



Polyvinyl alcohol/Starch/Carboxymethyl cellulose ternary polymer blends: Synthesis, Characterization and Thermal properties

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Abstract

Polymer blends were prepared from polyvinylalcohol, starch and carboxymethyl cellulose aqueous suspensions in the presence of H₂O₂ by solution casting method in the form of films. The prepared polymer blends were characterized by FTIR Spectroscopy, Scanning Electron Microscopy and XRD analysis. The thermal degradation of prepared polymer blends was investigated by thermogravimetry and derivative thermogravimetry analysis. The thermal stability of polyvinyl alcohol/starch/carboxymethyl cellulose blends is higher than that of polyvinyl alcohol/starch blends suggesting that the addition of carboxymethyl cellulose improved the thermal stability of polyvinyl alcohol/starch blends.

Keywords: polymer blends, polyvinyl Alcohol, starch, carboxymethyl cellulose, thermal stability.

1. Introduction

Polymer blends are physical mixtures of two or more structurally different homopolymer or copolymers and they interact through secondary forces with no covalent bonding. Polymer blending is a well-used technique whenever modification of properties is required, because it uses conventional technology at low cost. The usual objective for preparing a novel blend of two or more polymers is not to change the properties of the components drastically, but to capitalize on the maximum possible performance of the blend [1].

Polyvinyl alcohol (PVA) is a synthetic water-soluble polymer [2]. PVA is semicrystalline, non-toxic, better film and fiber forming, biocompatible, excellent chemical resistance, good mechanical properties and biodegradable synthetic polymer which is widely used in the biomedical field [3, 4]. It is a versatile polymer with many applications, and an important synthetic polymer whose backbone is mainly composed of C-C bonds that is biodegradable. It is the most readily biodegradable of vinyl polymers. It is readily degraded in waste water

activated sludge. The excellent chemical resistance, optical and physical properties of PVA resins has resulted in its broad industrial uses [5]. PVA is well suited to be blended with natural polymers since it is highly polar and can also be manipulated in water solution.

Among the water soluble natural polymers, starch is of interest. Starch(S) is a polysaccharide produced by higher plants as a means of storing energy. It is stored intracellular in the form of spherical granules that are 2-100nm in diameter. It is mostly water soluble, difficult to process and brittle. In principle some of the properties of starch can be significantly improved by blending it with synthetic polymers [6]. Owing to its complete biodegradability, low cost and renewability, starch is considered as a promising candidate for developing sustainable materials.

PVA is blended with starch as the starch is available in abundance at low price [7]. Starch possesses similar

function as PVA which is biocompatible and consumable by microorganism. When PVA and starch are blended together, the presence of hydroxyl groups tend to form strong hydrogen bonding among the molecules and subsequently lead to synergistic stability and better system integrity. [8].

Cellulose is the most abundant natural bio polymer and is readily available from renewable resources. It is an excellent fiber. Wood, cotton and hemp rope are all made of fibrous cellulose. Cellulose is made of repeat units of the monomer glucose. Cellulose is considered as a nearly inexhaustible raw material with fascinating structures and properties for the remarkable demand for environment friendly and biocompatible products.

Chemical functionalization of cellulose aims to adjust the properties of cellulose for different purposes, particularly as a chemical feedstock for production of cellulose derivatives for a variety of applications [9]. Chemical functionalization of cellulose include reactions of hydroxyl groups such as esterification, etherification, intermolecular crosslinking reactions, and macrocellulosic free radical reactions, particularly in the formation of graft cellulose copolymers to increase the usefulness of cellulose by altering its properties. These cellulose derivatives are grouped according to the processes and substituents. Chemical functionalization continues to play a dominant role in improving the overall utilization of cellulosic polymers. Broader and more specialized applications of advanced and trend setting materials based on this unique and renewable macromolecule will increase the demand for more diverse synthesis paths and derivatives [10].

Carboxy methyl cellulose (CMC) is one of the cellulose ethers which exhibits thermal gelation and forms excellent films. CMC films are generally odorless and tasteless, flexible and are of moderate strength, transparent, resistant to oil and fats, water soluble, moderate to moisture and oxygen transmission. Because of its polymeric structure and high molecular weight, it can be used as filler in biocomposite film production [11, 12]. The many important functions provided by this polymer make it a preferred thickener, suspending aid, stabilizer, binder and film-former in a wide variety of applications [13].

