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Preparation of PLA based biodegradable nanofibre films and their characterization

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Nanofibres have been obtained from sugarcane bagasse through different chemical treatments and mechanical grinding process. These nanofibres are then used for the preparation of their PLA-based biodegradable films by the solvent casing method using various weight percentages (0, 1, 2, 3, 4 & 5) of nanofibres. The morphological analysis, tensile properties, thermal property and optical properties of the films are characterized by field emission electron microscopy, tensile test, thermogravimetric analysis and UV-Vis spectrometers respectively. The film with 2 wt. % of nanofibre is found to offer the highest tensile strength (24.5 %) which is 57-55 % more than that of neat PLA film. The thermal and optical properties of PLA films are also significantly influenced by the incorporation of nanofibres. Based on the results obtained from the present study, the prepared biodegradable nanofibre films can be used in nanofabrics and for packaging applications.

Keywords: Biodegradable film, Nanofibre, Poly lactic acid, Sugarcane bagasse

1 Introduction

In the last decades, wide-spread use of non-biodegradable and non-recyclable petrochemical polymers in a number of applications from packaging to automobile has been a major cause of bad environmental impact. In order to overcome this issue, a good number of biocomposites have been developed so far by the researchers. Due to several advantages of natural fibres such as high strength and modulus, low density, biodegradability, recyclability and abundant availability, these fibres were reinforced in polymeric matrix to prepare the biocomposites[1-4]. These biocomposites are found partial biodegradable which motivates researchers for the development of complete biodegradable composites (green composites). Such types of composites can be prepared by using biopolymers (PLA, PHB, starch, chitosan and soy based polymers) as matrix and natural fibres (hemp, banana, sisal, rice husk, coir, bamboo and so on) as reinforcement.

Among biopolymers, poly lactic acid (PLA) has been frequently used because of its good strength and modulus, biodegradability, eco-friendliness and easy processing behaviours[5]. It can be produced from lactic acid by fermentation of agricultural products, like corn, potatoes, sugar beet, rice and agriculture waste[6]. PLA has been utilized in a number of applications such as packaging (i.e. food packaging, bottles and cups), automobile (i.e. under-the-hood components, visible interior parts and so on), and biomedical (i.e. orthopaedic devices, drug delivery systems and so on)[7, 8]. Some recent applications of PLA-based composites are mulch film, biodegradable PLA cups, tea bags, 3D printed micro coils and 3D printed human skull[9]. However, the pure PLA films have some drawbacks also, such as brittleness, low thermal stability, low water vapor and low oxygen barrier properties [5]. In order to overcome these drawbacks and to get enhanced properties, nano fillers (nanoparticles and nanofibres) were added into PLA[10, 11].

Cellulose is the most abundant material extracted from the plant fibres, such as hemp, rice husk, kenaf, abaca, flax, bamboo, sisal, jute, coconut husk, cassava bagasse, banana, sugarcane bagasse, etc.[11-14]. Cellulose of different shape and sizes has been used to prepare its composites for the several applications. The nano sized fillers in the biopolymer matrix contain fewer defects as compared to macro/micro size fillers. This fact accelerates the researchers to develop the nanofibres. Currently, nanofibres have been isolated using the various techniques, such as acid hydrolysis[15], enzymic hydrolysis[16], high pressure homogenization[17], grinding[18], and steam explosion and cryocrushing[19]. Pereda *et al.*[20] prepared the sodium caseinate/cellulose based film by the casting and drying. The improved tensile and barrier properties by incorporation of nanofibres was reported. The melt mixing process was used to prepare the cellulose nanofibre/PLA nanocomposites with maleated

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PLA (PLA-g-MA) as a compatibilizer, and enhanced physical and mechanical properties were obtained[21]. Savadekar and Mhaske[22] obtained nanofibres from cotton fibre by chemo-mechanical process subjected to prepare its starch based films, and observed that the film with 0.4 wt. % reinforcement showed 46.10 % improvement in tensile strength as compared to matrix.

The main aim of the present study is to prepare a biodegradable film with enhanced performance using nanofibres of sugarcane bagasse as reinforcement and PLA as matrix by the solvent casting method. The effect of varying percentages of nanofibres loading on the mechanical property (tensile), thermal stability, and optical properties (transmittance, absorbance and transparency value) of biodegradable PLA-based films is studied.

