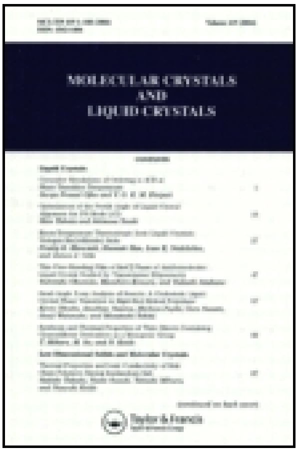

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Use of Primary Sludge from Pulp and Paper Mills for Nanocomposites

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Use of Primary Sludge from Pulp and Paper Mills for Nanocomposites

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Cellulose nanocrystals have been evaluated as reinforcement material in polymeric matrices due to their potential to improve the mechanical, optical, and dielectric properties of these matrixes. This work describes how high pressure defibrillation and chemical purification affect the sludge fiber morphology from micro to nanoscale. Microscopy techniques and X-ray diffraction were used to study the structure and properties of the prepared nanofibers and composites. Microscopic studies showed that the used individualization processes lead to a unique morphology of interconnected web-like structure of sludge fibers. The nanofibers are bundles of cellulose fibers having widths (5 to 30 nm) and estimated lengths of several micrometers.

Keywords Nanobiocomposites; nanocellulose; nanocomposite; polyurethane; pulp & paper sludge; sludge nanofibre

1. Introduction

The advantages of the presence of nanoparticles in composites include reduced weight, improved mechanical properties, better stress transfer, reducing the amount of dead load in many applications, mainly automotive and aeronautical [1].

The chemical, physical and biological properties of materials at the nanoscale have fundamental differences about their properties at the conventional level, because of quantum mechanical interactions at the atomic scale [2]. Nanotechnology brings multidisciplinary innovations in all areas of knowledge (chemistry, physics, agriculture, modern biology, among others) [3–5].

In the production of pulp and paper the average of 35% of the input material becomes waste in the form of general waste (sludge, lime sludge, ash from the boiler) and currently

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promoting some of these 56% of energy needed in the industry. The sludge waste is generated in two stages in the process of wastewater treatment. The primary sludge is obtained after the clarification process which is carried by primary sedimentation, and dissolved air flotation in which waste solids are removed. The secondary sludge came from secondary treatment that is usually a biological process in which microorganisms convert the waste into carbon dioxide and water while consuming oxygen [6]. Disposal of waste from pulp and paper is a difficult environmental issue since its majority is directed to landfills. While some waste is incinerated, some sold as a substrate for composting and applied in some forest areas, these practices are not common [7]. According to Son et al. [7], the utilization of waste paper was proposed as filling material in thermoplastic polymers. The use of fibers from the primary sludge for the production of composite materials can generate a lightweight, durable, non-abrasive, renewable, biodegradable and recyclable allowing competition with other artificial materials with less availability or environmental disadvantages and still helps with the disposal of industrial waste.

Currently, the debate is about the quantity and quality for future landfill space, which has been difficult to install and expensive to build and operate because of several restrictions, reducing their viability, and generate public opposition [6]. Therefore is essential to find a destination economically viable and environmentally sound to the sludge. In this situation, the production of nanocellulose seems to be a great opportunity, mainly because this sludge is already partially bleached, therefore it is interesting to use it as raw material due to its feature, less lignin, hemicellulose and other low molecular weight components, in a way to isolate the pure cellulose.

The cellulose (Fig. 1) is composed mainly of crystalline regions that it will result in important mechanical properties when dispersed in polymer for production of nanocomposites. Recent advances in producing bio-fibers, microfibrillated or nano-size fibers with high-strength and surface area offer manufacturing high-performance composites [8–10].

The cellulose polymer composites always face the interfacial problem between cellulose and polyolefins [14]. In this study hydrophilic polyurethane has been used as the matrix polymer. When the hydrophilic polyurethane is used as matrix, it is believed that no adhesion problem would occur and the dispersion would be much better.

