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Research Article

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Thermal and morphological characteristics of cellulose nanocrystals filled PVA/starch nanocomposites

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ABSTRACT

Among the natural polymers starch is of interest. It is regenerated from the carbon dioxide and water by photosynthesis in plants. Owing to its complete biodegradability, low cost and renewability, starch is considered as a promising candidate for developing sustainable materials. Blends of starch with synthetic polymers such as poly vinyl alcohol, aliphatic esters are prepared to achieve the desired performance for different applications. In such blends, the starch particles act as a promoter for plastic matrix biodegradation in applications such as drug delivery systems, hydrogels, bone cements and bone replacement or fixation devices. Nanocellulose can be used as a reinforcing filler to prepare composites with solutions of water soluble polymers, as well as with acrylic and other latex to change the viscosity and increase mechanical properties of dry composites. Of great importance has been the addition to biodegradable polymers, permitting both the improvement of thermo mechanical properties and acceleration in the rate of bio degradation.

Key words: polyvinyl alcohol, starch, nanocellulose, biodegradation.

INTRODUCTION

The severe environmental problems, including the increasing difficulties of waste disposal and the deepening threat of global warming caused by the non biodegradability of a number of polymers used in packing and agriculture field have raised concerns all over the world. To solve the problems caused by plastic waste, many efforts have been done to obtain an environmental friendly material. Most of the researches are focused on substitution of the petro based plastics by biodegradable materials with similar properties and low cost. These materials not only provide the convenience for daily life but also minimize the impact to the environment after being used [1].

Starch is one of the most abundant natural mixture polysaccharides, which makes it of great importance in food industry. Moreover, the natural availability, biodegradability [2], low cost, renewability [3] and its easiness to chemical changes have all made starch as useful natural product in various other applications. There has been growing interest in the development of starch based products, because starch is completely biodegradable, naturally abundant and cheap [4].

Poly vinyl alcohol is a versatile polymer with many applications, and it may be the only synthetic polymer whose backbone is mainly composed of C-C bonds that is biodegradable[5].It is well suited to be blended with natural polymers since it is highly polar and can also be manipulated in water solution[6]. It dissolves slowly in cold water, but at higher temperatures, it goes fairly fast into solution, more so around 90°C [7]. PVA is blended with corn starch as the starch is available in abundance at low price. Particularly, plant materials derived from renewable crops by-product or their industrially processed wastes offer a good source of fiber for applications [6]. Starch possesses similar function as PVA which is biocompatible and consumable by micro organism. When PVA and starch are blended together, the presence of hydroxyl groups (-OH) tend to form strong hydrogen bonding among the molecules and subsequently lead to synergistic stability and better system integrity. Both PVA and starch disperse homogeneously in solution cast film under the scanning electron microscopy [8].

Currently, numerous efforts are focused on the use of materials from renewable resources as reinforcement agents in nanocomposites. Among such materials cellulose nanocryatals (CNs) have attracted great interest due to their renewability, biodegradability, and spectacular mechanical properties [9]. CNs have high mechanical strength and elastic modulus values, which makes it an ideal component in many nanocomposites [10], arising from interactions between the crystalline and amorphous regions, as well as from the properties of these regions themselves. CNs can be isolated from renewable resources, including plants (Such as wood, cotton, wheat straw, rice straw etc), as well as from bacterial sources or animal tissue through acid hydrolysis [11].

In this work, CNs are isolated from rice straw and reinforced with PVA and Starch by physical cross linking method. The resulting polymer nanocomposite was analyzed by FT-IR, Scanning electron microscopy (SEM) and XRD analysis. Finally, the enhancement of the thermo mechanical properties was analyzed by thermal gravimetric analysis (TGA).