2 Materials and Methods

2.1 Materials

Poly lactic acid (PLA-4043 D) in pellets form was purchased from Nature-Tech India Pvt. Ltd. The fibres of sugarcane bagasse were provided by K.M. Sugar Mills, Faizabad, Uttar Pradesh, India. The chemicals, such as chloroform, acetone, sodium hydroxide and hydrochloric acid, were purchased from Science Corporation and UMA Scientific traders, Prayagraj, India.

2.2 Extraction of Nanofibres

Nanofibres from sugarcane bagasse were extracted through chemo-mechanical method consisting of alkali treatment, acid treatment and high speed mechanical grinding process. Dried fibres were soaked in 15 wt. % NaOH solution for 4 h at 25 °C, thereafter treated fibres were washed several times with distilled water to remove the remaining alkali. After drying the treated fibres in a hot air oven at 80 °C for 24 h, they were soaked in 1 mol HCl solution, prepared by adding 88.28 mL of HCl into 911.72 mL of distilled water, for 4 h at 80 °C. Further, the fibres were washed well with deionized water to get rid of acid HCL, and then treated fibres were again soaked in 2 wt.% NaOH solution for 4h at 80 °C to remove the remaining noncellulosic constituents. Then, these treated fibres were washed and dried in hot air oven. Finally, dried and treated fibres were grinded using high speed grinder at revolution of 1500 rpm for 20 min to obtain the nanofibres of sugarcane bagasse. The size of isolated nanofibre was measured by Dynamic Light Scattering (DLS) and its average size was reported as 53 nm (Fig. 1).

2.3 Preparation of Nanofibre Films

The solvent casting/evaporation method was employed for the preparation of nanofibre reinforced PLA films. PLA pellets were dried in a hot air oven before their uses. The PLA pellets were dispersed in 50 mL chloroform at 70 °C to make its solution. The mechanical stirring was applied to ensure the uniform mixing of PLA pellets into chloroform. The various amount of nanofibres (1–5 wt.%) was separately dispersed into PLA solution. To obtain a uniform dispersion of nanofibres into solution a magnetic stirrer was used. The resultant uniformly dispersed solution was placed in a hot air oven to remove the unwanted impurities from the solution and also to prevent the formation of air bubbles. Then the solution was cast in to glass petri dish of ~ 100 mm diameter. Finally, petri dish was kept at 30 °C for 3 days to get the films after complete evaporation of the solvent. The removed films were again dried for 24 h prior to their characterization. The prepared films were marked as: F0 = neat PLA film; F1= PLA film reinforced with 1 wt.% of nanofibres; F2= PLA film reinforced with 2 wt.% of nanofibres; F3= PLA film reinforced with 3 wt.% of nanofibres; F4 = PLA film reinforced with 4 wt.% of nanofibres; and F5= PLA film reinforced with 5 wt.% of nanofibres.

2.4 Field Emission Scanning Electron Microscope (FESEM)

The morphological analysis and element mapping of prepared neat PLA and nanofibre reinforced PLA (NC/PLA) films were captured using FESEM (Nova nano SEM 450) with energy dispersive X-ray (EDX) analyzer at IIT Kanpur, India. A very thin gold coating was applied to the films to make them conductive.

2.5 Tensile Test

Tensile properties of neat PLA and NC/PLA films were evaluated as per ASTM D882 – 97 on the universal testing machine (Tinius olsen, 10 kN) at a cross head speed of 1 mm/ min. The film samples were cut in a rectangular shape (80 mm × 15 mm) to perform the test. All the films were performed using rubber gripped holder at 24 °C and 50% relative humidity. To ensure that samples were straight in holder, pre-load was applied. Minimum five samples were tested of each film and their mean value were taken.

