

Fabrication and Characterization of PVA-Gelatin-Nano Crystalline Cellulose based Biodegradable Film: Effect of Gamma Radiation

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Abstract: Poly Vinyl Alcohol (PVA) films were prepared using solution casting. The Tensile Strength (TS), Tensile Modulus (TM) and Elongation at break (Eb) of the prepared films were found to be 23.58 MPa, 32 MPa and 302% respectively. Moisture content and water uptake analysis were also checked. Then, gelatin and nano crystalline cellulose (NCC) were incorporated into PVA film and again physico-mechanical properties were measured. The TS, TM and Eb values of PVA/Gelatin-based films were 23.57 MPa, 114.58 MPa, 48.10% respectively. On the other hand, PVA/Gelatin/NCC-based films showed the TS, TM, and Eb values of 32.92 MPa, 129.8 MPa, 58.5% respectively. Thermal degradation test was accomplished by Thermo-Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). Spectroscopic analysis was also done by Fourier Transfer Infra-Red (FTIR). The soil degradation test confirmed the inherent biodegradable nature of the films. The prepared bio-polymeric films were exposed to gamma radiation. It was found that at 6 kGy dose the mechanical properties of the films improved significantly.

Keywords: Polyvinyl Alcohol, Nano Crystalline Cellulose, Biodegradable, Gelatin, Gamma Radiation.

INTRODUCTION

Investigation is being carried out to design an eco-friendly packaging materials in place of petroleum-based synthetic polymers such as polyethylene (PE) and polypropylene (PP). Presently, synthetic polymers are widely used as packaging materials due to their excellent thermo-mechanical and barrier properties. Moreover, these synthetic polymeric materials are also low-priced. Synthetic polymers are non-biodegradable and a threat to the environment. It is high time to develop an alternative packaging films which are biodegradable in nature [1-2]. The biodegradable polymers which can replace the synthetic polymers include poly lactic acid, polycaprolactone, poly glycolic acid, chitosan, alginate, cellulosic materials. Bioactive packaging is an intelligent or smart system involving interactions between package or package components and food or internal gas atmosphere and complies with consumer demands for high quality, fresh-like, and safe products. It is the most favorable smart packaging systems for regulatory of spoilage and pathogenic micro-organisms. It is a ground-breaking approach to improve the condition of the packaging to extend shelf-life or expand safety or sensory properties while preserving the quality of the food [3-4].

Polyvinyl alcohol (PVA) is one of the most common water-soluble polymers produced on a huge scale commercially. PVA has great probability in various industrial applications, such as emulsifier, a stabilizer for colloid suspensions, adhesive. Because of its outstanding properties, such as good barrier property, high strength, good film-forming property and highly hydrophilic property, PVA has been used in the form of fibers, films, hydrogels, and glues. Because the melting point (T_m , typically 226 °C) and the decomposition temperature of PVA are very close, the thermal degradation also undergoes simultaneously during melting [5-6]. PVA is a semicrystalline polymer in which high physical interactions between existing polymer chains, due to the hydrogen bonding between hydroxyl groups. Hydrogen bonding also controls the thermal properties of PVA. PVA is a reasonable polymer which owns desirable properties such as water solubility, biocompatibility, and biodegradability [7-8].

Gelatin is a dissimilar mixture of water-soluble proteins of high average molecular mass which are absent in nature but can be derived by the hydrolysis of collagen, a protein of mammal external protective tissues, by boiling skin, tendons, ligaments, bones, etc. with water. It absorbs 5–10 times its weight of water to form a gel in solutions below 35–40°C. Commercially gelatin is obtained as a colorless or slightly yellow, transparent, brittle, practically odorless, tasteless sheets, flakes, or coarse powder [9-10]. There are unbounded potentials for amending the properties of gelatin due to the presence of bi and poly functional

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organic and inorganic compounds that can interact with the particular gelatin functions is very large indeed. Chemical modifications, aiming at an increase in the degree of protein cross-linking varied upon the reactivity of the protein constituents, the specificity of the modifying agent, the amino acid composition, and the reactivity of amino acid and the tri-dimensional structure of the protein molecule. Generally, chemical reactivity of proteins depends on the side chain, the amino acid composition and the free amino and carboxyl groups. The most responsive protein groups are serine (primary-OH), hydroxyproline (secondary-OH), threonine (secondary-OH), tyrosine (phenolic-OH), aspartic acid (-COOH), glutamic acid (-COOH), lysine (-NH₂) and arginine (-C(:NH).NH₂). Crosslinking of gelatin macromolecules is acknowledged for increasing the viscosity of the gelatin solutions, strength and melting points of gelatin gels [11-12].