In this work Polymer blends were prepared from PVA, starch and CMC in the presence of H₂O₂. The resulting blend films were characterized by FTIR, Scanning Electron Microscopy (SEM) and XRD analysis. Finally, the enhancement of thermal properties of the blend films was investigated by using TGA-DTG analysis.

2. Experimental

2.1 Materials

The polymers PVA and starch were purchased from Merck Company. The reagents like NaOH, isopropyl

alcohol, chloroacetic acid, methanol and ethanol were AR grade and used as such without any further purification.

2.2 Preparation of Carboxymethyl cellulose

Cellulose pulp powder (15 g) isolated from rice straw [14] was dispersed in 450mL isopropyl alcohol and stirred for about one hour. 50mL of 40% NaOH was added into the reaction mixture and further stirred for 30 min prior to adding chloroacetic acid (18 g). The mixture was covered with aluminum foil and placed in a hot air oven at 55°C for 3.5 hrs. The solid phase was separated and washed with 100mL of absolute methanol, neutralized with acetic acid (90%) and filtered using a Buchner funnel. The product was washed five times by soaking in 300mL of ethanol (70 %) for 10 min to remove undesirable byproducts. The final product was washed with 300mL of absolute methanol. The carboxymethyl cellulose obtained was dried overnight at room temperature.

2.3 Preparation of blend Films

Films were obtained by casting method. PVA (4.5 g) was solubilized in 60mL of distilled water at 75°C for 15 min and starch (1.5 g) was mixed with 40mL of distilled water at 75°C for 15min. CMC (0.3g) was solubilized in 20mL of distilled water at 75°C for 15min. Then PVA, starch, carboxymethyl cellulose solutions were mixed together and stirred with a magnetic stirrer for about two hrs. Finally 1% of H₂O₂ was added and stirred for about 5min. Then the solution was poured into the mold and dried at 4°C for one week. A blank film is also prepared without the addition of CMC.

2.4 FTIR Analysis

Infrared Spectroscopy plays a very important role in the physical characterization of polymers. The FTIR spectra of polymer blends were recorded in the range of 4000-650 cm⁻¹ on a Shimadzu FTIR- 470 infrared spectrometer by KBr disc technique.

2.5 XRD Analysis

The XRD pattern of the films was analyzed by Panalytical X'pert powder X'celerator Diffractometer using Cu K α radiation in the 2 θ range of 0-80° diffraction angle. The percentage of crystallinity and the crystalline index of the polymer blends were calculated from XRD data using the formulae,

$$\text{Percentage (\%) Crystallinity} = \frac{I_c}{I_c + I_a} \times 100$$

$$\text{Crystallinity Index} = \frac{I_c - I_a}{I_c}$$

Where, I_c is the intensity of crystalline phase and I_a is the intensity of amorphous phase.

2.5 Scanning Electron Microscopy

The morphology of the surface of the films was investigated using a Scanning Electron Microscope JOEL model JSM-6390LV(STIC Cochin).

2.6 Thermogravimetric Analysis

Athermogravimetric analysis was employed to measure the thermal weight loss of PVA/S/CMC ternary blend films in the temperature range from room temperature to 700°C with the heating rate of 10°C per min. under a nitrogen stream. The TG and DTG curves are plotted for each sample. The weight losses at different stages were analyzed.

3. Results and Discussion

3.1 FTIR Analysis

In the FTIR spectra of PVA/S blend (Figure 1) a strong and broad band at 3305 cm^{-1} corresponds to the OH stretching, indicating the presence of both the strong hydrogen bonding internally to OH or terminal vinyl group. The peaks at 2919 cm^{-1} and 2851 cm^{-1} are attributed to the asymmetric stretching of CH groups. The weak peak at 1645 cm^{-1} is due to the adsorbed water and the peak arising at 1416 cm^{-1} is the

characteristic peak of CH_2 bending with deformation. The peak at 1076 cm^{-1} is due to C-O-H bending and C-O stretching vibration coupled with O-H bending vibration and the band at 1003 cm^{-1} is due to the stretching of C-O group in C-O-C group. The peaks at 718 cm^{-1} – 558 cm^{-1} are the characteristic peaks of C-C stretching.

