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Experimental Studies of UV Irradiation Induced Changes in Optical, Mechanical and Microstructural Properties of PVA/Modified Cellulose Composite

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Abstract

Poly(vinyl alcohol) (PVA)/modified Cellulose composite films with 85:15 wt.% were prepared by solution casting method and subjected to UV irradiation for different intervals of time. The UV irradiation induced modifications in optical, mechanical and morphological properties were studied. The FTIR results confirm the chemical interaction between PVA and Cellulose. The optical absorption also supports the formation of crosslinked network in the polymer composite. The XRD result shows an increase in the amorphousness with increase in UV irradiation time. The Young's modulus (YM), tensile strength (TS), stiffness and percentage (%) elongation at break (% EB) of the composite films increase with increase in UV irradiation time. The Scanning Electron microscope (SEM) images confirm the

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photosensitive nature of the composite films, studied up to 72 hours UV irradiation.

Keywords: Cellulose, Crosslinking, Mechanical properties, poly (vinyl alcohol), UV irradiation

1. Introduction

In recent years, there has been growing interest in developing biopolymers in the field of tissue engineering, microchannel structures, due to their environment-friendly nature. Solid polymer composites obtained from natural polymers such as starch, chitosan, pectin, cellulose derivatives etc., have attracted attention due to their non-hazardous nature to the environment, when used in large amounts. The use of these biodegradable polymers has contributed to a reduction in environmental problems [1]. But due to their low mechanical, barrier, water resistance and thermal properties compared to the synthetic polymers, there has been a trend toward the production of degradable natural and synthetic polymers and natural/synthetic polymer composites [2, 3].

Among biodegradable synthetic polymers, cellulose is one of the most attractive polymers because of its availability, degradation, and good mechanical properties. It has the advantages of widespread availability, low cost, renewable, biodegradable, biocompatible and highly flexible. Cellulose-based biopolymer composites have come to the attention of researchers because of their chemical composition, presence of large amount of easily accessible hydroxyl units that can be used for the attachment of variety of functional groups, which gives it extremely good properties for application in many electrochemical devices, such as cellular phones, thin credit cards, and laptop, computers, electric vehicles, starting assist for diesel locomotives, military, and medical applications [1-4].

Recently, Chemical modification of cellulose is an important route for the production of multifunctional materials and the modified cellulose (mCellulose) has been used as reinforcements for various composites due to its excellent mechanical performance and fully biodegradable in a wide variety of environmental conditions [5]. The processes of chemical modifications of cellulose usually result

in lower degree of polymerization and weaker inter and intramolecular hydrogen bonding of the cellulose chains, which may lower the mechanical properties of the material. Therefore, alternative methods to enhance the mechanical performance are essential.

Blending is a convenient process for developing high strength polymer based materials. Blending of Cellulose and poly(vinyl alcohol) (PVA) is favorable, because, both of them are polar substances. Moreover, PVA is a synthetic water soluble polymer which is produced by hydrolysis of poly(vinyl acetate). It is a biodegradable polymer, highly hydrophilic, non toxic and low cost polymer with good mechanical strength, high thermal and chemical stability, and excellent film forming properties. The Cellulose and PVA have highly polar hydroxyl groups, tend to form inter and intramolecular hydrogen bonds. The formation of hydrogen bonds between hydroxyl groups of Cellulose and PVA tends to promote the localized stability and subsequently improve the miscibility. Further, there are only few reports on biodegradable polymers for use in electronic devices due to lack of mechanical strength. UV irradiation is simple and cheap procedure to improve mechanical properties and structural and functional units of the polymers can be controlled [1-3, 6-7]. It is based on photodegradation of polymers, i.e., the main chain scission leads to a decrease of molecular weight, and predominant cross linking to an increase of molecular weight.

In view of this, we have undertaken the investigating of the effect of UV irradiation on the compatible PVA:m Cellulose polymer composite film with 85:15 wt.% ratio. The effect of UV irradiation on optical, mechanical and morphological properties of PVA:mCellulose composite films were studied using Fourier Transform Infrared (FTIR) and UV-Visible spectrophotometer, X-ray diffraction, Universal Testing Machine (UTM) and Scanning Electron Microscope (SEM).