Nanocrystalline cellulose (NCC) is a stimulating nanomaterial for the construction of cheap, lightweight and very strong nanocomposites. NCC is found from native cellulose sources and composed of nanometer-sized rod like particles. The NCC used in this experiment is extracted from bleached softwood kraft pulp by controlled acid hydrolysis. Wood cellulose nanocrystals possesses cross-sectional dimensions of 6–7 nm and lengths ranging from 80 to 100 nm. NCC is estimated to show high stiffness since the Young's (elastic) modulus along the axis of the cellulose nanocrystals is 137 GPa or more. The tensile strength (TS) of the crystal structure was evaluated by modeling to be approximately 7.5–7.7 GPa. It is predicted that NCC nanocomposites may provide value-added materials with superior performance and extensive applications for the next generation biodegradable materials [13-14]. Cellulose nanocrystals are ordinary and have excellent reinforcing agent for thermoplastic polymers owing to their outstanding mechanical properties and large aspect ratio. Usually, dried NCC aggregates due to its small size, high surface energy, and strong intrinsic van der Waals forces [15-16].

Nowadays, there has been a continuous and rapid growth in the development and application of radiation techniques including gamma radiation. Gamma radiation is a type of ionizing radiation. Irradiation of polymers with high-energy gamma rays are responsible for the formation of very reactive intermediates in the forms of excited states, ions, and free radicals. These intermediates are almost spontaneously consumed in several reaction pathways which ultimately produce oxidize products, grafts, crosslinking, and scission of

main or side chains (degradation). The relative extent of these alterations depend on the nature of the polymer and the treatment condition during and after irradiation, and close control of these factors makes possible the modification of polymers by radiation processing [17]. The several advantages of gamma radiation are continuous operation, minimum time requirement, less atmospheric pollution, and curing at ambient temperatures. Radiation induced processes also have many advantages other than conventional methods. Catalysts or additives are not required to initiate the reaction, as absorption of radiation energy by the polymer backbone generally initiates a free radical process. Moreover, the radiation dose rate can effortlessly control and make the reaction easier and precise. Finally, radiation processing is temperature liberated and is therefore a zero activation energy process is considered [18].

In this study, the purpose was to fabricate a biodegradable film using the PVA, Gelatin and NCC and observe the thermo-mechanical properties and changes due to radiation dose.

MATERIALS AND METHODS

Materials

PVA was purchased from MERCK-Germany, having molecular weight 145000 g/mol and 99% hydrolyzation. The purified gelatin was obtained from Merck-Germany. The Nano Crystalline Cellulose (NCC) was extracted from bleached softwood kraft pulp. The particle size was 8-12 nm and length had a range of 80-100 nm. Deionized water was collected from the laboratory of Institute of Radiation and Polymer Technology.

Preparation of Biodegradable PVA-Based Films Using Solution Casting

1gm of PVA crystals was weighed by electronic balance and taken into a petri dish. Then the measured PVA was taken and poured into 100ml hot deionized water. A magnetic stirrer was placed to ensure the homogeneous mixing of PVA. Then the lid of the beaker was sealed using a glass plate. The temperature was also checked with the interval of time to maintain the parameters. It took about 2hour to dissolve the PVA completely. Then the warm solution was cast in a glass mold. After 24hrs at Relative Humidity (RH) 65% and temperature at 30°C the film was dried and then peeled off using a spatula and was stored in a desiccator containing blue silicon beads

prior to characterization. Thus the control sample was prepared. After that, 1gm of gelatin was taken in different beaker and marked to 100ml by the freshly prepared base solution. Then the 10% NCC of the total weight was added to the PVA-Gelatin solution and mixed using Ultrasonicator. Finally the film was casted into the silicon paper covered glass mold and kept in desiccator for further characterizations.

Evaluation of Mechanical Properties

Tensile strength (MPa) and elongation at break (%) of the films were examined by the Universal Testing Machine (Hounsfield series, model, INSTRON 1011, UK) with a crosshead speed of 10 mm/min. The experiment was carried out according to ASTM D 638-01. The size of the experimental sample were: 80 mm × 10 mm.

