

PREPARATION AND CHARACTERIZATION OF POLYMERIC MATERIAL OF CELLULOSE ACETATE-POLYVINYL ALCOHOL FILM

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Abstract

This work is mainly concerned with the preparation of polymeric material from cellulose acetate with polyvinyl alcohol (PVA) and glutaraldehyde as used as cross linker and the study of their characteristics. The films were prepared by mixing various proportions of cellulose acetate with various proportions of polyvinyl alcohol and fixed proportion of glutaraldehyde by blending, casting technique. The prepared films were investigated according to physicochemical parameters such as thickness, tensile strength, elongation at break, tear strength and physicochemical parameters such as water uptake and swelling properties. The optimum ratios for preparing films were chosen according to their physicochemical properties. The most favorable conditions for preparing film namely CPF 3 was found to be 20 mL of 2 % w/v cellulose acetate, 80 mL of 4 % w/v PVA and 25 mL of 0.025 M glutaraldehyde. It was found that the film CPF 3 possessed 27.30 MPa of tensile strength, 24.60 % of elongation at break and 58.90 kNm⁻¹ of tear strength. All prepared films showed plain, clear, smooth surface, flexible, highly transparent and light white colour. The prepared films can be used in packaging materials.

Keywords: Cellulose acetate, polyvinyl alcohol, films, tensile strength

Introduction

The importance of polymeric materials has increased in recent years due to their unique properties and the potential to be beneficial for resource conservation. Novel polymeric materials are a key research field at Fraunhofer IFAM for adhesive bonding, paint/lacquer technology and fiber reinforced plastics. These materials are opening up a host of new technical opportunities (Cascone, 1997).

Cellulose acetate which is an abundant natural fiber resource with an excellent tensile strength is widely used in oral pharmaceutical products and is regarded as a nontoxic, nonirritant and biodegradable material (Liu *et al.*, 2012). Among its wide array of applications, cigarette filters, high absorbent diapers, semipermeable membranes for separation processes, fibers, films for biomedical domain and mats for transdermal drug delivery can be included. In addition, a long term antimicrobial effect for wound healing application (Ragauskas, 2016).

Cellulose acetate is an environmental friendly substance for making membranes since it is a non-toxic material and low can be available at cost. Membranes made from cellulose acetate have been used for brackish water or seawater desalination and for filtering methanol, ethanol and urea in a reverse osmosis process. Cellulose acetate was used for its excellent film forming properties (Darunee and Tripo, 2008).

Synthetic polymers have been widely used in biosensors poly (vinyl alcohol) solid supports. The hydrogels most commonly known are PVA and their copolymers and their structures can be controlled by physical and chemical crosslinking of chains. PVA is a synthetic water-soluble hydrophilic polymer. The basic properties of PVA are dependent on the degree of polymerization or on the degree of hydrolysis. It has been widely used in adhesives, emulsificants, in the textile and paper industry applications and in the attainment of amphiphilic membranes for enzyme immobilization. Most recently, PVA has been used in pharmaceutical and biomedical

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applications for controlled drug release tests due to its degradable and non-toxic properties. Chemical crosslinking is a highly versatile method to create and modify polymers, where properties can be improved, such as mechanical, thermal and chemical stability. Also, a novel class of materials called organic-inorganic hybrids would combine properties of organic polymers with ceramics. Hybrids would combine properties of organic polymers with ceramics. These different components can be mixed at length scales ranging from nanometer to micrometer, in virtually any ratio leading to the so-called hybrid organic-inorganic (Zhang *et al.*, 2009).

The aim of this research is to prepare and characterize the polymeric material of cellulose acetate-polyvinyl alcohol film. The prepared polymeric material films have been assessed according to their physicochemical properties.

Materials and Methods

All specific chemicals used were cited in details in each experimental section. The apparatus consists of conventional laboratory glass ware and modern equipment. Some of the instruments used in the experiments are Balance (Precision Balance, AWS, PN-2100A, China), Magnetic Stirrer Oven (Universal Oven, Memmert, UFB-400, Germany), Furnace (Thermo scientific, USA), melamine plate, FTIR (Fourier Transform Infrared Spectrophotometer, Shimadzu, IR Prestige-21, Japan), SEM (Scanning Electron Microscope, Evo-18, Brandi cars ZEISS, Germany) and TG-DTA (DTA-60H, Hi-TGA 2950) thermal analyzer.