2. Experimental

2.1 Materials

The PVA was procured from SDFCL (sd fine-chem limited) Mumbai, India, with molecular weight $M_w \approx 125,000$ and its degree of saponification is 86%-89%. The fibre used in this work was commercial microcrystalline cellulose supplied by Loba Chemie, India, 2-(Trifluoromethyl) benzoylchloride, pyridine were purchased from Aldrich and used as received.

2.2 Modification of Cellulose

Initially, the calculated amount of Cellulose was treated with sodium hydroxide solution at room temperature and stirred for 2 hrs. Then, the solid obtained was filtered off, and after that, the salt formation was confirmed by solubility test, since it is freely soluble in water. Then the salt was treated with 2-(Trifluoro-methyl) benzoylchloride in presence of pyridine as a base cum solvent and stirred overnight at 100 °C. Then, dumped into water; solid obtained was filtered off. This product was confirmed by IR analysis, which shows the absence of peak at 3332 cm^{-1} .

2.3 Preparation of Films

The PVA and mCellulose with 85:15 by wt.% was added to doubly distilled water at room temperature and then allowing the solution to stir for 36 hours for complete dissolution. The solution so obtained was poured on to a cleaned glass plate and dried at room temperature. After drying, the film was peeled from the plate and kept in vacuum desiccators for further study. The thickness of the film is in the range of 100-200 μm measured using Mitutoyo-7327 dial thickness gage of accuracy 0.001mm. The prepared PVA:mCellulose composite films with 85:15 wt.% was subjected to UV irradiation for different intervals exposure time with 254 nm UV lamp.

3. Sample Characterization

The prepared PVA:m Cellulose composite films with 85:15 wt.% are irradiated under UV lamp G6T5, purchased from GE Lighting

of short wavelength (254 nm) with 6 W power, with irradiance of $17.7 \mu\text{W}/\text{cm}^2$ and UV output intensity of 1.7 W. The samples were placed at a distance of 5 cm from the UV lamp in a tightly sealed wooden box. Fourier transformation infrared spectroscopy (FTIR) analysis was carried out using SHIMADZU FTIR-8700 Spectrophotometer in the wave number range $4000\text{--}400 \text{ cm}^{-1}$ with the scanning resolution of 4 cm^{-1} and recorded in transmittance mode. The UV-visible spectra were recorded using Shimadzu-1800 spectrophotometer in the wavelength range of 195–800 nm. The XRD measurements were performed using Bruker D8 advance X-ray diffractometer with Ni-filtered, $\text{Cu-K}\alpha$ a radiation of wavelength 1.5406 \AA with graphite monochromator. The morphologies of the prepared composite films were examined using JEOL JSM-6390LV SEM with resolution of 3 nm specimen holder of diameter 10 mm. Mechanical properties of the prepared composite films were measured with Lloyd LRX plus universal testing machine (UTM) equipped with a 5 kN load cell. The film samples in the form of strips of 50 mm x 25 mm sizes were fixed in grips and the mechanical measurements were performed at room temperature with a constant rate of 25 mm/min and gauge length of 50 mm.

4. Result and discussion

4.1 FTIR studies

The FTIR analysis was carried out to compare the changes in the structure of cellulose and PVA with respect to different intervals of UV exposure time are shown in Fig. 1. The IR bands of cellulose at 3429 cm^{-1} and 2930 cm^{-1} are due to -OH and C-H vibrations respectively. The band at 1729 cm^{-1} is assigned to C=O stretching vibration and at 1645 cm^{-1} corresponds to O-H bending of adsorbed water. The intensity of the band at 1426 cm^{-1} assigned to C-H bending of polymer matrix. The IR bands at 1267 cm^{-1} and 1091 cm^{-1} are assigned to CH_2 wagging and C-O stretching of PVA respectively [6]. These bands are shifted to 3443, 2918, 1719, 1636, 1406, 1258, 1058 cm^{-1} respectively for UV irradiated composites. The intensity of the composite film drastically decreased with increase in UV irradiation time, can be attributed to the formation of new products due to photochemical reactions [3]. The shift in the 3429