In the FTIR spectrum of CMC (Figure 2), a broad band at 3360 cm^{-1} is due to the stretching of O-H group and a band at 2915 cm^{-1} due to the stretching of C-H group. However, a carbonyl (C=O) peak at 1590 cm^{-1} , a $-\text{CH}_2$ peak at 1414 cm^{-1} and an ether peak at 1046 cm^{-1} confirmed the introduction of a $-\text{OCH}_2\text{COO}$ -group into the cellulose molecule [15-17].

In the FTIR spectra of PVA/S/CMC blend film (Figure 3) a strong and broad band at 3297 cm^{-1} corresponds to the OH stretching. The peak at 2920 cm^{-1} is attributed to the asymmetric stretching of CH groups and a peak at 1257 cm^{-1} is assigned to the stretching vibration of C-O group. A carbonyl (C=O) peak at 1601 cm^{-1} , a $-\text{CH}_2$ peak at 1429 cm^{-1} and an ether peak at 1029 cm^{-1} confirmed the introduction of CMC into the PVA/S film. The peaks from 841-579 cm^{-1} are the characteristic peaks of C-C stretching.

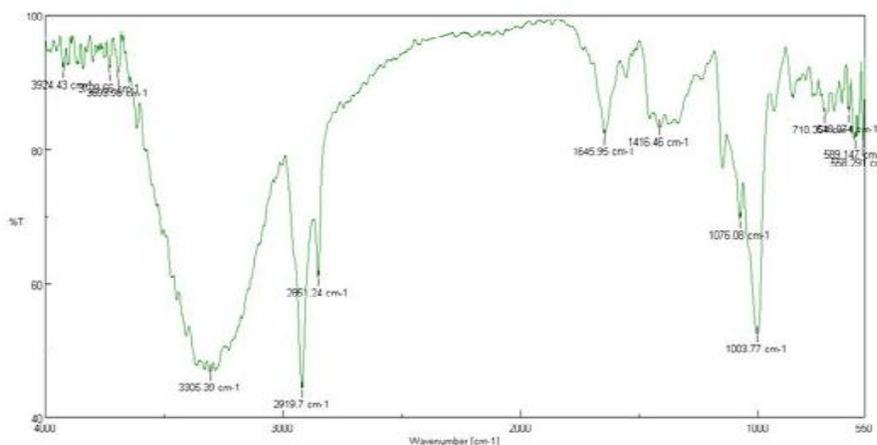


Figure 1. FTIR Spectra of PVA/S film

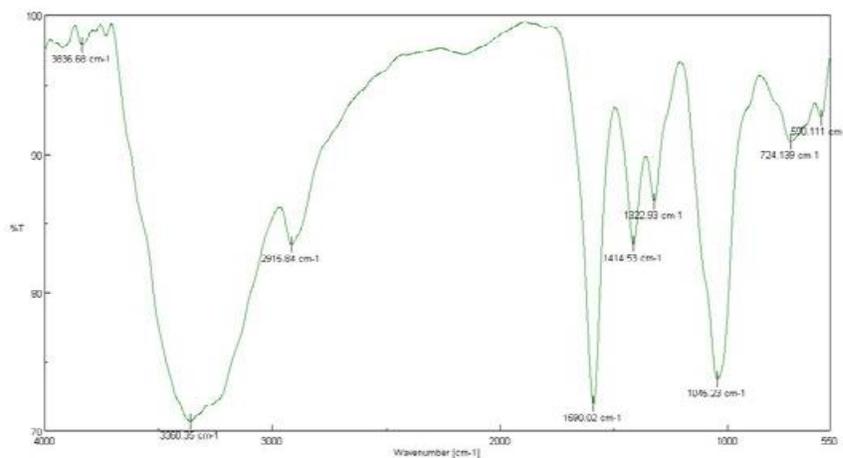


Figure 2. FTIR Spectra of CMC

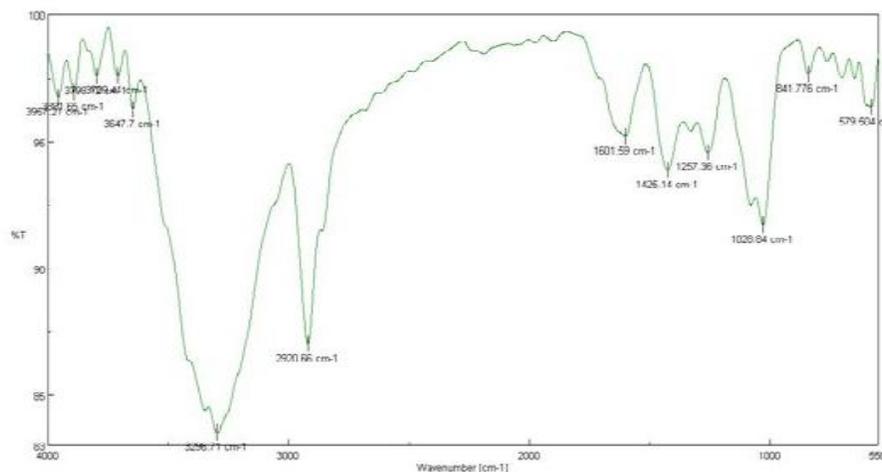


Figure 3: FTIR spectra of PVA/ S/CMC film

3.2 XRD Analysis

The XRD patterns of CMC, PVA/S and PVA/S/CMC are shown in Figures 4-6. When PVA is blended with starch, two diffraction peaks appeared at $2\theta = 20.05^\circ$ and $2\theta = 41.49^\circ$. The crystallinity and the crystallinity index of the above blend are 64.7% and 0.6

respectively. The addition of 5% CMC to the above blend changes the intensity of diffraction peaks. The intensity of diffraction peaks are highly increased and the change in crystallinity and crystallinity index are observed from 64.7% to 71.42% and 0.45 to 0.6 respectively.