Collection of Samples

In the experiments, commercial cellulose acetate, polyvinyl alcohol (Molecular weight 20,000, degree of hydrolysis 98 %) and glutaraldehyde were purchased from the British Drug House (BDH) Chemical Ltd, England. All other chemicals used were of analytical reagent grade.

Determination of Physicochemical Properties of Cellulose Acetate and Polyvinyl Alcohol

The physicochemical properties (moisture content, ash content, solid content, bulk density and pH) of the samples were determined by conventional methods and the results are presented in Table 1.

Characterization of Cellulose Acetate and Polyvinyl Alcohol

FT IR analysis

FT IR analysis was performed in order to characterize the functional groups of samples. A Perkin-Elmer Spectrum GX, USA was used for FT IR analysis. The FT IR spectra of cellulose acetate and polyvinyl alcohol are shown in Figures 1 and 2 and the description data are presented in Tables 2 and 3.

SEM analysis

The morphology of prepared cellulose acetate and polyvinyl alcohol was studied by using Scanning Electron Microscope (JSM-5160, JEOL Ltd., Japan) for analysing micro and macro pores present on the surface of the samples. The scanning electron micrographs of cellulose acetate and polyvinyl alcohol are shown in Figures 3 and 4.

Preparation of Cellulose Acetate and Polyvinyl Alcohol Films

In this research, all of the cellulose acetate - polyvinyl alcohol films were prepared by blending casting method.

On the Aspect of the Preparation of Cellulose Acetate - Polyvinyl Alcohol Films

Clear solution of PVA 4 % w/v was prepared by dissolving 4 g of PVA in 100 mL of water by stirring with magnetic stir for 20 min at room temperature, to get a clear solution. Clear solution of cellulose acetate 2 % w/v in acetone by stirring with magnetic stir for 30 min at 100 °C. Next, (40, 30, 20, 10, 0) mL of the prepared CA solution and (60, 70, 80, 90, 100) mL of prepared PVA solution and were thoroughly mixed by stirring each pair in the given order for 20 min. The polymer solution was cooled to room temperature and (0.025 M, 25 mL) glutaraldehyde was slowly added and allowed to undergo gelation for 10 min. The solution was casted onto cleaned and dried melamine plate at room temperature for three days.

Determination of the Physicochemical and Physicomechanical Properties of Cellulose Acetate - Polyvinyl Alcohol Films

The physicochemical and physicomechanical properties (thickness, tensile strength, elongation at break, and tear strength) of the prepared CPF films were determined by the conventional method and modern techniques. The resulting data are presented in Table 4 and Figures 5, 6 and 7.

Determination of the Water Uptake Properties of Cellulose Acetate - Polyvinyl Alcohol Films

The water uptake of the prepared CPF 3 films are shown in Figure 8 and the resulting data are presented Table 5.

Determination of the Degree of Swelling Properties of Cellulose Acetate - Polyvinyl Alcohol Films

The degree of swelling of the prepared CPF 3 films are shown in Figure 9 and the resulting data are presented in Table 6.

Characterization of the CPF 3 Film

FT IR analysis

The FT IR spectrum of CPF 3 film is shown in Figure 10 and the description data is presented in Table 7.

SEM analysis

The scanning electron micrograph of CPF 3 film is presented in Figure 11.

TG-DTA analysis

Thermal analysis of the sample was determined by a DTA-60H (Hi-TGA 2950) thermal analyzer. The sample (*ca.* 5 mg) was required and measured in the temperature range 0~600 °C at 20.00 °C/min and nitrogen gas at 50.00 mL/min. The TG-DTA thermogram of CPF 3 film is shown in Figure 12 and the description data is presented in Table 8.

Determination of Biodegradation

Soil Burial Test

Biodegradation of prepared CPF 3 films were determined by soil burial test examining the morphology changes. Sample geometry on degradation was also recorded by photo. The physical appearances of CPF 3 films are shown in Figure 13.