EXPERIMENTAL SECTION

The polymers PVA and starch obtained from E-Merck Ltd. (India) were used as such without any further purification. The reagents like NaOH, hypochlorite and H_2O_2 were AR grade.

i) Preparation of cellulose from rice straw

Cellulose was isolated from rice straw by soda pulping method. 10g of powdered rice straw sample was boiled with 200ml of 18% NaOH solution for one hour. The resulting mixture was filtered off and washed with distilled water to free the fibers. The resulting sample was then collectively bleached with hypochlorite in alkaline medium. The bleached sample was dried at 80^{o}C in the oven for 8h to obtained cellulose pulp.

ii)Preparation of Cellulose Nanocrystals

The obtained cellulose pulp was then hydrolysed with 65 wt % sulfuric acid at 55^{o}C for 45 min under vigorous mechanical stirring. The resulting suspension was cooled in an ice bath and filtered through No.1 glass sinter to remove unhydrolysed material and finally washed with deionised water by successive centrifugations until neutral pH. Finally the suspension was sonicated and a few drops of chloroform were added to avoid degradation. The suspension was kept refrigerated until use.

iii)Preparation of PVA/Starch-CNs composites

PVA (4.5g) was dissolved in 60 ml of water and starch (1.5g) in 40ml of water. The two solutions were mixed with vigorous mechanical stirring. 1% of CNs were mixed with 20 ml of water and sonicated to about 5 min. It was then added to the above suspension and continuously stirred for about 2 hours. Finally 1% of H_2O_2 was added and stirred for about 5min. Then the solution was poured into the mould and freeze dried for one week.

RESULTS AND DISCUSSION

Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR characteristic absorption bands of PVA/starch blend which can be assigned to the vibrations arising due to C=O,C-H,C-OH,C-O bonds are shown in Fig.1. A strong and broad band at 3306 cm^{-1} was assigned to the characteristic absorption peak of the stretching vibration of –OH. Hydroxyl group from residual water also contribute to the peak intensity. The peak at 2917 cm^{-1}was attributed to the asymmetric stretching of C-H. The weak peak at 1645 cm^{-1}was assigned to the adsorbed water and the peak arising at 1416 cm^{-1} to the -CH_2 bending with deformation. The peak at 1076cm^{-1}was attributed to the-C-O-H- bending and C-O stretching vibration coupled with O-H bending vibration.

The presence of CNs produced distinctive changes in the shape and intensity of the peaks (Fig.2). This is explained by the strong interactions present, mainly due to hydrogen bonding or network between the hydrophilic CNs reinforced nano particles and the PVA/starch continuous polymer matrix. Support of this explanation is provided by the band observed at 3306 cm^{-1}, which is characteristic of the stretching O-H from the intermolecular and intramolecular hydrogen bonds. The shape of this band was substantially different when comparing neat and the CN filled PVA/starch composite[9].