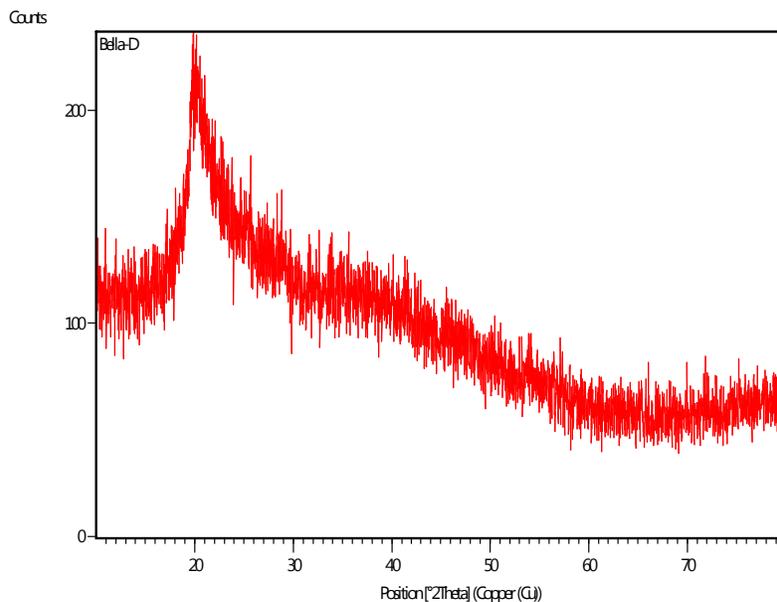


Figure 4: XRD pattern of CMC

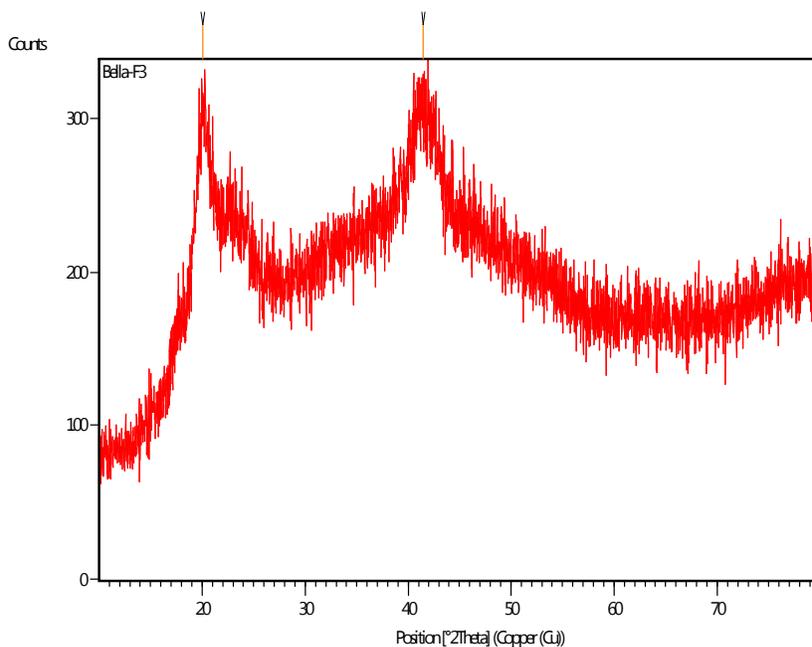


Figure 5: XRD pattern of PVA/S

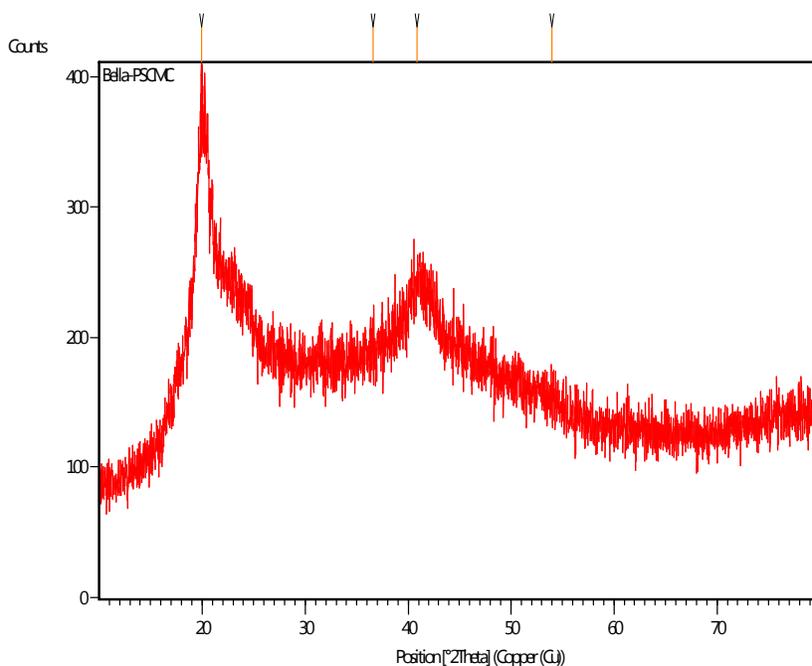


Figure 6: XRD pattern of PVA/S/CMC

3.3 Scanning Electron Microscopy

The SEM image of PVA/S blends (Figure 7) shows agglomeration and almost uniform dispersion of starch on the surface of the PVA. SEM image of CMC shows

the particles are in tubular structure (Figure 8). The SEM image of PVA/S/CMC blends (Figure 9) shows CMC is well distributed in the PVA/S matrix and exhibited considerable cohesion with the polymer.