Results and Discussion

Table 1 shows that the physicochemical properties (moisture content, ash content, bulk density, and pH) of the cellulose acetate and polyvinyl alcohol determined by the conventional methods. The pH values of samples were determined by pH meter. The moisture content of cellulose acetate and polyvinyl alcohol were determined by oven drying method at 115-120 °C to obtain constant weight. It can be observed that moisture content of the cellulose acetate is 15.24 %, ash content is 5.00 %, solid content is 84.76 %, bulk density is 52.50 g mL⁻¹ and pH is 6.20. It can be observed that moisture content of the polyvinyl alcohol is 33.00 %, ash content is 6.50 %, solid content is 67.00 %, bulk density is 0.30 g mL⁻¹ and pH is 6.70.

Table 1 Physicochemical Properties of Cellulose Acetate and Polyvinyl Alcohol

No.	Physicochemical Properties	Cellulose Acetate	Polyvinyl Alcohol
1.	Moisture content (%)	15.24	33.00
2.	Ash content (%)	5.00	6.50
3.	Solid content (%)	84.76	67.00
4.	Bulk density (g mL ⁻¹)	52.50	0.30
5.	pH	6.20	6.70

Characterization of Cellulose Acetate and Polyvinyl Alcohol

FT IR analysis

Figure 1 shows the FT IR spectrum of cellulose acetate. The spectrum of CA shows a weak and broad band at 3369 cm⁻¹, 2919 cm⁻¹, 1728 cm⁻¹, 1437 cm⁻¹, 1019 cm⁻¹. These peaks are assigned to the O-H stretching of hydroxyl group, C-H asymmetric stretching, C=O symmetric stretching acetyl group, C-H stretching of CH₃, C-O-C asymmetric stretching for ether bridge and pyranose ring, respectively. The presence of PEG in the spectrum is manifested only as an outstanding increase of the signal for OH groups and CH stretching at 3289 cm⁻¹.

Figure 2 shows the FT IR spectrum of polyvinyl alcohol. The main peak of PVA observed at at 3305 cm⁻¹, 2916 cm⁻¹, 1714 cm⁻¹, 1423 cm⁻¹, 1248 cm⁻¹, 943 cm⁻¹. These peaks are assigned to the O-H stretching of hydroxyl group, C-H as symmetric stretching, C=O carbonyl stretching, C-H bending of CH₂, C-O stretching acetyl group, C-C stretching, respectively.

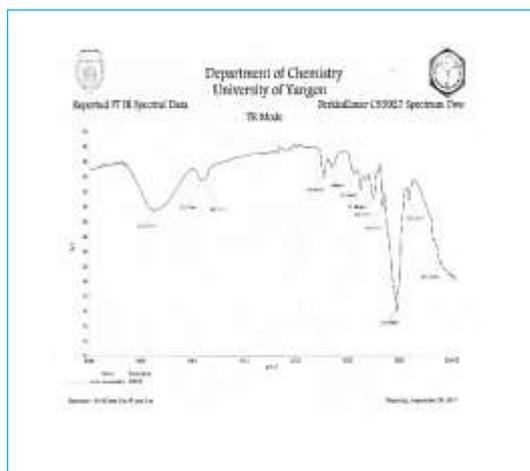


Figure 1 FT IR spectrum of cellulose acetate

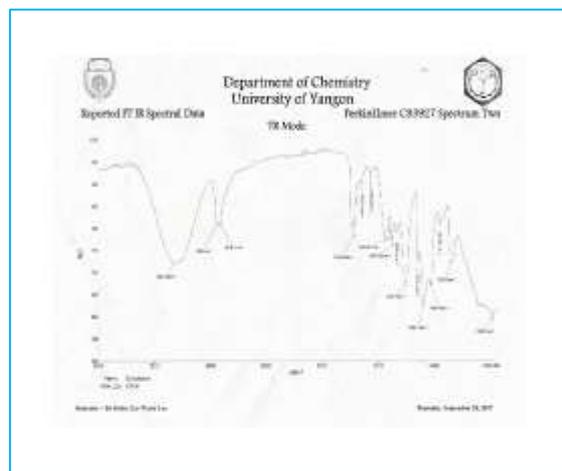


Figure 2 FT IR spectrum of polyvinyl alcohol

Table 2 FT IR Band Assignments of Cellulose Acetate

Observed wave number (cm ⁻¹)	Literature wave number (cm ⁻¹)	Band assignment
3369	3200-3600	O-H (stretching)
3289	3330-3500	O-H and C-H (stretching)
2919	2850-2940	C-H (stretching)
1728	1695-1735	C=O (symmetric stertching)
1437	1400-1480	C-H (bending ester methyl group)
1019	1320-1380	C-O-C (asymmetric stretching of ether)