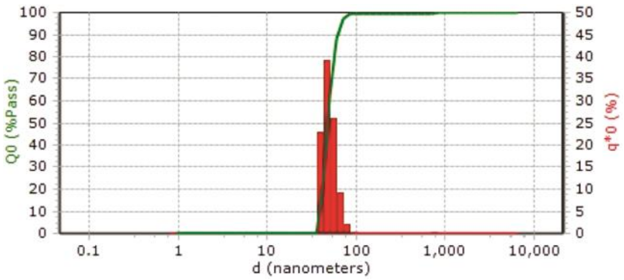

Fig. 1 — Particle size distribution of nanofibre of sugarcane bagasse

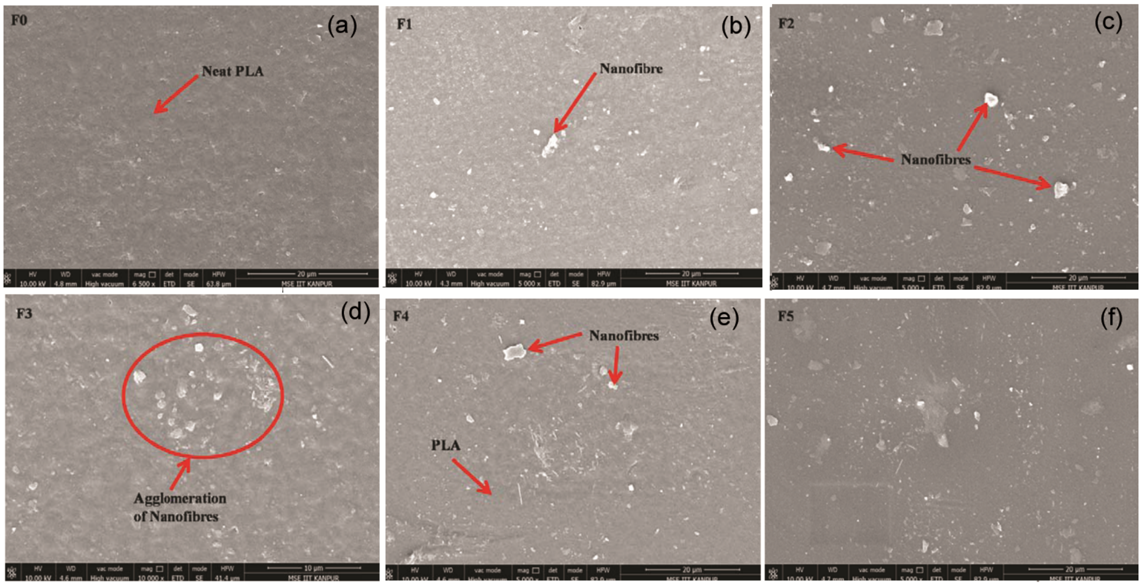

Fig. 2 — FESEM images of PLA based films reinforced with: (a) 0 wt.% nanofibre, (b) 1 wt.% nanofibre, (c) 2 wt.% nanofibre, (d) 3 wt.% nanofibre, (e) 4 wt.% nanofibre and (f) 5 wt.% nanofibre

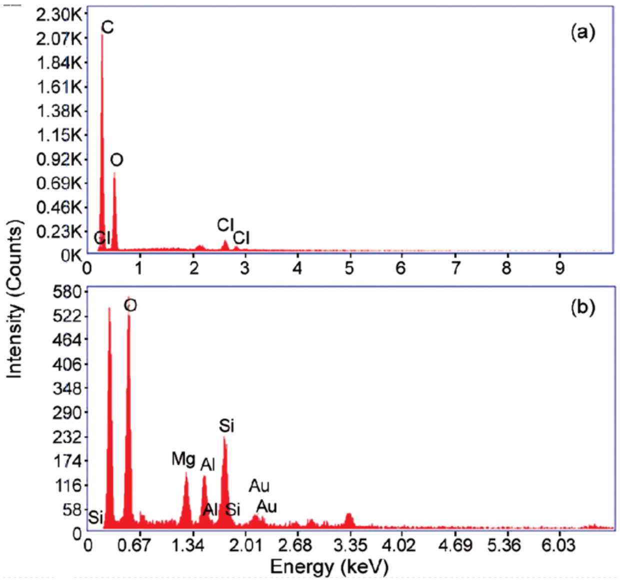

Fig. 3 — EDX image of films (a) neat PLA and (b) F2 (2 wt. %)

2.6 Thermogravimetric Analysis (TGA)

The thermal stability of the nanofibres films was measured by Thermogravimetric analysis using TGA instrument (TGA, STA 409 Netzsch). The test was performed in a temperature range 30-500 ˚C with a heating rate of 10 ºC/min in a nitrogen atmosphere at a flow rate of 20 mL/min.