cm^{-1} band to 3443 cm^{-1} (hydroxyl groups and inter/intramolecular interactions) indicates the decrease in crystallinity of the PVA:mCellulose composite with increase in irradiation time. The ester formation in the PVA:mCellulose matrix takes place between the carboxylic group of mCellulose and $-\text{OH}$ groups of PVA with increase in the irradiation time, results in crosslinking network between the two polymers. For the highest UV irradiation time (72 hours), the polymer resulted in the elimination $-\text{OH}$ groups in PVA:mCellulose. FTIR spectra also show a band at 1426 cm^{-1} assigned to C-H bending vibration together with plane deformation of O-H, meaning that both C-H and O-H bonds are cleavages during irradiation.

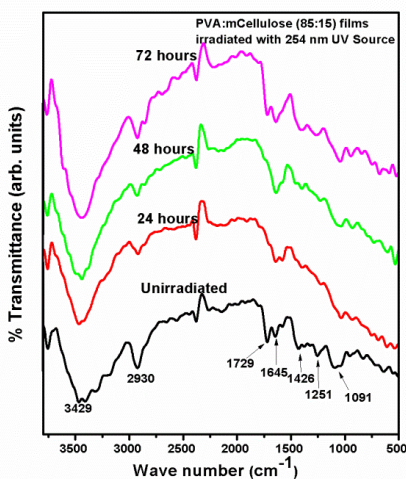


Fig. 1. FT-IR spectra of un-irradiated and UV irradiated PVA:mCellulose (85:15) composite films for different intervals of UV exposure time with 254 nm UV lamp

4.2 UV-Visible absorption studies

The UV-Visible absorption spectra of unirradiated and UV irradiated PVA:mCellulose composite films are shown in Fig. 2. It is clear that there is no absorption band in the visible region for all the investigated samples, since the films are transparent. The shoulder type peak at 213 nm is assigned to $n \rightarrow \pi^*$ transition and the absorbance increases with increase in UV irradiation time.

The broad peak observed around 274 nm with UV irradiation is assigned to $n \rightarrow \pi^*$ inter-band transition, which is shifting to 281 nm for 24 hours and 48 hours, and shifted to 280 nm for 72 hours UV irradiation composite films. The shift of absorption peaks towards higher wavelength region is due to the formation of free radicals or cross linking [8]. The broadening of the absorption peaks with the irradiation time is attributed to the formation of an extended system of conjugated bonds, i.e. the formation of defects in the polymer matrix, which may further results of new energy levels leading to the broadening of the peaks.

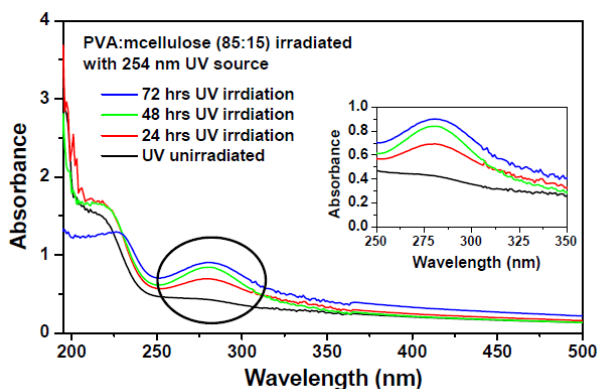


Fig. 2. UV-Visible absorption spectra of unirradiated and UV irradiated PVA:mCellulose composite films for different intervals of UV exposure time.

4.3 XRD studies

X-ray diffraction (XRD) analysis is a well known technique used for phase identification of materials, both in crystalline and amorphous regions. Cellulose is a semi-crystalline polymer and even after its chemical modification, the cellulose remains semi-crystalline, leading to conclusion that the initial crystallinity was retained. Pure PVA is also a semi-crystalline polymer, contains crystalline and amorphous regions [8].