*(Silverstein *et al.*, 2003)

Table 3 FT IR Band Assignments of Polyvinyl Alcohol

Observed wave number (cm ⁻¹)	Literature wave number (cm ⁻¹)	Band assignment
3305	3200-3600	O-H (stretching)
2916	2850-2940	C-H (stretching)
1714	1705-1750	C=O (stretching)
1423	1260-1440	C-H (bending of CH ₂)
1248	1050-1330	C-O (stretching of acetyl group)
943	750-1300	C-C (stretching)

*(Silverstein *et al.*, 2003)

SEM analysis

Surface morphology of cellulose acetate and polyvinyl alcohol are presented in Figures 3 and 4. It is obviously seen that large non-uniform cavities and pores are on the surface of the cellulose acetate whereas the fibrils with uncrosslinks nature of PVA is observed.



Figure 3 SEM photomicrograph of cellulose acetate

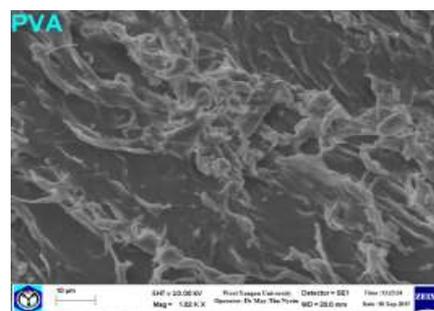


Figure 4 SEM photomicrograph of polyvinyl alcohol

On the Aspect of the Preparation of Cellulose Acetate - Polyvinyl Alcohol Films Determination of the Physicomechanical Properties of Cellulose Acetate - Polyvinyl Alcohol Films

For all of the prepared films, physicochemical and physicomechanical parameters were determined. Among these parameters, tensile strength is more specific than other for determining films quality. CPF 1, CPF 2, CPF 3, CPF 4 and CPF 5 films were prepared. The results of the physicochemical and physicomechanical properties of CPF 1 to CPF 5 films are presented in Table 4 and Figures 5, 6 and 7. The most favorable conditions for preparing film namely (CPF 3) was

found to be with 20 mL of 2 % w/v cellulose acetate, 80 mL of 4 % w/v PVA and 25 mL of 0.025 M glutaraldehyde. It was found that CPF 3 has the highest tensile strength among them. Moreover, the water uptake tests of the films are also found to be satisfactory. The film CPF 3 has the equilibrium water uptake percentage among them in Table 5. Therefore, film CPF 3 was chosen to make the most suitable film.

Table 4 Physicomechanical Properties of Films with Various Proportions of Cellulose Acetate - Polyvinyl Alcohol Films

Properties	Cellulose Acetate - PVA Films				
	CPF 1	CPF 2	CPF 3	CPF 4	CPF 5
Thickness (mm)	0.10	0.11	0.19	0.23	0.18
Tensile strength (MPa)	15.20	19.40	27.30	18.20	17.20
Elongation at break (%)	17.90	22.00	24.60	20.40	18.28
Tear strength (kN/m)	38.40	48.80	58.90	52.60	52.00

CPF 1 = (2 % w/v, 40 mL) C + (4 % w/v, 60 mL) P + Glutaraldehyde (0.025 M, 25 mL)

CPF 2 = (2 % w/v, 30 mL) C + (4 % w/v, 70 mL) P + Glutaraldehyde (0.025 M, 25 mL)

CPF 3 = (2 % w/v, 20 mL) C + (4 % w/v, 80 mL) P + Glutaraldehyde (0.025 M, 25 mL)

CPF 4 = (2 % w/v, 20 mL) C + (4 % w/v, 90 mL) P + Glutaraldehyde (0.025 M, 25 mL)

CPF 5 = (2 % w/v, 0 mL) C + (4 % w/v, 100 mL) P + Glutaraldehyde (0.025 M, 25 mL)