2.7 UV-Vis Spectrometer

Optical properties (transmittance, absorbance and transparency value) of the nanofibres films were measured using ultraviolet – visible (UV – Vis) spectrometer (UV-3600 Plus, Shimadzu, Japan) in wavelength range 190 - 800 nm. The transparency value (TV) was calculated by the following equation:

$$\mathrm{TV} = \log\,[T\,(600\ \mathrm{nm})/\,X\,(\mathrm{mm})] \qquad \ldots (1)$$

where T is the transmittance; and X, the thickness of film (0.015- 0.025 mm).

3 Results and Discussion

3.1 FESEM Results

SEM microstructures of neat PLA (F0) and NC/PLA films (F1, F2, F3, F4 and F5) are shown in Figs 2 (a-f). In Fig. 2 (a), a smooth surface and complete absence of voids can be observed for neat PLA film F0. The effect of nanofibre concentrations on its dispersion and surface roughness can be seen in each nanofibre film. The homogeneous distribution of nanofibre in to PLA matrix is found for 2 wt.% of nanofibre concentration. On increasing the nanofibres concentrations above 2 wt.%, degree of agglomeration and decrease in homogeneity can be seen, as depicted in Figs 2 (c-f). Further, the increase in surface roughness can also be observed with an increase in concentration of nanofibres. Fig. 2 (c) shows a good dispersion of nanofibre in to PLA matrix without an agglomeration for film F2. A uniform dispersion of the nanofibres is responsible for the effective stress transfer and enhanced crystallinity, resulting in improved mechanical properties[11, 23]. Hence, enhanced mechanical properties can be expected for the film F2. In Fig. 2 (d-f), agglomeration and nonuniform dispersion due to overloading of nanofibres can be seen, which may be a reason for their reduced mechanical properties. In addition, the elemental composition of neat PLA film and nanofibres reinforced film F2 is also obtained by Energy–Dispersive X-ray (EDX) analysis [Figs 3 (a) & (b)]. Some elemental contents, such as C, Cl and O, are found to be present in PLA film, whereas nanofibres film is consisting of C, O, Mg, Al, Si and Au due to presence of nanofibres.

3.2 Tensile Properties

Tensile strength and elongation-at-break (%) of neat PLA and NC/PLA films are depicted in Fig. 4. It can be easily observed that each composite film offers the higher values of tensile strength than that of neat PLA film which shows a positive effect of nanofibres reinforcement. This can be explained on the basis of the fact that reinforcing materials with a high aspect ratio (length/diameter), due to their high specific surface area, provides the better reinforcing capacity, resulting in increased strength[20, 24-26]. It has also been reported that high surface contact area and formation of the intermolecular hydrogen bond between nanofibres and PLA matrix may also be a cause of enhanced mechanical strength[27]. Another, appropriate reason for enhancement in tensile strength may be due to improved crystallinity index after chemical treatments[26, 28, 29]. It is also noticed that tensile strength increases with an increase in nanofibres content up to 2 wt.% and then decreases. Similar types of results have also been reported in published literatures[20, 30, 31].

