend shows better dispersion among all the clay filled samples in the polymeric matrix. With better dispersion the surface activity of the nano clay also improves. This leads to better adhesion of the clay with the polymer chains, leading to improved thermal stability of the blend. Thus the energy involvement for any type of phase change increases with better dispersed clay filled samples. This is the reason that 2% clay filled starch-PVA blend shows increase in onset temperature and the energy involvement compared to unfilled starch-PVA blend. The DSC results of the starch-PVA based samples are tabulated in Table 2 and Figures 5a and 5b).

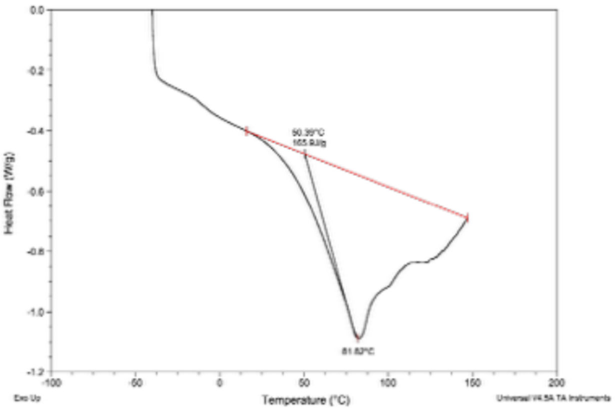

Figure 5a: DSC curve of starch-PVA based samples. **a:** DSC curve of starch -PVA blend at 50:50 ratio.

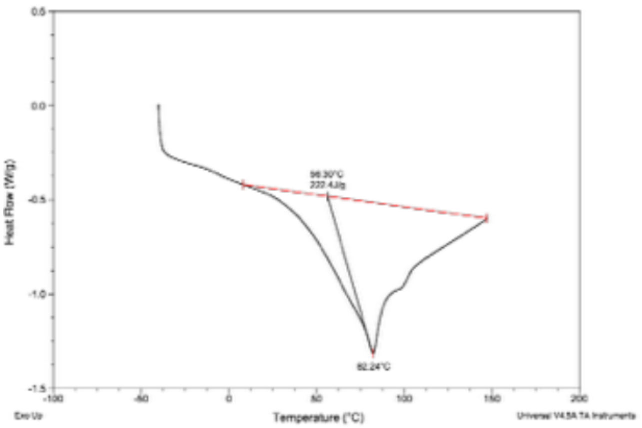

Figure 5b: DSC curve of starch-PVA blend (50:50 ratio) with 2% nano clay.

Sample	Onset Temperature (°C)	Peak Temperature (°C)	Energy Involved (J/g)
PVA-starch blend	50.39	81.82	165.9
PVA-starch + 2% nano	56.3	82.24	222.4

Table 2: DSC results of starch-PVA samples.

Conclusions

Starch PVA blend is a biodegradable blend made from sustainable resources. This blend may be used for various applications which include food packaging, biodegradable packaging etc. as a single material or in combination with other materials. For these above mentioned applications, the studies of mechanical and thermal properties are important. Nanofillers are well known material to enhance both mechanical and thermal studies. Hence the study of thermal stability of starch-PVA nano composites is important.

The present study reveals in the XRD data that the nano fillers are well dispersed in the polymer matrix and exfoliated as there is no peak of nano clay layers till 10° angle in 1%, 2% and 3% loading. The dispersion of the nano clay is best in case of 2% loading. The crystallinity peak of the base material that is the starch-PVA blend is also low in case of 1% and 2% loading of nano clay. In case of 3% loading of nano clay, the polymer crystalline peak intensity increases significantly indicating poor dispersion of the nano clay in the blend matrix.

The TGA studies of the unfilled and filled starch-PVA blend and pure PVA shows that addition of starch to PVA matrix has reduced the thermal stability of PVA. But addition of nano clay at 1%, 2% and 3% loading has increased the stability. The best stability among all the clay filled samples is shown by 2% clay loaded starch-PVA sample again confirming the optimum dispersion of the nano clay in the blend matrix.

DSC has been done for two representative samples the unfilled starch-PVA blend and 2% nano clay filled starch-PVA blend. The DSC results are in accordance with the XRD and TGA data. The 2% clay filled blend shows higher energy involvement during the phase change confirming good interaction between the nano clay particles and polymer blend matrix.

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