Determination of Thermal Properties

Thermal properties of biopolymeric films were investigated by thermo gravimetric analysis (TGA). TGA was performed under nitrogen atmosphere from room temperature to 800°C at a rate of 10°C/min with a TGA-50 instrument (Shimadzu Cooperation, Japan). The weight of the sample varied from 2 to 3 mg. the maximum temperature range for this instrument was from room temperature to 800°C and the cell was made of alumina. Thermal properties were evaluated using differential scanning calorimetry (DSC). DSC was performed using DSC-60 (Shimadzu Cooperation, Japan), under liquid nitrogen atmosphere and temperature ranges from room temperature to 400°C. The heating rate was 10°C/min and weight of sample varied from 2 to 3 mg.

Characterization Using Spectroscopic Method

A spectrum two spectrophotometer (Perkin-Elmer) equipped with an attenuated total reflectance (ATR) device and a high linearity lithium tantalite (HLLT) detector was used for recording the spectra. The device was used for analysis of solids. Spectrum 10TM software was used for spectral identification. Films were stored in a desiccator containing blue silica gel for 72 minutes at room temperature. The films were then placed on a zinc selenide crystal, and the analysis was performed within the spectral region of 650–4000cm⁻¹. After attenuation of total reflectance and baseline correction, spectra were normalized with a limit ordinate of 1.5 absorbance units.

Assessment of Physical Properties

Weighted test specimens were immersed into glass beakers containing 50ml of deionized water. The test was carried out for 30minutes at 30°C temperature. After 30minutes, samples were withdrawn from the beaker, wiped out properly for removing the surface moisture and then reweighed. Water uptake of the films was measured by a weight difference methodology. The equation for water uptake was as follows: Water uptake (%) = (Wwet – Wdry)/Wdry × 100, where Wwet indicated the weight of the sample after immersion in water and Wdry represented the weight of the film before immersion. Moisture content analysis was done by using KERN-D85. It runs at 120°C and gives the moisture content result on percentage basis.

Determination of Crystalline Properties

Crystallinity of the samples were determined using the X-Ray Diffraction (XRD) process. The XRD spectra of NCC was analyzed by the Rigaku ULtima IV X-RAY diffractometer (Rigaku Americas Corporation, Japan). The ultima IV was equipped with unique and patented cross beam optics (CBO). The sample was cut into a square shape with the length of less than 1.5 cm.

Analysis of Surface Morphology

Surface morphology of the samples were evaluated using Scanning Electron Microscopy (SEM). The SEM analysis was done using the machine purchased from JEOL, Japan. The samples were cut into shapes of 1cm × 1cm.

Degradation Test of the Film

The biodegradability test of the films in soil medium was investigated. For this purpose, sample biopolymeric films were weighed individually and buried in the garden soil for a period of 7 days. After that, samples were taken out from soil carefully and degradation of the samples was inspected visually.

Irradiation Effect

The PVA-Gelatin-NCC based biopolymeric films were taken in an air tight zipper poly bag. Then the films were exposed to gamma rays, generated from a Co-60 source in the Institute of Radiation and Polymer Technology, Atomic Energy Research Establishment, Savar, Dhaka. The doses of radiation were 6kGy. Prior to analysis, the samples were kept in a desiccator for 24hours.

RESULTS AND DISCUSSIONS

Physico-Mechanical Properties of the PVA-Based Biopolymeric Films

Fabricated films of PVA, PVA-Gelatin and PVA-Gelatin-NCC were experimented about their physico-mechanical properties before and after radiation dose. Significant changes were found which are illustrated into Tables 1 and 2.