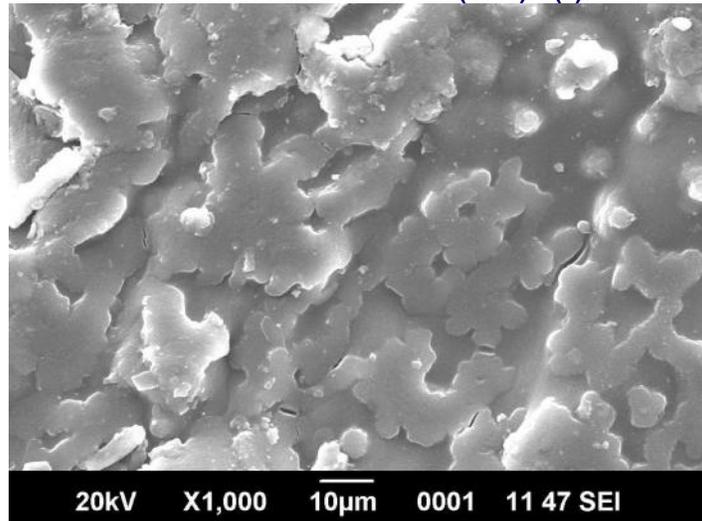


Figure 7: SEM image of PVA/S film

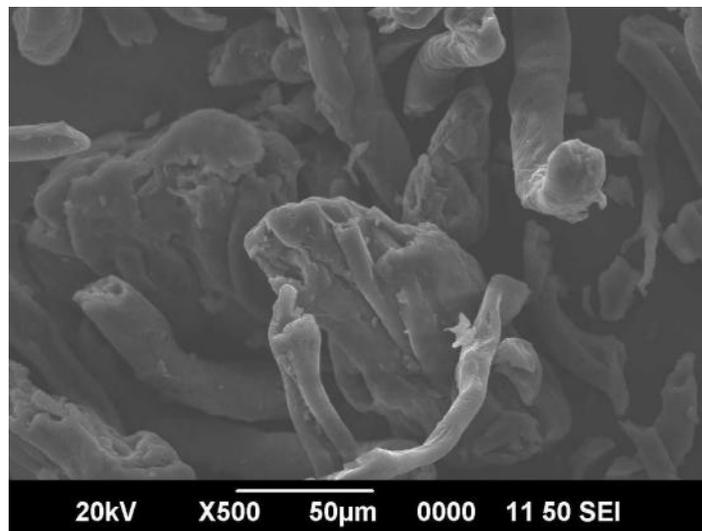


Figure 8: SEM image of CMC

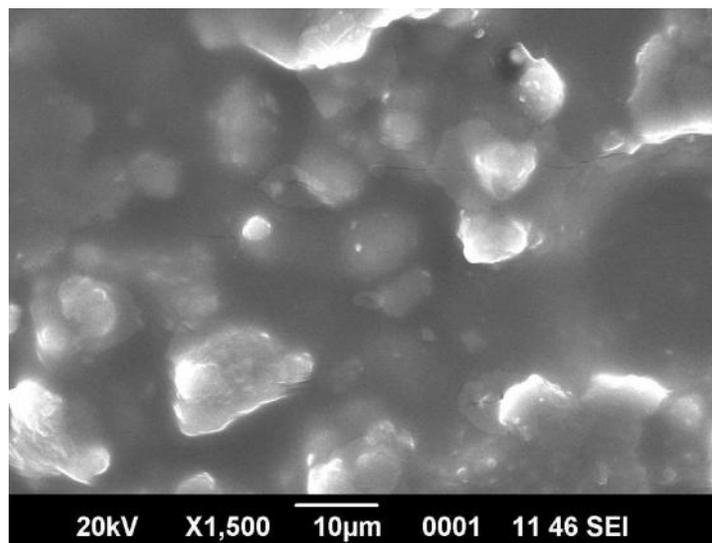


Figure 9: SEM image of PVA/S/CMC film

3.4 Thermal Analysis

The TGA/DTG curves of PVA/S and PVA/S/CMC blends are shown in Figures 10 and 11. The thermal decomposition temperature (T_{50}) of PVA/S/CMC blend shifted toward higher temperature compared to PVA/S blend (Table 1). This means that the addition of CMC increases the thermal stability of PVA/starch blends. This is due to the increase in crystallinity of the polymer blend after the addition of CMC and the molecular interaction between PVA, starch and CMC in the polymer blends.

The DTG curves of the prepared blends exhibited three distinct weight loss stages. The first stage of degradation represent the volatilization of easily degraded components, while the second stage exhibits the major mass loss predominantly the characteristic degradation of polymer structure (water elimination of PVA, decomposition of starch and decomposition CMC). The third stage of weight loss shows the decomposition of main chain of PVA [18-21].

