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Thermal degradation and hemocompatibility of polyurethane cellulose nanocomposites

K. J. Jasmine Jerlite

Research Scholar (Reg No:18113112032038), Department of Chemistry, Nesamony Memorial Christian College, Marthandam, Tamil Nadu, India

N. T. Nevaditha

Department of Chemistry, Nesamony Memorial Christian College, Marthandam, Tamil Nadu, India. Affiliated to Manonmaniam Sundaranar University, Abishekapatti, Tirunelveli- 627012, Tamil Nadu, India

Abstract---Bio based polymers are reinforced with natural fibers as a good candidate to the replacement of synthetic materials. In this work biobased polyurethane cellulose nanocomposites (PUCNs) prepared from hydroxylated olive oil and diphenyl methane - 4, 4 - diisocyanate, in the presence of dibutyl tin dilaurate as catalyst and incorporated with varying concentration of cellulose nanocrystals. The polyurethane cellulose nanocomposites films have been characterized by FTIR, XRD, SEM and TGA/DTA studies. The compatibility of the nanocomposites is evaluated by invitro hemolytic assay method. The FTIR analysis indicates the presence of the cellulose nanocrystals in the polyurethane matrix. The formation of urethane linkage is confirmed by the stretching vibrations of the peak around 3330 cm^{-1} . XRD diffraction pattern of the samples shows a increase of 2% crystallinity by the addition of cellulose nanoparticles. The average size of cellulose nanocrystals is calculated as 16nm. SEM images shows a rod like structure of cellulose nanocrystals and the fine dispersion of cellulose nanocrystals in the polymer matrix. The degradation of PUCNs is more pronounced in different chemical environments than polyurethane. Thermogravimetric analysis observed that the addition of cellulose nanocrystals increases the thermal stability of PUCNs upto 300°C . Hemolytic assay displays the excellent non hemolytic nature of polyurethane nanocomposites.

Keywords---polyurethane, cellulose, nanocomposites, hemolytic assay.

Introduction

Nowadays there is a growing interest on biopolymer based nanocomposites, to make eco-friendly and highly economic products from renewable sources. Renewable or biobased polymeric materials such as cellulose, starch, poly lactic acid have several advantages as biodegradability, renewability and sustainability. It is used in pharmaceutical, food packaging and agriculture technologies [1]. Vegetable oils are viewed as one of the main kinds of renewable feed stock [2]. They are structurally versatile, highly pure, stable and flexible for chemical transformations [3,4]. Polyurethanes from vegetable oils have become one of the most remarkable polymers as they exhibit a high performance and versatility, being utilized in a tremendous scope of industrial and engineering applications such as foams [5,6], coatings [7], medicinal products [8,9] and adhesives [10]. The use of nanotechnology in the field of polymer science has prompted the creation of nanocomposite polymers.

Cellulose is one of the most abundant material and limitless natural macromolecule in the field of polymer. [11]. Cellulose nanocrystals have gained high thought of reinforcing filler on account of their key attributes like very high specific mechanical property. Cellulose nanocrystals (CNC) are commonly produced using acid hydrolysis of cellulosic materials dispersed in water, in general concentrated sulphuric acid is used which dissolves the amorphous regions of cellulose and the crystalline regions are left alone [12]. The CNCs scatterings obtained using sulfuric acid are stable due to the grafting of sulfate ester groups on the surface of the whiskers, which stabilize the aqueous whisker suspensions by electrostatic repulsion [13]. The hydronium ions enter the amorphous regions of cellulose chains and promotes the hydrolytic cleavage of the glycosidic bonds [14]. Nanocellulose is utilized for health care applications such as personal hygiene products, cosmetics and biomedicines [15].

Cellulose nanocrystals kept up polymer nanocomposites can retain the transparency of the polymer matrix. It is considered a sustainable material due to its biodegradable nature [16]. The importance has been the addition of nanocellulose to biodegradable polymers, which permits both the improvement of mechanical properties and speeds up the rate of biodegradation. [17]. When polyurethanes are used as long-term blood-contacting materials, proteins can accumulate rapidly on the material surface, thus platelets are activated, and then blood coagulation and thrombosis occur [18]. There have been significant developments in recent years in shape memory materials, tissue engineering, and coronary stents for use as biocompatible materials [19].