Table 1 describes the mechanical properties and moisture content analysis of the four PVA-based Gelatin-NCC biopolymeric films. In this table, mechanical evaluation of the tensile strength (TS), tensile modulus (TM) and elongation at (Eb) are shown. Moisture content denotes the physical properties of the biodegradable films. From the data, we can clearly visualized the mechanical properties of PVA, PVA-Gelatin and PVA-Gelatin-NCC films. The TS, TM and Eb values of PVA film were found to be 23.58 MPa, 32 MPa and 302% respectively and for PVA-Gelatin film these values were found to be 26.2 MPa, 115.58 MPa and 48.10% individually. With the incorporation of 10% NCC into PVA-Gelatin film the mechanical properties were increased significantly. The TS, TM and Eb values were obtained to be 32.92 MPa, 129.8 MPa and 58.5% correspondingly. The outstanding properties were found for the incorporation of NCC can be explained from the structures of PVA, Gelatin and Cellulose. The presence of protein molecules in gelatin forms carbonyl groups, hydrogen bonds, nitryl bonds, etc. But, incorporation of NCC in PVA-Gelatin film increases the stiffness and and

strength. The moisture contents of the films eg, PVA, PVA-Gelatin and PVA-Gelatin-NCC were found 21.3, 20 and 18.7% respectively.

The Table 2 demonstrates the physico-mechanical properties of the PVA, PVA-Gelatin and PVA-Gelatin-NCC-based biopolymeric films after the 6 kGy radiation dose. Radiation dose significantly changed the TS, TM and Eb values of the films. After radiation the TS, TM Eb values of PVA films were 27 MPa, 62.5 MPa and 314.5%, for PVA-Gelatin film those were denoted 29.32 MPa, 157.8 MPa and 54.10% separately. Addition of NCC improved the mechanical properties drastically. The TS, TM and Eb values were found to be 40.38 MPa, 139.7 MPa and 14.9% respectively. The moisture content percentage was found for PVA, PVA-Gelatin and PVA-Gelatin-NCC films were recorded 18%, 19.8% and 14.9%. After radiation the cross-linking was responsible for this drastic changes into mechanical properties. Water uptake test was carried out upto 30 minutes of the films before and after radiation. The water uptake percentages are showed in Table 3.

Table 3 illustrates the water uptake percentages of PVA, PVA-Gelatin and PVA-Gelatin-NCC-based biopolymeric films before radiation dose. The water uptake percentages of the films raised gradually then after a certain time the water uptake percentages reduced. With the immersion into deionized water the film tried to absorb water upto 100% and even higher. After reaching the peak level, the films started to dissolve into water and reduced its weight rapidly. Gelatin had better water barrier properties than PVA because of the presence of protein structures which

Table 1: Physico-Mechanical Properties of the PVA-Gelatin-NCC-Based Biopolymeric Non-Irradiated Films

Sample No.	Sample Film	Tensile Strength (TS) (MPa)	Tensile Modulus (TM) (MPa)	Elongation at break (Eb) (%)	Moisture Content (%)
1.	PVA	23.58	32	302	21.3
2.	PVA-Gelatin	26.2	115.58	48.10	20
3.	PVA-Gelatin-NCC	32.92	129.8	58.5	18.7

Table 2: Physico-Mechanical Properties of PVA, PVA-Gelatin and PVA-Gelatin-NCC-Based Biopolymeric Irradiated Films

Sample No.	Sample Film	Tensile Strength (TS) (MPa)	Tensile Modulus (TM) (MPa)	Elongation at break (Eb) (%)	Moisture Content (%)
1.	PVA	27	62.5	314.5	18
2.	PVA-Gelatin	29.32	157.8	54.10	19.8
3.	PVA-Gelatin-NCC	40.38	139.7	62.8	14.9

Table 3: Data of Water Uptake Percentages of PVA-Based Non-Irradiated Films

Sample No	Soaking Time	PVA	PVA-Gelatin	PVA-Gelatin-NCC
1.	5	45	63	58
2.	10	85	85	76
3.	15	112	101	94
4.	20	98	119	90
5.	25	85	94	68

Table 4: Data of Water Uptake Percentages of PVA-Based Irradiated Films

Sample No	Soaking Time	PVA	PVA-Gelatin	PVA-Gelatin-NCC
1.	5	56	60	63
2.	10	84	88	75
3.	15	102	111	98
4.	20	95	120	91
5.	25	78	92	82

helped to withstand more time while immersing into deionized water. Incorporation of NCC improved the surface morphology which helped to be more resistant to water.

The Table 4 describes the water uptake percentages of PVA, PVA-Gelatin and PVA-Gelatin-NCC-based biopolymeric films after irradiation. After irradiation, the water uptake percentages decreased significantly for the biopolymeric films. It is clearly visualized from the table that, after radiation the NCC based film showed the lowest water uptake properties. After gamma irradiation, the cross-linking among the PVA-Gelatin-NCC were rearranged. This rearrangements resulted into this lower water uptake percentages for all the films.