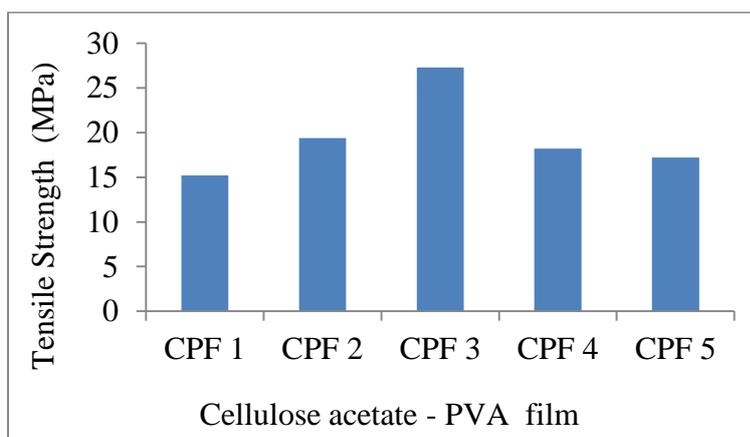


Figure 5 Tensile strength of cellulose acetate- polyvinyl alcohol films

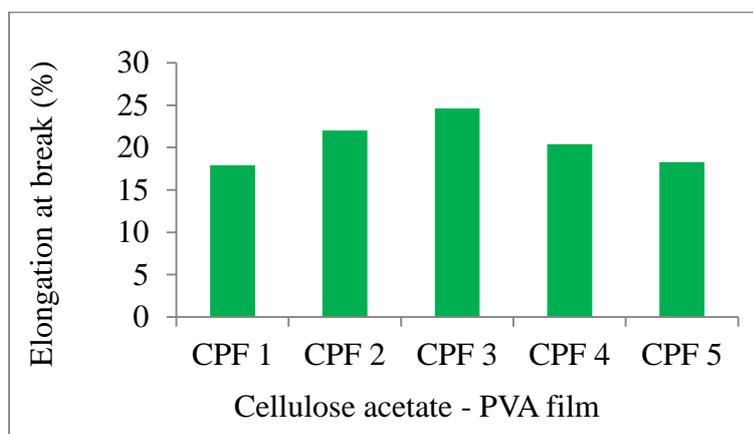


Figure 6 Elongation at break of cellulose acetate- polyvinyl alcohol films

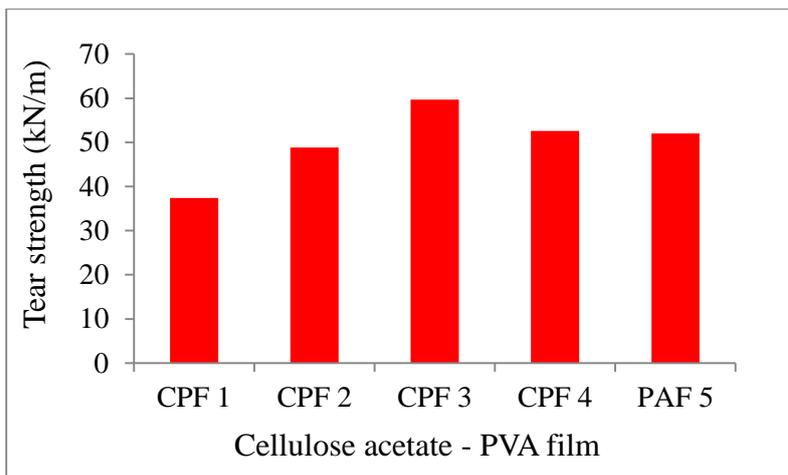


Figure 7 Tear strength of cellulose acetate- polyvinyl alcohol films

Determination of Water Uptake Properties of Cellulose Acetate - Polyvinyl Alcohol Films

The degree of water uptake was investigated with increasing immersion time. The water uptake was one of the most significant parameter when a film to be used as packaging materials. The water uptake was the amount of water entrapped in the matrix including bound water. The water absorption properties of CPF 3 films were studied for varying time intervals such as 10 min, 20 min, 30 min, 40 min, 50 min and 60 min. The water uptakes as a function of time for CPF 3 films are shown in Table 5 and Figure 8.