The present work is to study the biocompatibility of polymer nanocomposites synthesised using olive oil based polyurethane and nanocellulose. The nanocomposites samples are characterized by spectroscopic methods and studied for its degradability at different chemical parameters. The biocompatibility of the polymer nanocomposites have been studied by hemolysis method.

Materials and Methods

Olive oil was commercially obtained from marbilyagsan.tic.izmir turkey. Diphenyl methane - 4,4- diisocyanate(DMDI) and dichloro methane were commercially obtained from Merck. Benzoyl peroxide was received from spectrochem (Mumbai).dibutyl tin dilaurate, cellulose and ethylene glycol dimethylacrylate were obtained from sigma Aldrich.

Synthesis of polyurethane cellulose nanocomposites (PUCNs)

The polyurethane cellulose nanocomposites was synthesised in the ratio of NCO/OH 1:2 (w/w). Hydroxylated olive oil and Diphenyl methane - 4, 4 - diisocyanate were individually dissolved in dichloromethane and suspended in the three necked 250 mL flask. The reaction was initiated by using benzoyl peroxide. The catalyst dibutyl tin dilaurate and the cross linker ethylene glycol dimethyl acrylate were added to the reacting mixture. Then the polyurethane mix was added with the required quantity of nanocellulose crystals. The reaction was carried out at 40°C with continuous stirring for 2 hrs. until the solution became viscous. The resultant solution was poured into glass plate dried and cured in an oven at 60°C for 12 h. The sample was removed from the glass plate.

Table 1. Formulations of the olive oil based polyurethane cellulose nanocomposites

Samples	Ratio (NCO:OH)	of cellulose	of cellulose
PUCN1	1:2	1	
PUCN2	1:2	2	
PUCN3	1:2	3	
PUCN4	1:2	4	

Characterization

Fourier transform infrared spectroscopy

FTIR spectra were determined with an FTIR affinity 1 Shimadzu fourier transform infrared spectrometer. The polymer samples were recorded at 400-4000cm⁻¹.

Scanning electron microscope

The polyurethane cellulose nanocomposites for scanning electron microscope were observed in Quanta FEG-250 SEM which permits to achieve a resolution of 1.4 nm even at 1kv electron landing voltage.

X Ray Diffraction

X Ray Diffraction studies were performed using aX'Pert Pro-PAalytic diffractometer with monochromatic Cu - k α radiation. The percentage of Crystallinity was calculated by % of Crystallinity = $I_c / (I_c + I_a) \times 100$ Where, I_c -

Intensity of crystalline peak Ia – Intensity of amorphous peak Crystallinity index was calculated by Crystallinity index = $I_c - I_a/I_c$

Chemical resistance test

Chemical resistance test was carried out according to ASTM D3137. The degradation of samples in 5% hydrochloric acid and 5% sodium hydroxide were studied. The percentage of weight loss was calculated.

Thermal studies

Thermal analysis was carried out by TGA/DTA on a TA instruments NJA-STA 2500 regulus at a heating rate of 10°C min, from room temperature to 800°C under nitrogen atmosphere.

Hemocompatibility test

Hemocompatibility test is carried out according to the standard method using phosphate buffer saline solution.

Results and Discussion

Fourier Transform Infrared Spectroscopy

The FTIR spectrum of polyurethane in figure 1. shows a absorption peak at 3356 cm^{-1} is attributed to the NH stretching and 1527 cm^{-1} is NH bending vibration of polyurethane (PU). FTIR spectra of Polyurethane cellulose nanocomposites (PUCNs) shows the extensive formation of urethane linkages is confirmed by their characteristics absorption of NH stretching vibration at 3340 cm^{-1} and the corresponding bending vibration at 1526 cm^{-1} . The absorption bands at 2953 cm^{-1} and 2823 cm^{-1} are due to C-H asymmetric and symmetric stretching vibrations of methylene groups in the polyurethane backbones. Small peaks at 1455 cm^{-1} , indicates the CH_2 bending vibrations of polyurethanes. The absorption band at 1720 cm^{-1} corresponding to the carbonyl group The urethane carbonyl absorption is observed at 1597 cm^{-1} for the bonded CO- O stretching. The deformations of cellulose rings can be identified by their absorption bands in the region 1412 cm^{-1} and 1000 cm^{-1} . While the absorption for C-C ring stretching band is appeared at 1152 cm^{-1} . The other characteristics bands of pyranose ring stretching vibration band is observed at 1017 cm^{-1} . The presence of two bands at 942 cm^{-1} and 1054 cm^{-1} represents C-O and C-O-H stretching vibrations, respectively that confirms the presence of cellulose nanocrystals in polyurethane composites.