Cellulose fibers attract considerable interest as reinforcing fillers for thermoplastic polymers especially those with a relatively lower melting point like polypropylene, high and

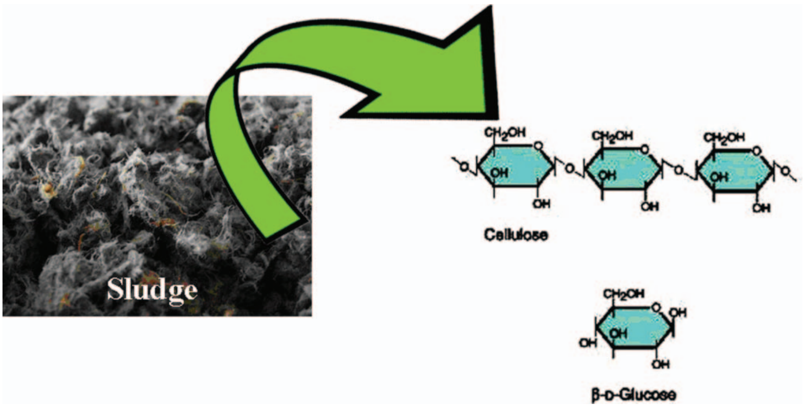

Figure 1. The repeating unit of cellulose.

low density polyethylene. Sludge from paper mills consists mainly of two components, fine cellulose fiber and inorganic materials, and can offer a number of benefits, as a substitute for the typical inorganic reinforcing fillers in manufacturing thermoplastic polymer composite.

A high percentage of the solid residues in the pulp and paper industry is paper sludge produced during wood pulping and papermaking operations. Because of the high cost of paper, the paper manufacturing industry is very interested in reducing the paper sludge disposal cost through recycling and reuse. The use of paper sludge to produce wood-based materials may be an innovative way to recycle paper sludge. Therefore, it may have potential application in particleboard production as an alternative to wood utilization. Through various studies, paper sludge has been demonstrated capable of serving as new reinforcing filler in the manufacturing of thermoplastic polymer composites [11,12]. These authors showed that the density and tensile properties of the composite increased as the concentration of the paper sludge increased, whereas izod notched and unnotched impact strengths slightly decreased.

Taramian et al. [13] characterized the mechanical properties and water resistance of particleboard made from paper sludge. The results indicated that the mechanical properties of the produced particleboards are negatively affected by the use of paper sludge (may be due to the inorganic materials present). The strengths of the UF-bonded board decreased much more than those of MDI-bonded board as paper sludge content increased.

A bleached kraft pulp from softwood was used as the cellulose source for obtaining cellulose nanofibrils prepared by 2,2,6,6-tetramethylpiperidine-1-oxy radical (TEMPO)-mediated oxidation of native celluloses followed by mechanical disintegration of the oxidized celluloses in water TEMPO-mediated oxidation. The pulp contained approximately 90% cellulose and 10% hemicelluloses. Composite films were produced with this nanocellulose and PET. This final product contains individualized nanofibrils with random orientation, the films had higher Young's modulus (ca. 10 GPa) and lower elongation (ca. 5.1%) and the oxygen permeability of the films was lower than that of the PET films [15].

The polyurethane resins show great versatility and can be used in different industries. These resins can be obtained with densities ranging from 6 to 1220 kg/m^3, which may present as a highly flexible elastomer or harder, or as engineering plastic [16]. The polyurethane are an important and very versatile class of polymer materials, with desirable properties, such as its high abrasion resistance, tear strength, excellent shock absorption, flexibility and elasticity.

Its applications are varied and include flywheel, panels, seats, bumpers in the automotive industry, mattresses and seats in the furniture industry, shoes soles, nucleus of skis and boards in the windsurfing sport and leisure industry, adhesives, refrigerators, heaters, biomedicine, etc [17,18].

Polyurethanes have been used in several applications such as biomedical, coatings, adhesives and composites [18,19]. Polyurethanes form a copolymer structure which can be adjusted by formulating the polyurethane based on different isocyanate/polyol or altering the properties of the polyurethanes with different fillers and reinforcements [19]. Polyurethanes have been reinforced with certain fillers such as talc, mica and glass fiber in the form of polymer matrix composite material increasing the tensile strength, decreasing the elongation to break and discolouring the polymer [20–22]. The aim of this study was to examine the effect of fibrillation of pulp and paper primary sludge cellulose fibers using a high pressure steam treatment and compare the reinforcing effect of nano sized cellulose fibrils in the polyurethane matrix. Earlier studies made on polyurethane and cellulose both as micro and nanocomposites have been reported [23,24] but high crystalline nanofibrils of sludge fibers prepared by steam explosion process have not been utilized in a polyurethane matrix before.