Table 5 Water Uptake of Cellulose Acetate -Polyvinyl Alcohol Films

Films	Water Uptake (%)					
	10 min	20 min	30 min	40 min	50 min	60 min
CPF 1	10.2	12.8	15.7	17.6	20.4	26.9
CPF 2	15.5	18.6	20.5	22.4	26.0	28.6
CPF 3	19.3	22.4	25.6	27.3	24.2	32.4
CPF 4	22.1	24.7	27.3	29.5	32.4	34.6
CPF 5	25.4	28.0	31.5	33.6	37.8	40.2

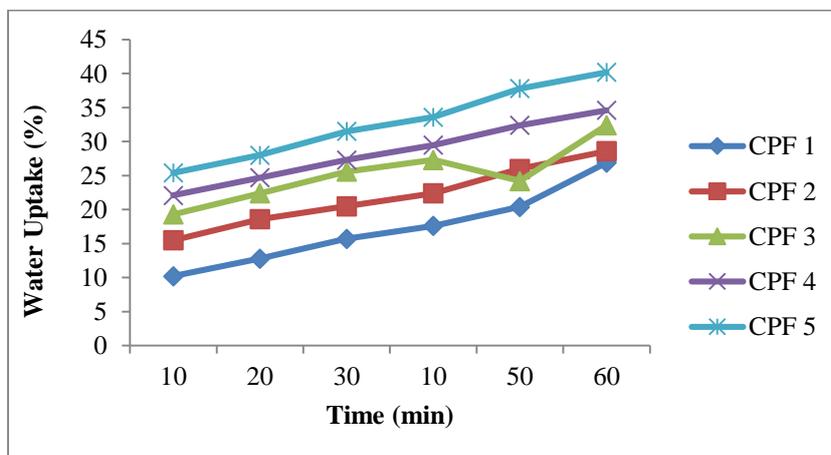


Figure 8 Water uptake of cellulose acetate - polyvinyl alcohol films as a function of contact time

Determination of Degree of Swelling Properties of Cellulose Acetate - Polyvinyl Alcohol Films

The degree of swelling of CPF 3 films with different compositions are shown in Table 6 and Figure 9 as a function of immersion time in distilled water at room temperature. For a given blend composition time, mostly the degree of swelling increased with increasing immersion time. The degree of swelling of CPF 3 films from 10 min to 60 min was slightly difference for all prepared films.

Table 6 Degree of Swelling of Cellulose Acetate - Polyvinyl Alcohol Films

Films	Degree of Swelling (%)					
	10 min	20min	30min	40mn	50 min	60min
CPF 1	8.3	11.2	13.7	16.2	19.36	21.1
CPF 2	12.4	13.6	15.9	18.3	22.6	25.3
CPF 3	15.5	17.2	17.2	20.4	21.4	23.6
CPF 4	19.2	21.4	21.4	23.0	25.9	27.2
CPF 5	21.4	24.6	24.6	26.4	29.8	30.8

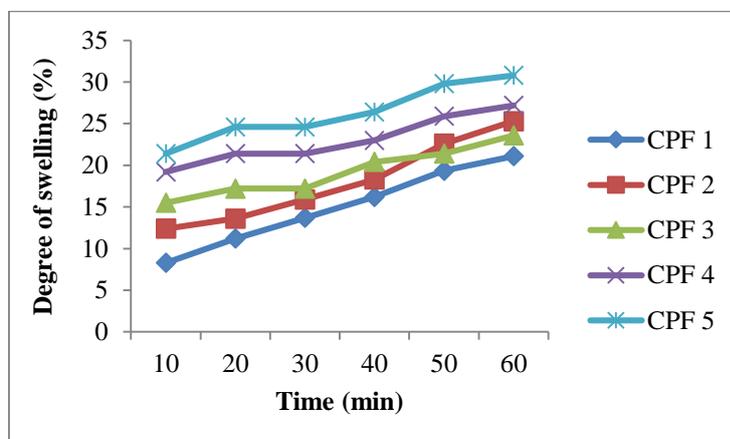


Figure 9 Degree of swelling of cellulose acetate - polyvinyl alcohol films as a function of contact time

Characterization of CPF 3 Film

FT IR analysis

Figure10 shows the FT IR spectrum of CPF 3 film. The bands at 3271 cm^{-1} , 2922 cm^{-1} , 1648 cm^{-1} , 1416 cm^{-1} , 1328 cm^{-1} , 1087 cm^{-1} , 832 cm^{-1} may be due to O-H stretching, C-H stretching, C=O (stretching), C-H (bending of CH_3), C-H (bending of CH_3), C-O (stretching of CH-OH) and C-C (stretching) respectively.