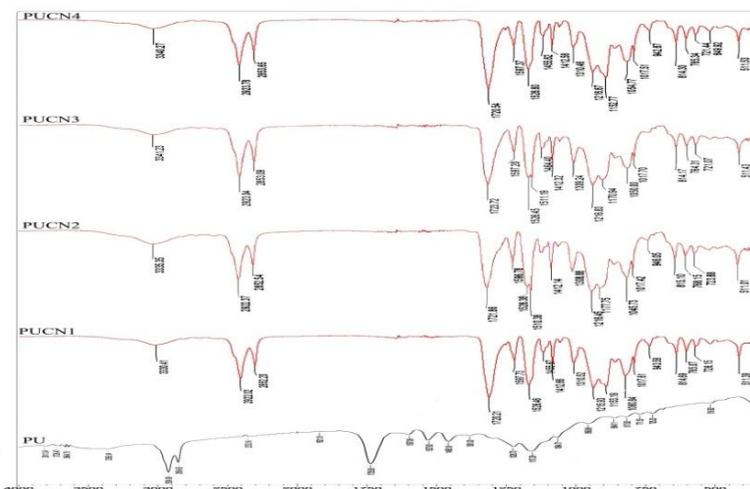


Fig.1. FTIR spectra of PU and PUCNs

Table 2. FTIR assignment of PUCNs

Assignment	Wave number (cm ⁻¹)				
	PU	PUCN1	PUCN2	PUCN3	PUCN4
NH stretching	3356	3330	3335	3341	3340
CH asymmetric stretching	2954	2922	2922	2923	2923
CH symmetric stretching	2854	2852	2852	2853	2853
Carbonyl group	1735	1720	1721	1723	1720
CO-O stretching		1597	1598	1597	1597
NH bending	1527	1526	1526	1526	1526
CH ₂ bending		1455	1412	1464	1455
C-O stretching		1215	1216	1216	1216
C-C ring stretching		1153	1177	1170	1152
C-OH stretching		1060	1045	1050	1054
Pyranose ring stretching		1017	1017	1017	1017
C-O stretching		943	946	-	942

X Ray Diffraction

XRD studies of CNs, PU and PUCNs have been conducted to compare the crystalline behaviour of the nanocomposites. The XRD pattern of cellulose nanocrystal is shown in figure 2.(a) having a sharp peak at $2\theta = 22.58^\circ$ ($d = 3.9 \text{ \AA}$) and the crystallinity is 71.42%. The particle size of cellulose nanocrystals is found to be 16nm. The PU film shows a diffraction peak at $2\theta = 19^\circ$ with 72% crystallinity and in PUCNs the angle of diffraction is shifted from 19 to 20.5 by the addition of cellulose nanocrystal. From Table 3. The crystallinity of PUCNs is significantly increased from 76.1% to 77.7%. The addition of cellulose nanocrystals increases the crystallinity of polyurethane cellulose nanocomposites.

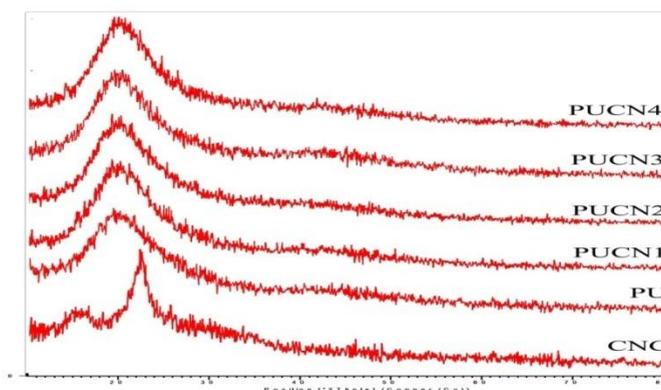


Fig.2. XRD spectra of a- cellulose nanocrystals, b-PU, c-PUCN1, d- PUCN2,e- PUCN3 and f-PUCN4