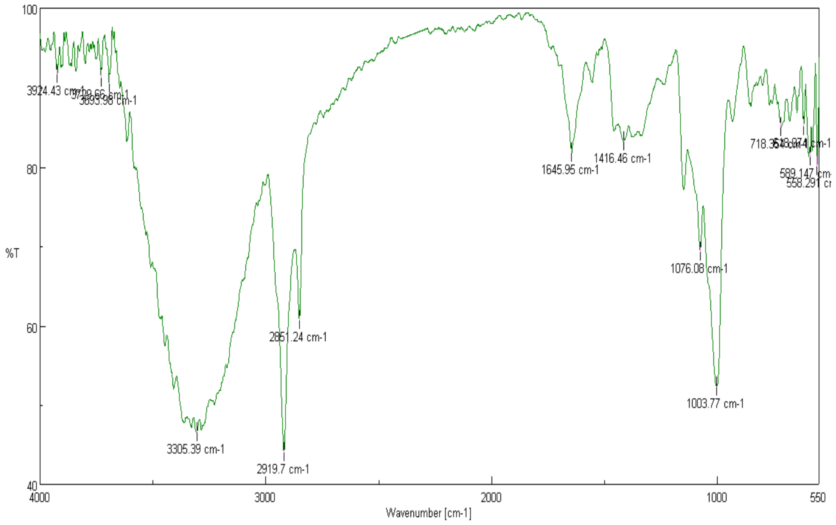

Fig.1. FTIR spectra of PVA/starch film

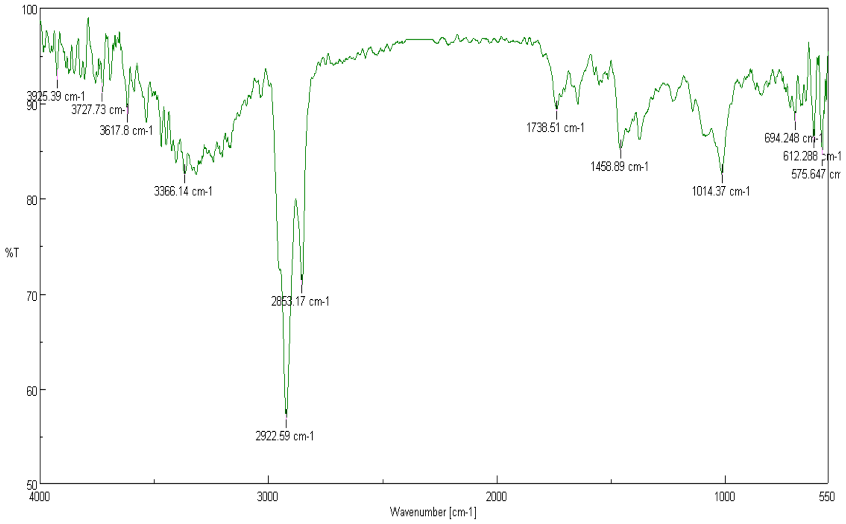

Fig.2. FTIR spectra of PVA/Starch- cellulose film

XRD analysis

The mean particle size of cellulose can be calculated from XRD analysis by using the Scherrer equation as follows.

$$D = \frac{0.89\lambda}{\beta cos\theta}$$

Where λ is the wavelength of X-ray source (Cu K_a= 1.5406 A^0), and β is the full width half maximum (FWHM) of the X-ray diffraction peak at the diffraction angle θ. The result shows that the average particle size of cellulose is 6nm, which confirms the nanocrystalline nature of cellulose.

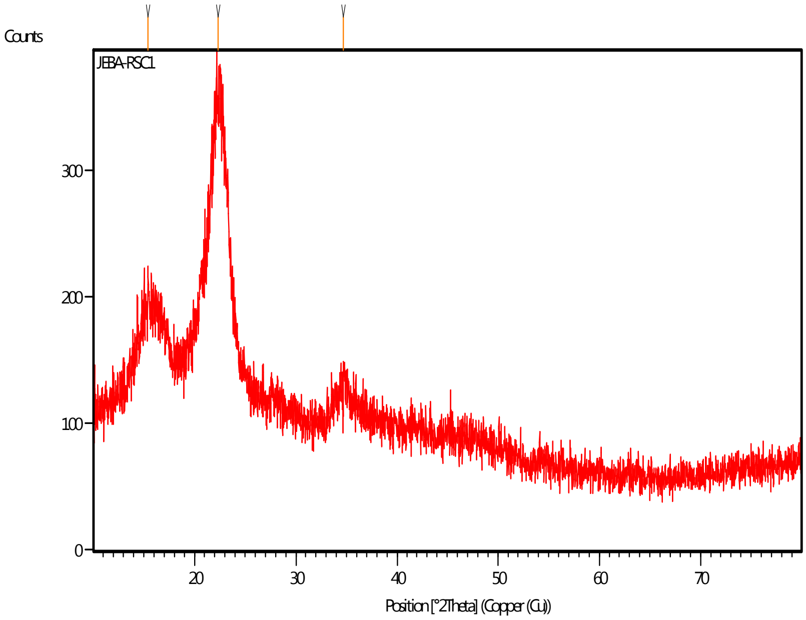

Fig.3.XRD of cellulose

Scanning Electron Microscopy (SEM)
The SEM photomicrograph for the PVA/Starch is shown in Fig.4.which shows the uniform distribution of PVA and starch throughout the surface.

The SEM photomicrograph for the CNs filled PVA/Starch is shown in Fig.5. Fibers were well distributed throughout the matrix and exhibited considerable cohesion with the polymer. The smooth, flexible, strong blends showed the presence of regions with fiber aggregates.