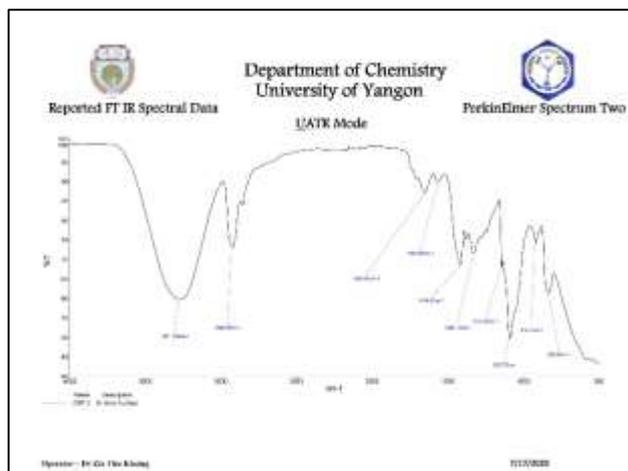


Figure 10 FT IR spectrum of CPF 3 film

Table 7 FT IR Band Assignments of CPF 3 Film

Observed wave number (cm ⁻¹)	Literature wave number (cm ⁻¹)	Band assignment
3271	3200-3600	O-H (stretching)
2922	2850-2940	C-H (stretching)
1648	1705-1750	C=O (stretching)
1416	1260-1440	C-H (bending of CH)
1328	1300-1350	C-H (bending of CH ₃)
1087	1000-1125	C-O (stretching of CH-OH)
832	750-1300	C-C (stretching)

*(Silverstein *et al.*, 2003)

SEM analysis

Surface morphology of CPF 3 is presented in Figure 11. Generally, the images show that the cellulose was homogeneously dispersed in the PVA matrix. The white dots, having different sizes on the film can be considered as cellulose. The amount of these smaller white dots was found to increase with increasing cellulose content indicating that these smaller white dots were mostly indicating of cellulose dispersed in PVA matrix.

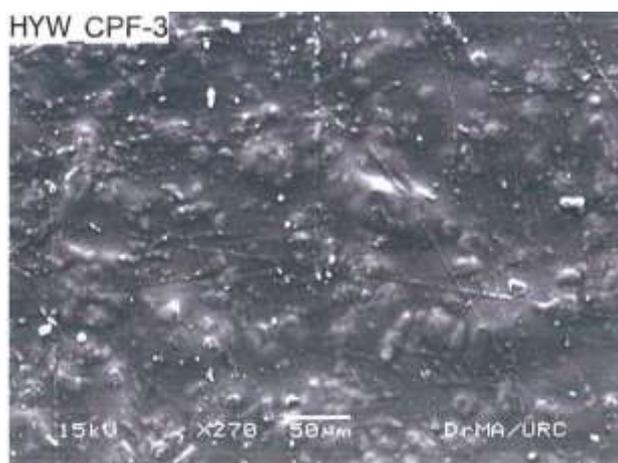


Figure 11 SEM photomicrograph of CPF 3 film

TG DTA analysis

Thermal stability of film CPF 3 is shown in Figure 12. It was investigated by TG-DTA analysis. On the basis of the thermogram of CPF 3 film, in first stage, the weight loss % about 8.16 % that was found within the temperature range of 38 °C to 80 °C. This is due to the dehydration of surface giving an endothermic peak at 63.70 °C. In the second stage, the weight loss % about 22.76 % was found within the temperature range of 80 °C to 300 °C. This is due to the decomposition of polymer backbone giving an endothermic peak at 275.32 °C. In the third stage, the weight loss % about 55.57 % that was found within the temperature range of 300 °C to 600 °C. This is due to the degradation of polymer backbones and burning into char giving an exothermic peak at 493.17 °C in Table 7.