Table 3. Percentage of Crystallinity of polyurethane cellulose nanocomposites

Samples	Percentage of crystallinity	Crystallinity index
PU	72	0.61
PUCN1	76.1	0.68
PUNC2	76.7	0.69
PUNC3	77.2	0.70
PUNC4	77.7	0.71

Scanning electron microscope analysis

In figure 3 (a) the cellulose nanocrystals are found to be rod like structure. Figure 3 (b) is the surface of the PU film which is fracture like structure showing the soft segments of methylene groups of olive oil and diphenyl methane -4, 4 - diisocyanate. The surfaces of the PUCNs are rough and agglomerates of cellulose nanocrystals are observed in the images of the composites even at lower concentrations. The roughness of the surfaces increases with the increase in the amount of cellulose content. The fine dispersion of cellulose nanocrystals in the polymer matrix is due to the interaction between the hydrogen bond of cellulose hydroxyl groups and the urethane groups. In figure 3 (b) and 3 (c) the surface of PUCNs shows a grain like appearances of cellulose nanocrystals in the polymer structure. In fig 3.(d) and 3(e) surface of the PUCN3 film is smooth and dense with spherical nanocrystals. The higher percentage of nanocrystals facilitates the formation of aggregated form of cellulose nanocrystals.

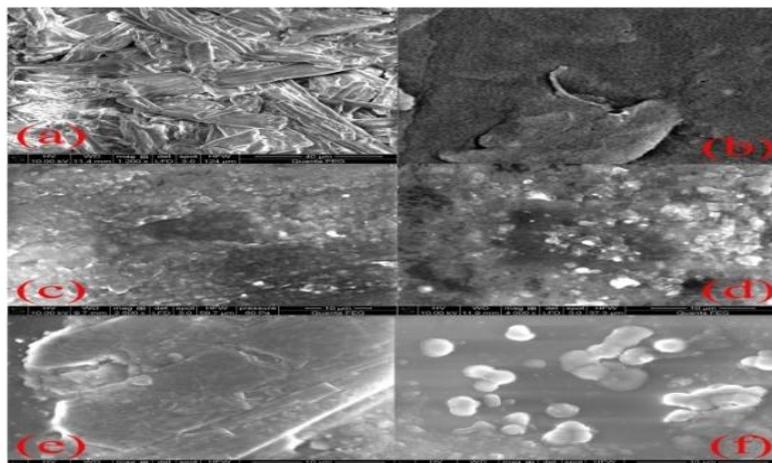


Fig.3: SEM images of a) cellulose nanocrystals b) PUCN1 c) PUCN2 d) PUCN3 e) PUCN4

Chemical resistance test

The chemical resistance test for PU and polyurethane cellulose nanocrystals (PUCNs) composite films have been analyzed in 5% of sodium hydroxide and 5% hydrochloric acid. When exposed to 5% NaOH for 72 hrs. the swelling of the film starts after 1hr and reaches maximum within a day. In 5% sodium hydroxide 2.5% weight loss has been observed in PU and it is increased to 18.8% of weight loss in PUCNs. In 5% hydrochloric acid 2.1% weight loss in PU and attained an increase of 17.8% weight loss in PUCNs followed by degradation of the PUCNs into small pieces.