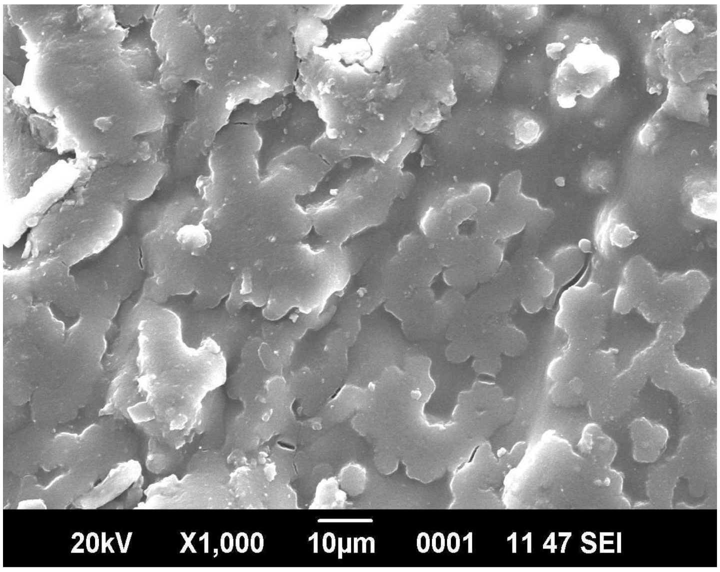

Fig.4. SEM image of PVA/starch film

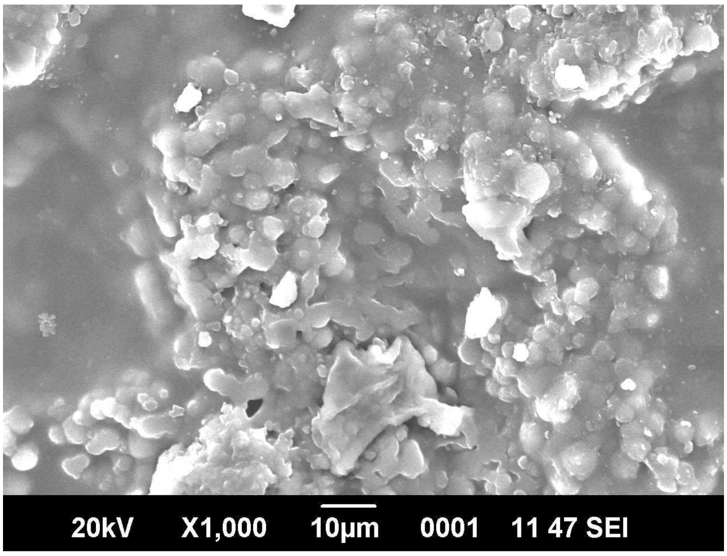

Fig.5. SEM image of PVA/starch - cellulose film

TGA-DTA

TGA has been extensively used in the study of polymeric systems. This analytical technique used to determine thermal stability and its fraction of volatile components by monitoring the weight loss of the sample in a chosen atmosphere as a function of temperature. Table.1. shows the TGA experimental results of PVA/starch, PVA/starch-CN composites. The samples were measured in the temperature range from 40^{o}C to 730^{o}C with a constant rate of 10^{o}C /min under nitrogen atmosphere. The TGA and DTA curves show that all samples exhibited three distinct weight loss stages. The first stage presents the loss of weakly physisorbed water while second stage exhibits the decomposition of side chain PVA. The third stage shows the decomposition of main chain of PVA [8].

The thermal decomposition of PVA/starch- CN filled nanocomposites shifted toward higher temperature compared to PVA/starch blend (Fig.6,7). This can be concluded that the addition of cellulose nanocrystals increases the thermal stability of PVA/starch blend and there is a molecular interaction between PVA, Starch and cellulose.