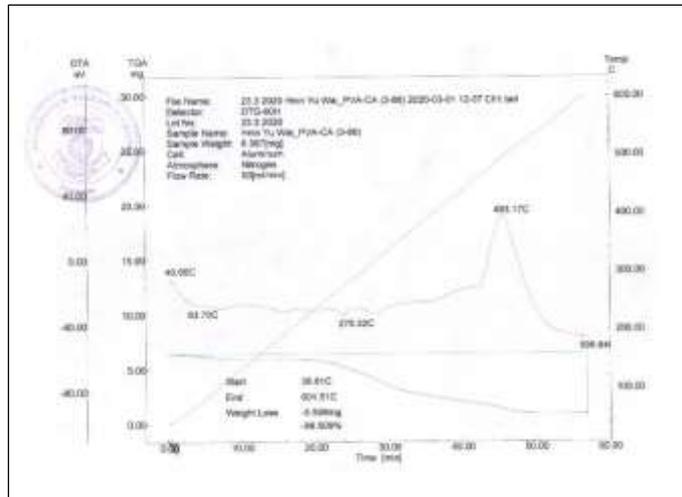


Figure 12 TG TDA thermogram of CPF 3 film

Table 8 Thermal Analysis Data of CPF 3 Film

Sample	TG		DTA		Remarks
	Break in Temperature (°C)	Weight loss (%)	Peak Temperature (°C)	Nature of peak	
CPF 3	38-80	8.16	63.70	endothermic	Dehydration due to surface water
	80-300	22.76	275.32	exothermic	Decomposition of polymer backbone
	300-600	55.57	493.17	exothermic	Degradation of polymerbackbones and completely burn

On the Aspect of Biodegradation

The environment friendly degradable plastic has been developed by gelling the cellulose acetate with the synthetic polyvinyl alcohol (PVA) polymer. One of the objectives of development of CPF 3 film is to make easy throw away materials from degradable plastic to alleviate waste disposal problems by means of environmental degradation. In this work, biodegradation of CPF 3 film was tested by soil burial method actual condition of waste disposal. Uniformly sized samples were buried in the soil from waste disposal. The physical appearance of CPF 3 films buried in the soil is shown in Figure 13. The Figure 13 shows biodegradation nature of CPF 3 film for 3 months

interval. These figures clearly showed significant deformation of films observed at films at each investigation period.

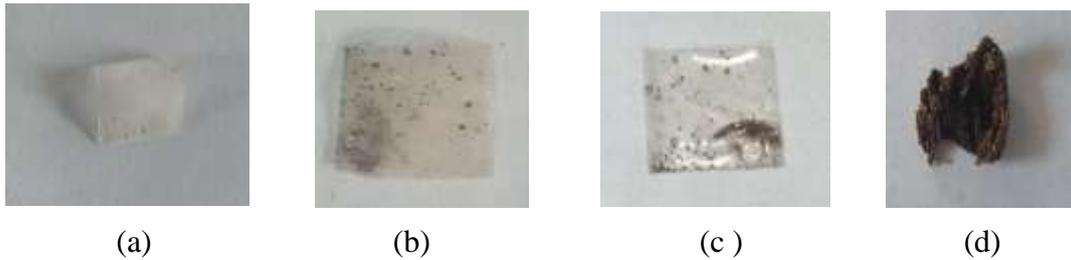


Figure 13 The physical appearances of CPF 3 film (a) Before burial test (b) After one month (c) After four month (d) After seven month

Some Possible Application of Prepared Films

The prepared cellulose acetate - polyvinyl alcohol films will be widely used in packaging materials. The photographs of CPF films are presented in Figure 14 and the photograph of the prepared food packaging box is in shown Figure 15.



Figure 14 Photographs of CPF film



Figure 15 Photograph of the prepared food packaging box

Conclusion

Polymeric materials consisting of cellulose acetate and polyvinyl alcohol films were prepared. The various types of cellulose acetate - polyvinyl alcohol films were prepared by blending, casting technique. According to the physicomechanical properties such as tensile strength, elongation at break (%) and tear strength, the optimum conditions was achieved by using 80 mL of polyvinyl alcohol and 20 mL of cellulose acetate. All prepared cellulose acetate - polyvinyl alcohol films showed plain, clear, smooth surface, flexible, transparent to light white

colour. According to physicochemical properties, film (CPF 3) sample was chosen as optimum conditions for the preparation of cellulose acetate - polyvinyl alcohol films. The prepared cellulose acetate - polyvinyl alcohol film will be widely used in packaging materials.

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