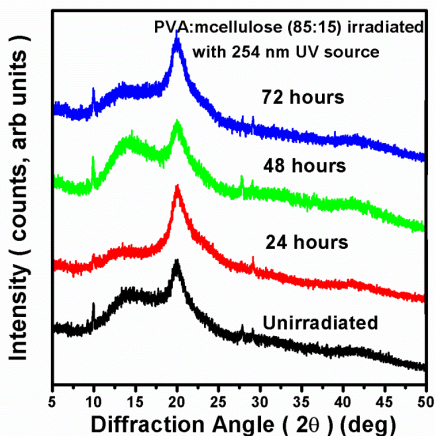


Fig. 3. XRD patterns of Unirradiated and UV irradiated PVA-mCellulose (85:15) composite for different irradiation times.

The XRD patterns of the UV irradiated PVA:mCellulose films with different irradiation times are shown in Fig. 3. The XRD patterns for 24 hours does not show much variation, but for 48 and 72 hours irradiated composite films, the semicrystalline peaks at 20.2° shifts toward lower angle and a shoulder peak (amorphous phase) at $2\theta = 13\text{--}17^\circ$ changes in to amorphous halos with decrease in intensity reveals the suppression of crystallinity from 86% for pure blend to 63% for 72 hours UV irradiation in PVA:mCellulose blend as shown in the Table 1. The UV irradiation also alters the crystallite size within the PVA/mCellulose blend, confirming microstructural modifications in PVA: mCellulose composite.

Table 1: XRD results of UV irradiated PVA:mCellulose blend.

| UV irradiation exposure time (hrs) | 2θ (deg) | Crystallinity (%) | Crystallite size P (nm) |
|------------------------------------|-----------------|-------------------|---------------------------|
| 0 | 20.20 | 86 | 4.92 |
| 24 | 20.15 | 77 | 4.76 |
| 48 | 20.02 | 65 | 4.83 |
| 72 | 19.94 | 63 | 5.10 |

4.4 Mechanical studies

The mechanical stress-strain curves of the PVA-mCellulose of unirradiated and UV irradiated composite films are shown in Fig. 4 and the variation of Young's modulus (YM), Tensile strength (TS), stiffness and % elongation at break (%EB) are depicted in Fig. 5. With the increase in UV irradiation time, the increase in YM, TS, stiffness and %EB is observed (up to 48 hours) in PVA: mCellulose composites. This increase is may be due to the inter-crosslinking between the neighboring cellulose molecules in the polymer composites and also due to absence of two opposing phenomena (photo-crosslinking and photo-degradation) under UV radiation. For 72 hours UV irradiated composites, the higher value of TS, YM, %EB is maintained indicating that, there is no main chain broken and degrade into fragments [9, 10].

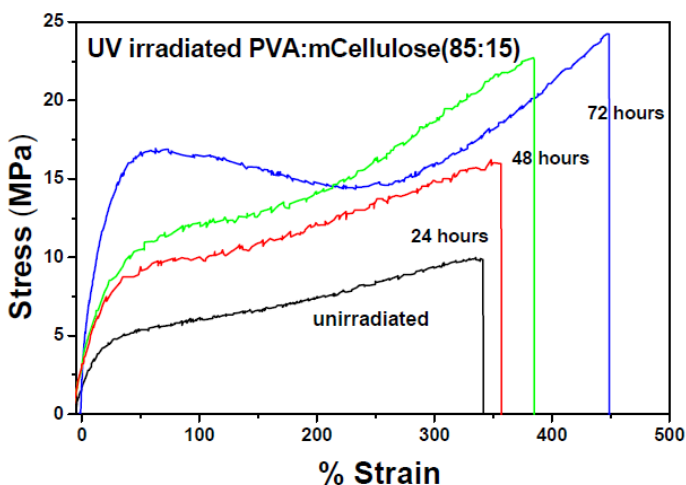


Fig. 4. Stress - strain curves of unirradiated and UV irradiated PVA:mCellulose composite.