Table 1: Decomposition temperatures at 10, 50 and 90% mass loss of prepared blends

Sample code	Temperature (°C)			
	T ₀	T ₁₀	T ₅₀	T ₉₀
PVA/S	39	257	300	450
PVA/S/CMC	40	290	340	460

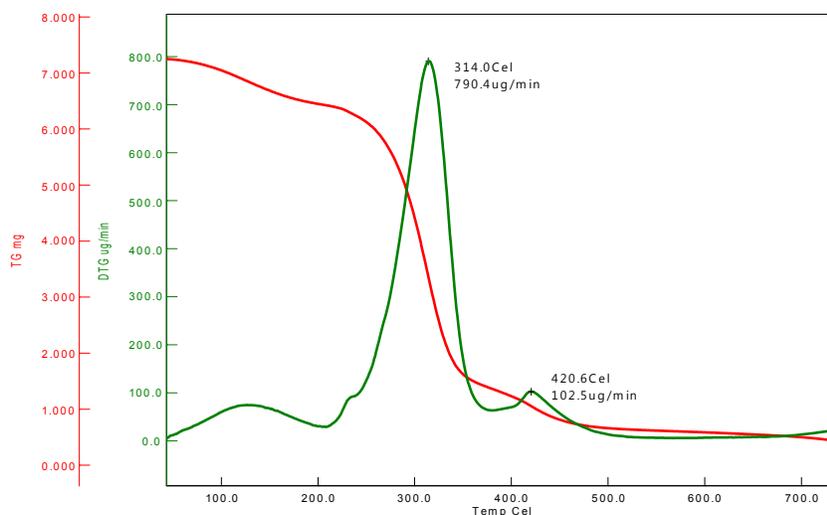


Figure 10: TG/DTG of PVA/S film

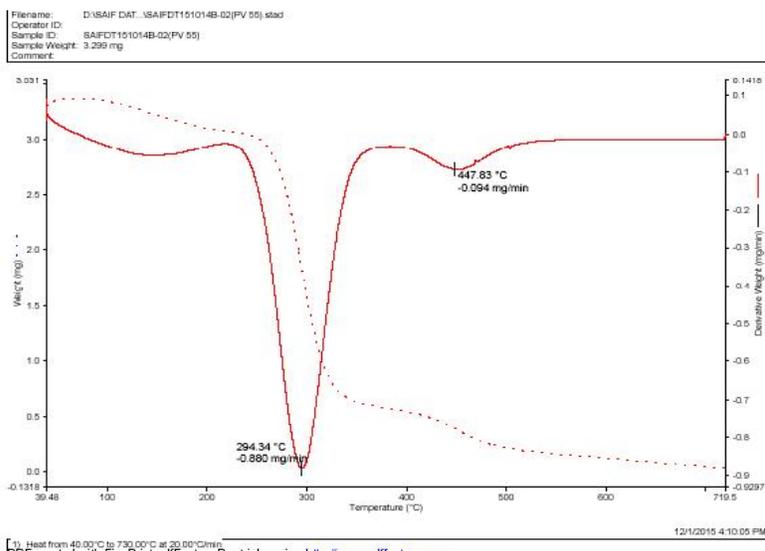


Figure 11: TG/DTA of PVA/S/CMC film

4. Conclusion

In this work PVA/S blend films were prepared with and without the addition of CMC. The prepared blend films were characterized by FTIR, XRD and SEM analysis. The thermal properties of the films were studied by TGA – DTG analysis. When CMC is added to PVA/S blends have shown better dispersion and improved thermal and morphological properties. Sharp IR signals indicate the presence of CMC within the PVA/S matrix. SEM images show the uniform dispersion and complete blending of CMC with PVA and starch matrix, XRD pattern shows the addition of CMC increases the crystallinity of the polymer and so the thermal stability is significantly high for blends with CMC than without CMC. The TGA – DTG results showed that the addition of CMC in the film structure improve the thermal property significantly. The thermo gravimetric analysis of prepared blend films indicated that, the thermal stability of PVA/S blend films was improved by the addition of CMC.

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