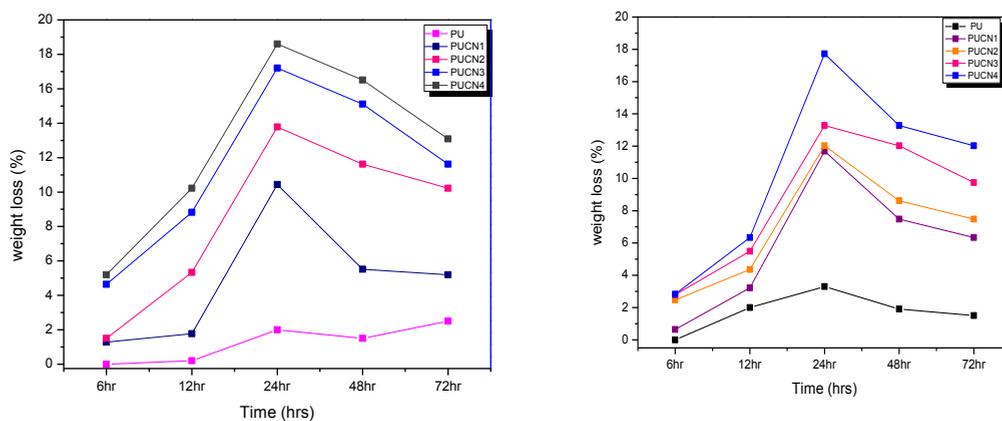


Fig.4. Chemical resistance of a) 5% NaOH b) 5% HCl

Thermal studies

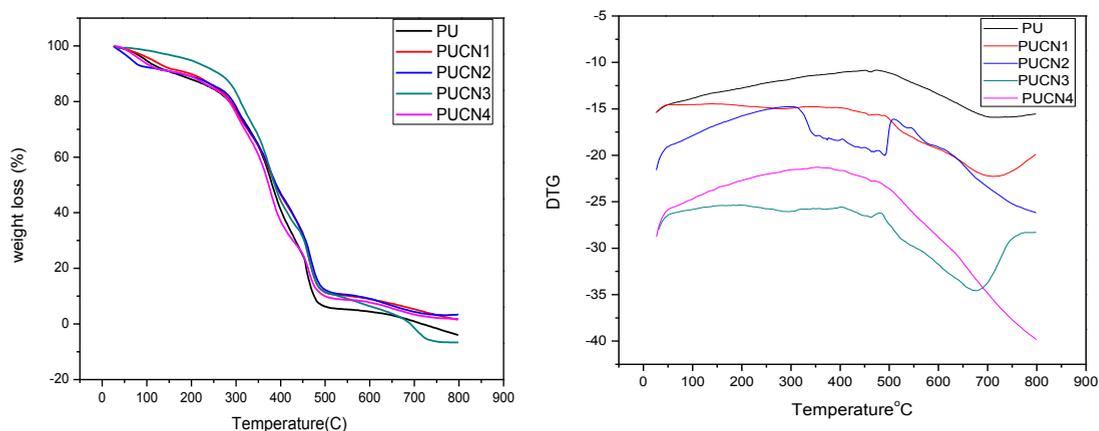


Fig.5. a)TGA andb) DTG curves for the PU and PUCNs

Table 4.Formulation of TGA

Sample	T onset (°C)	T max (°C)	tTT final (°C)	Residue
PU	100	250	470	0.19
PUCN1	120	270	490	1.56
PUCN2	1130	280	494	3.41
PUCN3	150	300	498	6.64
PUCN4	120	290	480	1.77

Fig 5a) shows the TGA/DTG curves of PU and PUCNs having various percentage of cellulose nanocrystals. The TGA profile PUCNs showed three stages of weight loss. In the first stage, a weight loss around 150 °C which may be due to the loss of water molecules. The intense peak at 186°C is attributed to cellulose depolymerisation and dehydration and decomposition of glycosyl units. In the second stage the weight loss around 25% occurs at temperature range 250 - 300°C is accompanied by the decomposition of glucosidic linkages in the cellulose chain. In the third stage a maximum weight loss of 40% at 350°C due to the decomposition of hard segments of urethane linkages, which leads to the dissociation of the polyol and isocyanates. The temperature range 400 – 500 °C corresponds to the decomposition of ester groups or soft segments in the backbone of the polyurethanes. The PU film is thermally stable in contrast to the other films. In the DTG curves three distinct exothermic peaks is observed at 450°C for PU. The PUCNs having three distinct exothermic peaks at 300, 380 and 460°C which indicates the degradation of cellulose and polyurethane. In TGA the total percentage of weight loss is found to be 99.8% in PU and PUCNs is 97.96, 95.87, 99.59 and 98.15% respectively. The thermal degradation increases with an increase in the cellulose nanocrystals content in the polymer matrix.