Thermal Properties of the PVA, PVA-Gelatin and PVA-Gelatin-NCC-Based Biopolymeric Films

Thermal properties were measured into two ways, one was thermo-gravimetric analysis and other was differential scanning calorimetry.

Thermo-Gravimetric Analysis (TGA)

The thermo-gravimetric analysis of the PVA, PVA-Gelatin and PVA-Gelatin-NCC based biopolymeric films was described in Figure 1.

From the graph we could get a clear view about the thermal decomposition of the films with the increase in

the temperature. For all of the film, temperature within 100°C the unbound water, under 200°C the chemically bound water, other decomposition temperatures were evaluated for the breakage of bonds between PVA and biopolymers. At last, ash content was varied to 3-6 % on average for the films. For PVA film, there was a decomposition at 348.52°C due to breakage of C-C bond. The thermogram of PVA-Gelatin had a sharp decrease at 478.7°C, which was mainly due to the cleavage of C=N bond due to the presence of protein molecules in gelatin. NCC also had 2 steps decomposition. 1st one was at 114.24°C and mass loss was 18.5%. This occurred due to cleavage of hydroxyl

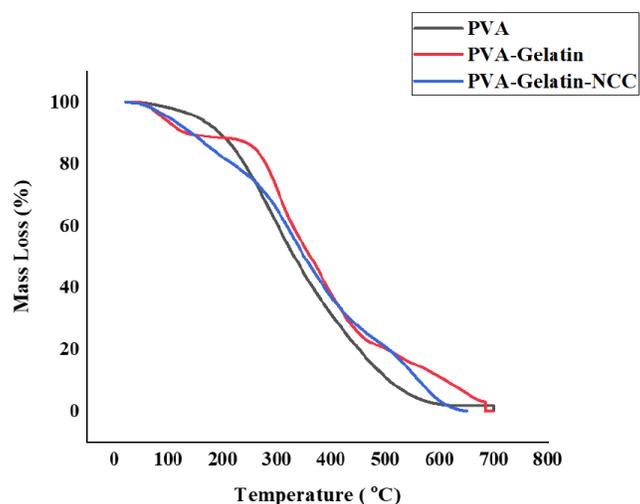


Figure 1: Graphical representation of thermo-gravimetric analysis for PVA, PVA-Gelatin and PVA-Gelatin-NCC films.

groups in polysaccharides and water vaporization. Secondly the decomposition occurred around 678.25°C and mass loss is 85.51%. This occurs due to the breakage of glycosidic bond and hydrogen bonds. It is noticed that TGA properties improved significantly with 10% NCC film and it could withstand about 800°C for fully decomposition.

Differential Scanning Calorimetry (DSC)

The thermal degradation of PVA, PVA-Gelatin and PVA-Gelatin-NCC-based biopolymeric films by differential scanning calorimetric method was illustrated in Figure 2.

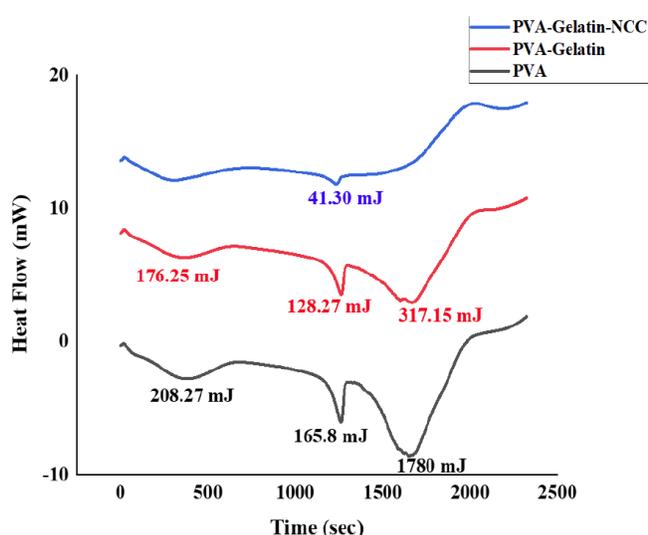


Figure 2: Graphical representation of differential scanning calorimetry for PVA, PVA-Gelatin and PVA-Gelatin-NCC-based biopolymeric films.