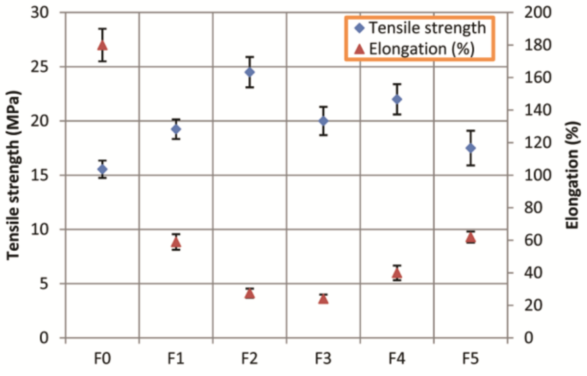

Fig. 4 — Tensile properties of PLA based nanofibre films

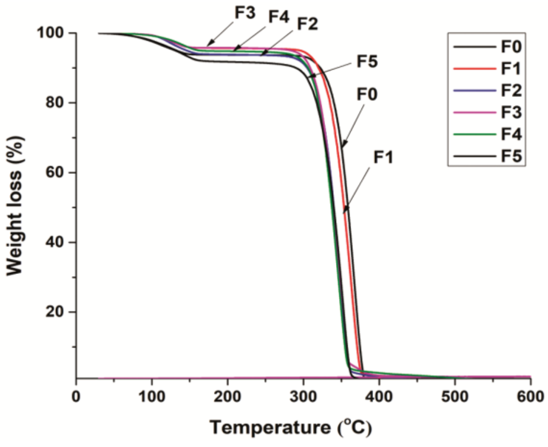

Fig. 5 — Weight loss *vs* temperature graph of PLA based nanofibre films

Film F2 has the highest tensile strength (24.5 MPa), which is 57.55 % higher than that of neat PLA film F0. The highest tensile strength of film F2 can be owing to the homogeneous distribution of nanofibres into PLA matrix, which offers an effective stress transfer. The homogeneous distribution in film F2 has already been confirmed from FESEM analysis. On the other hand, a decrease in tensile strength with an increase in nanofibres concentrations can be due to agglomeration/non-uniform dispersion of nanofibre in PLA matrix[20, 32]. The highest elongation-at-break (180 %) is shown by neat PLA film as compared to all the nanofibres reinforced films. The highest elongation of neat PLA film shows its better ductility. Elongation-at-beak of nanofibres films decreases with increase in nanofibre concentration due to rigid nature of nanofibres, thus showing their reduced ductility. Again, this finding is found to be in agreement with the results published in literature[20, 32].

3.3 Thermogravimetric Analysis (TGA)

Percentage of change in weight loss against the temperature of neat PLA and NC/PLA films is depicted in Fig. 5. The values of weight loss at different temperatures of the films are also illustrated in Table 1. Natural fibres are consisting of many constituents that have different degradation temperatures due to their different chemical structures. The ranges of decomposition temperature of main constituents are: hemicelluloses (220-315 °C), cellulose (315 - 400 °C) and lignin (200 - 700 °C)[32]. Initial low temperature weight loss of the films starts at around 40 °C and goes to 100 °C, due to the evaporation of loosely bound moisture absorbed by the films[33-38]. At this stage, lower thermal stability is shown by PLA film, which may be credited to higher moisture absorption. It is also interesting to observe that the film F5 has lower thermal stability, which may be due to a higher concentration of nanofibres. The second stage of degradation starts at 200 ºC due to the degradation of constituents of the nanofibres. On increasing the temperature above 350 °C, a sudden drop in weight can be seen due to the decomposition of cellulose. At 380 °C, more than 96% of weight loss for the films can be observed. A sudden drop in weight against the temperature of the films in the range 350-380 °C (which is the degradation temperature range of cellulose) confirms the presence and purity of cellulose and removal of lignin after chemical treatments and mechanical grinding.

3.4 UV-Vis Spectrometer Analysis

The optical properties, like transmittance and absorbance, of neat PLA and NC/PLA films have been measured using UV-Visible spectroscope. The UV transmittance and absorbance spectra of the films are measured in wavelength range 200–800 nm, and obtained results are presented in Figs 6 (a) and (b) respectively. At different wavelengths, the percentage of transmittance and absorbance of these films are also presented in Tables 2 and 3 respectively. The neat PLA film exhibits the higher transmittance as compared to all the NC/PLA films, as expected. However, on increasing the nanofibre concentration, transmittance of the films decreases, as also reported in literature [39-41]. The lowest transmittance as shown by film F5 can be due to a higher concentration of nanofibres. It is interesting to observe that transmittance increases with increase in wave length also. For visible light (wave length more than 400 nm), the maximum and almost saturated transmittance is shown by nanofibres films including neat PLA film. Transparency value is an important parameter for optical property analysis which is inversely proposal to transmittance; higher transparency value offers the lower transmittance and vice-versa[39]. Furthermore, the transparency value of the films decreases with the addition of nanofibres. Similar results have also been reported by other researchers[39, 42]. The lowest transparency value (1.37) is associated with neat PLA, whereas its highest value is associated with film F5 due to higher nanofibres concentration, as shown in Table 2.