Hemocompatibility test

Red blood cells may lead to hemolyzation when contacting with implant biomedical materials. The hemolysis evaluation of blood with polyurethane cellulose nanocomposites are shown in table. Based on the standard of relative hemolytic tests, permissible hemolysis rate of biomaterials should be lower than 5%. The American society for testing and materials, the hemocompatibility of materials have been defined as the rate of hemolysis (>5% of hemolysis), slightly hemolysis (2-5% of hemolysis) and non hemolysis (0- 2% of hemolysis) materials were defined. In 10 -100 μ g/ml the hemolysis rate is less than 2% of the red blood cells indicates the polyurethane cellulose nanocomposites as nonhemolysis materials implying its excellent hemocompatibility. When compared to PU and PUCN3, polyurethane cellulose nanocomposites is hemocompatibility than polyurethane.

Table 5. Percentage of hemolysis

S.No	Concentrations (μ g/ml)	Hemolysis (%)	
		PU	PUCN3
1	10	0	0
2	20	0	0
3	40	0	0.03 \pm 0.2
4	60	0.64 \pm 0.84	0.03 \pm 0.2
5	80	8.92 \pm 1.05	0.99 \pm 0.68
6	100	11.23 \pm 1.15	1.52 \pm 1.27

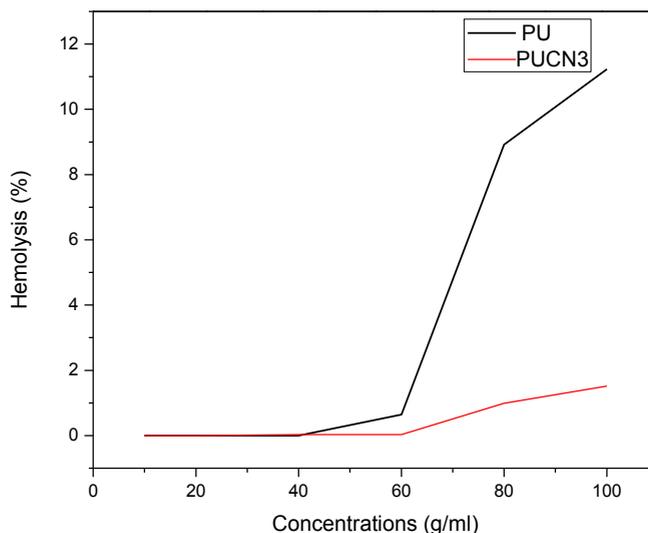
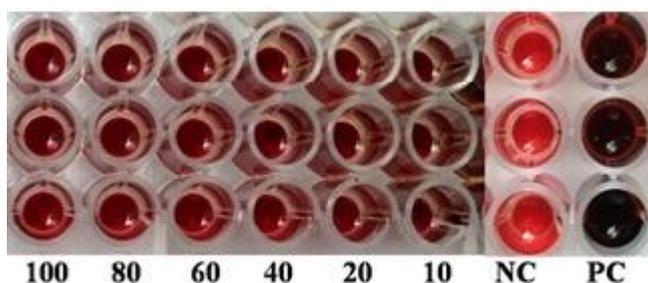


Figure 4. Percentage of hemolysis



Conclusion

Cellulose nanocrystals are obtained by acid hydrolysis from cellulose. The cellulose nanocrystals are used as fillers for the synthesis of polyurethane cellulose nanocomposite. It is confirmed by FTIR spectroscopy. In XRD shows the angle of deviation of peaks from $19 - 20^\circ$ is due to the addition of cellulose nanocrystals in the polymer matrix. SEM images showed that the cellulose nanocrystals are fine dispersion within the polymer matrix. In chemical resistance test the degradation of PUCNs increases. The presence of nanocrystals in the polymer matrix increases the chemical degradation upto 19%. In TGA curve PUCNs are thermally stable upto 300°C and start degradation due to the presence of ester groups. The percentage of hemolysis of PUCNs is $<2\%$ showing better biocompatibility than the polyurethane. Thus polyurethane cellulose nanocomposites are a promising material to be used in medical devices and implanting.

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