From the thermograms we got a view about the change of enthalpy of PVA due to presence of Gelatin and NCC. The heat of enthalpy for PVA film was found to be 168.86 mili joule at the glass transition (T_g) of 227.70°C. PVA-Gelatin film showed T_g at 225.69°C with the change of enthalpy 124.26. On the other hand, PVA-Gelatin-NCC film had a heat enthalpy 119.64 mili joule at 226.08°C. These DSC data indicated how the PVA and PVA-Gelatin films changed at glass-transition temperature with the incorporation of nano crystalline cellulose.

Spectroscopic Analysis of PVA and PVA-Gelatin-NCC-Based Films

Figure 3 demonstrated the Fourier Transform Infra-Red Spectroscopic analysis of PVA, PVA-Gelatin and PVA-Gelatin-NCC based biopolymeric films.

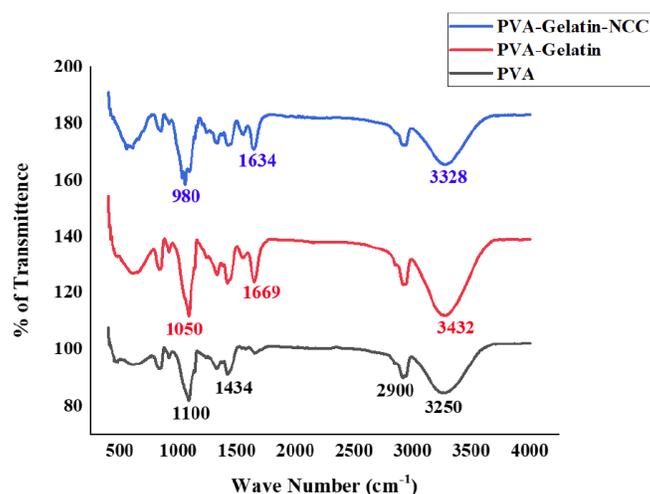


Figure 3: Graphical representation of Fourier Transform Infra-red Spectroscopy of PVA, PVA-Gelatin and PVA-Gelatin-NCC-based films.

The graph represented the functional groups present in the biopolymers due to vibration. The PVA showed a characteristic peak at 1100 cm^{-1} for the functional carboxyl group present in PVA structure. The other characteristic peaks were found at 2900 cm^{-1} for the C-H stretching bond and at 3250 cm^{-1} for the O-H bond due to the Hydrogen bond present in PVA film. Specific peak was found at 1669 cm^{-1} for the PVA-Gelatin film which was characteristic of the C=N bond between PVA and gelatin. For the NCC spectroscopy, a sharp peak was obtained at 980 cm^{-1} for the C-H bond. The C-O-C asymmetric bands present at 1634 cm^{-1} and O-H stretching vibration at 3328 cm^{-1} which were found in the spectrum. These could be obtained from the absorbed water molecule by the cellulose.

Crystalline Properties of PVA-Gelatin-NCC-Based Films

The typical X-ray diffraction patterns (XRD) of PVA, PVA-Gelatin and PVA-Gelatin-NCC-based biopolymeric film and their blend sample with NCC, at room temperature, in the scanning range $3^\circ \leq 2\theta \leq 70^\circ$ were shown in Figure 4.

PVA shows crystalline peak at 2θ value of 19.85. The sample was polymeric film, so most of the peak shows the amorphous nature. Gelatin is a protein based polymer and contains high amount of amines and amides groups. Mostly, it doesn't show that much crystalline properties. It shows little bit crystalline structure which is observed on 2θ value 19.12. With the incorporation of NCC into the film the crystalline properties increased significantly. The crystalline peaks are available at 2θ value of 19.65. These values are

assigned to a mixture of (110), (200) and (201) respectively.