Further, the absorbance of neat PLA and NC/PLA films is shown in Fig. 6 (b), and its values at different wavelength is presented in Table 3. A good blocking capacity to UV light (< 400 nm) is presented by all the films. It can be observed that all the NC/PLA films including neat PLA film have capability to block the light up to 400 nm wavelengths; however films are not found much efficient above 400 nm wavelength. Each PLA-based nanofibre film offers the better absorbance than the neat PLA film. The lowest and highest absorbance is seen for neat PLA film and film F5

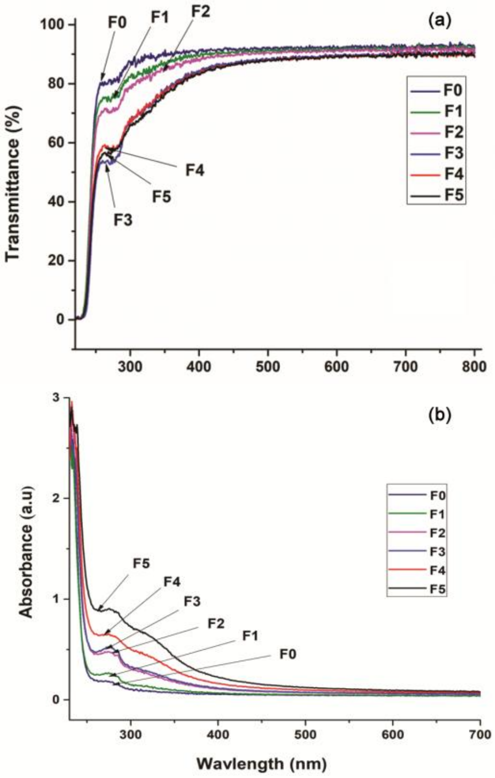

Fig. 6 — Optical properties of PLA based nanofibre films (a) transmittance and (b) absorbance

Table 1 — TGA results of nanofibre films

Temperature, °C	Weight loss, %					
	F0	F1	F2	F3	F4	F5
50	0.23	0.04	0.03	0.02	0.02	0.09
100	2.17	0.67	0.64	0.64	0.75	2.38
150	6.07	4.11	5.32	4.06	4.23	6.98
200	6.23	4.32	6.14	4.22	5.20	8.23
250	6.28	4.44	6.32	4.39	5.39	8.58
280	6.37	4.63	6.72	4.84	5.94	9.27
300	6.70	5.32	8.70	6.89	8.25	11.53
350	32.44	42.56	73.71	78.53	79.37	72.12
380	98.95	97.79	97.95	97.14	96.99	99.54

Table 2 — Transmission results of nanofibre films

Film type	Nanofibre wt. %	Transmission, %			
		Wavelength (280 nm)	Wavelength (350 nm)	Wavelength (600 nm)	Transparency value (T_V)
F0	0	81.30	90.56	92.39	1.37
F1	1	75.58	86.80	91.77	1.49
F2	2	71.49	85.34	91.32	1.57
F3	3	55.19	77.95	89.40	1.94
F4	4	58.49	77.65	89.35	1.95
F5	5	58.14	76.84	89.15	1.99

Table 3 — Absorbance results of nanofibre films

Film type	Nanofibre wt. %	Absorbance (a.u)		
		Wavelength (280 nm)	Wavelength (350 nm)	Wavelength (600 nm)
F0	0	0.17	0.07	0.04
F1	1	0.24	0.10	0.04
F2	2	0.45	0.18	0.06
F3	3	0.51	0.19	0.06
F4	4	0.63	0.29	0.08
F5	5	0.88	0.43	0.09

respectively. The higher blocking capacity to UV light makes the PLA-based nanofibres films suitable for packaging applications.

4 Conclusion

The biodegradable nanofibres films have successfully been developed using the solvent casting method and their mechanical, thermal and optical properties are studied. Based on the experimental outputs from the present study, following conclusions can be drawn:

4.1 The highest value of tensile strength is presented by the film with 2 wt. % nanofibres, credited to optimal loading and uniform distribution of nanofibres.

4.2 Good thermal stability is revealed by the PLA-based nanofibre films owing to the presence of nanofibres of high degradation temperature.

4.3 The films exhibit the good blocking capacity to UV light and its transparency values are increased by incorporation of nanofibres.

4.4 Based on the fruitful results, the newly prepared nanofibres films can be proposed for packaging applications. Further, this nanofibres film can also be used as a filter material (like face masks/respirators), because nanofibres have enhanced capture efficiency due to their very high surface area per unit mass.

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