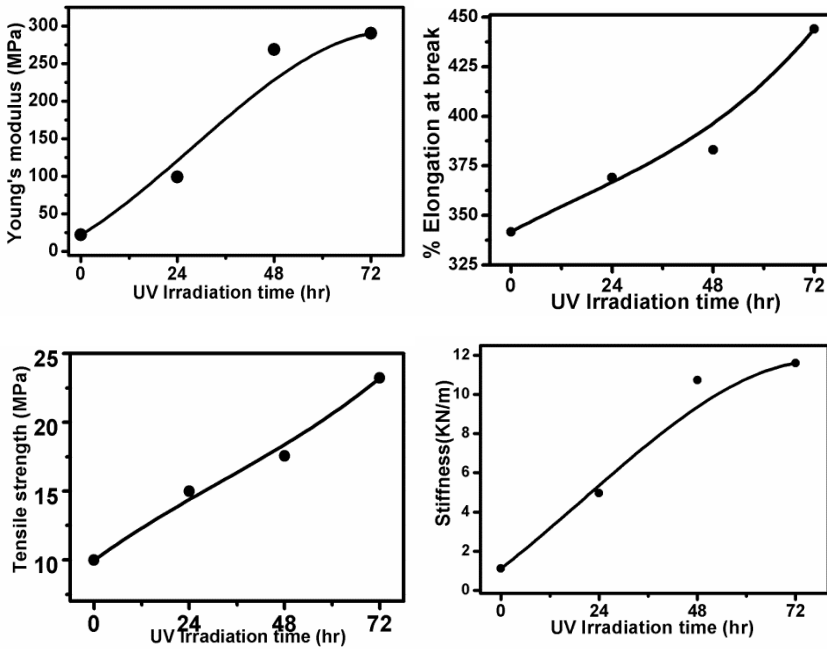


Fig. 5. Young’s modulus (YM), tensile strength (TS), stiffness and % elongation at break (%EB) against different intervals of UV irradiation in hours (hr).

4.5 Morphological studies

The surface morphologies of unirradiated and UV irradiated PVA:mCellulose (85:15) composite films are shown in Fig. 6. In the pure PVA:mCellulose (85:15) composite film the fibre is less visible, since a composition of mCellulose is only 15wt.% and smooth morphology is closely related to the amorphous nature of the composite. The SEM micrographs of UV irradiated PVA:mCellulose composite films exhibit a smooth and homogeneous surface with no pores and interface layer, indicating the complete miscibility and amorphous nature [10]. Whereas there is no roughness of the film surface and formation of small pores are found in UV irradiated films indicating only photo-crosslinking process has taken place and not the photo-degradation in the PVA:mCellulose composite [11].

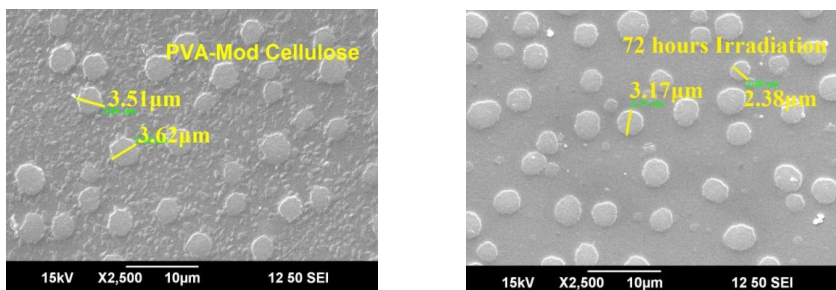


Fig. 6. SEM micrographs of unirradiated and 72 hours UV irradiated PVA:mCellulose (85:15) composite films.

5. Conclusions

The PVA:m Cellulose composites (85:15 wt.%) prepared by solution casting method and irradiated with UV source for different intervals of time. The FT-IR studies confirm the chemical interaction between PVA and mCellulose and structural changes upon UV irradiation. The UV-Visible absorption study reveals the formation of crosslinking network. The XRD results show that the UV irradiation modifies the microstructure of PVA:mCellulose composite, results in increasing amorphous nature. The increase in YM, TS, %EB and stiffness with increase in UV irradiation time confirms only photo-crosslinking and not the photo-degradation process. The SEM study of the UV irradiated films reveals that the surface of the composite has high photo-sensitivity.

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