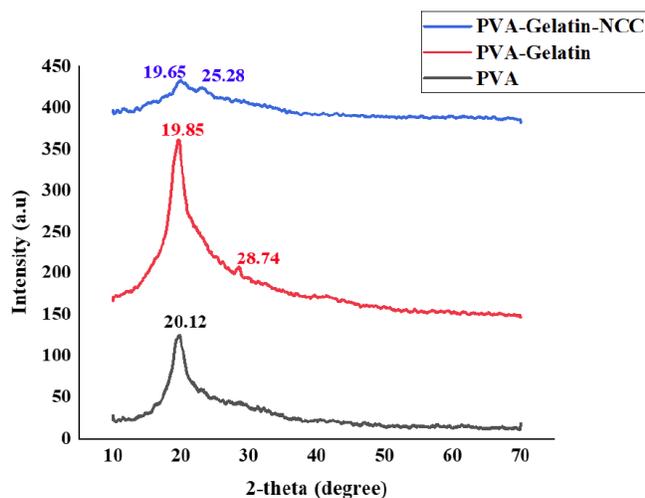


Figure 4: Graphical representation of X-Ray diffraction of PVA-Gelatin-NCC-based films.

Surface Morphological Analysis of PVA-Gelatin-NCC-Based Films

Figure 5 represented the surface morphology analysis images of PVA, PVA-Gelatin and PVA-Gelatin-NCC films.

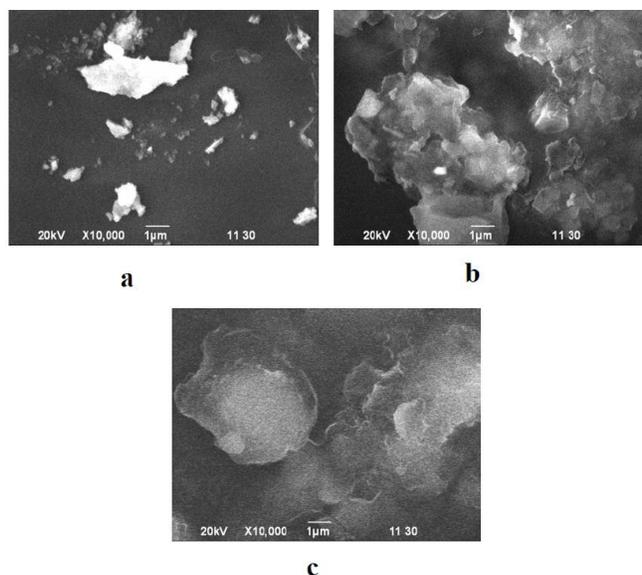


Figure 5: Scanning electron microscopic images of (a) PVA, (b) PVA-Gelatin and (c) PVA-Gelatin-NCC films.

The image (a) showed the homogeneous surface of PVA. From the image, the presence of moisture or any volatile particle was confirmed. In image (b) the heterogeneous nature was noticed due to mixing with gelatin. The third (c) image described the surface morphological changes due to addition of nano

crystalline cellulose. Nano particle present in small amount changed the surface morphology with the existence of glycosidic bonds in cellulose structure.

Biodegradability Tests of PVA-Gelatin-NCC Films

The PVA, PVA-Gelatin and PVA-Gelatin-NCC films were cut into small strips and placed in soil media for 7 days. It was observed clearly that the films were attacked by microorganism present in soil. After 7 days, the films were again buried back to the soil from a month. After that period of time, the films were found to be difficult to handle, as they got decomposed. So, this films were environment friendly and biodegradable in nature.

Effect of Radiation Dose in PVA-Gelatin-NCC Films

Gamma radiation produced free radicals and ions which initiated the crosslinking among PVA-Gelatin-NCC. The cross-linking properties had significant changes with the physical and thermo-mechanical properties of the films. Due to radiation dose, the mechanical properties of PVA, PVA-Gelatin and PVA-Gelatin-NCC-based films were improved. The tensile strength of the films were increased to 14.5%, 11.9% and 22.7% respectively. The tensile modulus and elongation properties were significantly improved. The moisture content of the films were decreased for the addition of NCC into PVA-Gelatin film. The water uptake percentages were drastically decreased after radiation.

CONCLUSION

The fabrication of biodegradable film using PVA, gelatin and nano crystalline cellulose was done successfully. The addition of NCC showed drastic changes with its thermo-mechanical and physical properties. Spectroscopic analysis was also carried out using Fourier Transform Infra-Red Spectroscopy and crystallinity by X-Ray Diffraction process. The surface morphological changes were investigated by Scanning Electron Microscopy and a significant modification was observed due to addition of NCC. Degradation test was successfully supported by using soil media. The fabricated films showed excellent thermo-mechanical properties that are well suited to be used as packaging materials.

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