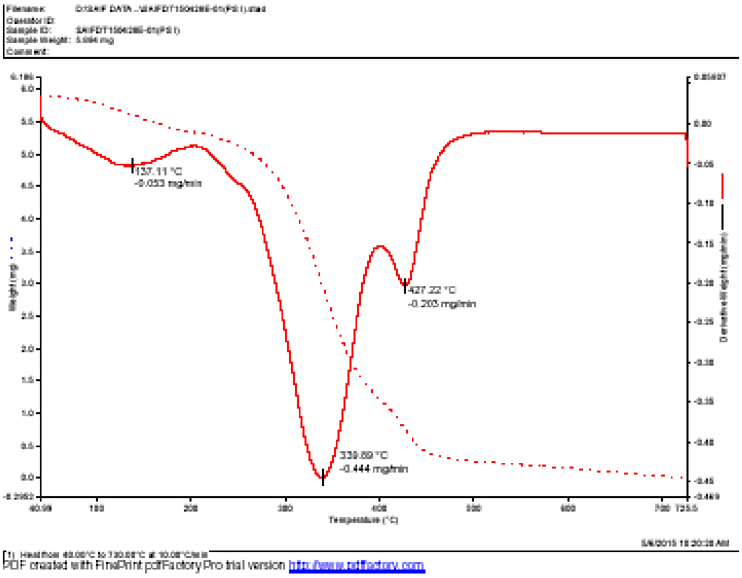

Fig.6. TGA-DTA curve of PVA/starch film

Table -1. Thermal characteristics of prepared blend and composite

Temperature(°C)	T_0	T_{10}	T_{20}	T_{50}	T_{90}
PVA/Starch	55	220	290	340	427
PVA/Starch-CN	55	220	305	356	432

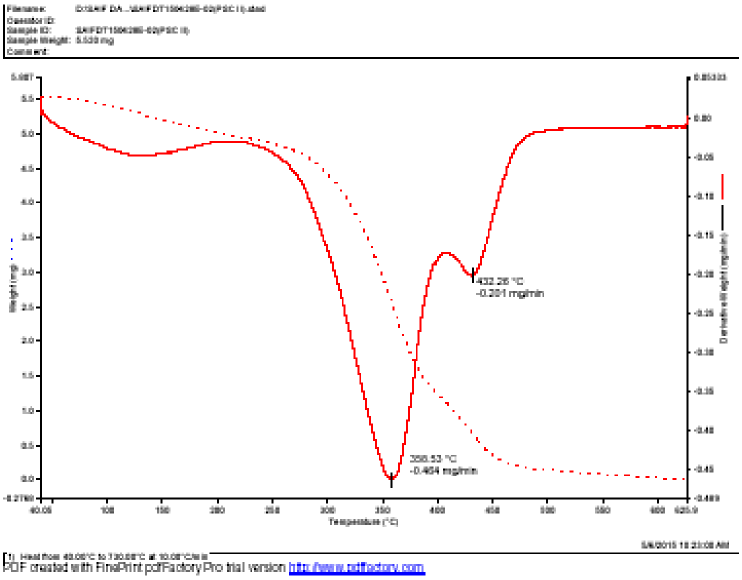

Fig.7. TGA-DTA curve of PVA/starch-cellulose film

CONCLUSION

PVA is a synthetic water soluble and biodegradable polymer. PVA has excellent mechanical properties and compatibility with starch, PVA/starch blend is assumed to be biodegradable since both components are biodegradable in various microbial environments. Development of nanocomposites based on nanocellulosic materials is a rather but rapidly evolving research area. Cellulose is abundant in nature, biodegradable, relatively cheap and is promising nano scale reinforcement material for polymers. The combination of biodegradable, renewable polymers is particularly attractive from an environment point of view. Further more, application of nanocellulosic fillers improves polymer mechanical properties and thermal properties in a more efficient manner than is achieved in conventional micro- or macro- composite materials. Packaging in one area in which nanocellulose reinforced polymer films could be of interest and, as shown, it is possible to produce such films with high transparency and with improved oxygen barrier properties. High oxygen barrier is often a requirement for food and pharmaceutical packaging applications and such improvement may be a key for capturing new markets.

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