2. Experimental

2.1 Materials

The materials used for the study includes sludge fibers were supplied by the company Superpolpa from Iaras – SP, Brazil, Sodium hydroxide (NaOH), Acetic acid (CH_3COOH), Sodium hypochlorite (NaClO) and Oxalic acid ($C_2H_2O_4$) of analytical purity grade were purchased from Merck and Co., Inc., Methylene di-*p*-phenyl-diisocyanate (MDI, 99%, Sigma Aldrich), 1,4-butanediol (BD, 99%, Sigma Aldrich), 2, 2′-(Methylimino)diethanol (MIDE, 99%, Sigma Aldrich), and *N, N*-dimethylformamide (DMF, 99%, Sigma Aldrich) and polycaprolactone diol (PCL-diol) with $M_n = 530$ were used as received. Methylene di-p-phenyl-diisocyanate (MDI) was purified through vacuum distillation, while 1,4-butanediol (BD) was distilled with calcium hydride (CaH_2) in a vacuum to eliminate moisture. DMF was distilled over calcium hydride (CaH_2) at the atmospheric pressure under nitrogen protection. MDI was chosen because it is widely used in synthesis of biomedical polyurethanes due to its reactivity and PCL-diol was chosen because of its biodegradability.

2.2 Isolation of Cellulose Nanofibrils

Pulp and paper primary sludge were treated with 2% NaOH (fiber to liquor ratio 1:10) in an autoclave and kept under 138 kPa pressures for a further period of 1 hour. Pressure was released immediately. The sludge fibers were removed from the autoclave and the fibers were washed in water until it was rid of alkali. The steam exploded fibers were bleached using a mixture of NaOH and acetic acid (27 g and 78.8 g respectively) and a mixture of 1:3 sodium hypochlorite solutions. The bleaching was repeated six times. After the bleaching the fibers were thoroughly washed in distilled water and dried. The steam exploded bleached fibers were treated with oxalic acid of 11% concentration in an autoclave until it attained a pressure of 138 kPa. The pressure was released immediately. The autoclave was again set to reach 138 kPa and the fibers were kept under that pressure for 15 minutes. The pressure was released and the process repeated eight times. The fibers were taken out washed until the washings no longer decolorized $KMnO_4$ solution to make sure that the washings are free from acid. The proceeded nanofibrils were suspended in water and kept stirring with a mechanical stirrer of type RQ-1.27 A and 8000 rpm for about 4 hours until the fibers are dispersed uniformly.

2.3 Processing of Nanocomposites

The preparation of polyurethane-cellulose nanocomposite is as follows:

2.3.1 Synthesis of Degradable PUs. Degradable PUs were synthesized using a two-step method. The stoichiometry of the PU synthesis reaction was approximately 2:1:1 of hard segment (diisocyanate)/soft segment (PCL-diol)/chain extender (1, 4-BD). The MDI was dissolved in 50 mL DMF and PCL-diol were added drop wise into the MDI solution. This mixture was allowed to react at 60°C for a period of 3 h. The solution was cooled to 25°C, 100 mL DMF was added, and then 5% (w/v) chain extender in DMF was added drop wise to the reaction mixture and stirred for 18 h. After the reaction was finished, the polymer solution was precipitated in distilled water, and dried in a vacuum oven at 60°C for at least 48 h before further use and characterization.

2.3.2 Preparation of PU Thick Films. Polymer films were prepared by solvent casting. The synthesized PUs were dissolved in tetrahydrofuran (THF) at a concentration of 4% (w/v). Polymer solution (12 mL) was then poured into levelled 5 cm PTFE casting plates and cast into thick films at room temperature. Casting plates were covered to prevent dust from contaminating the films and excessive fast casting, which may induce bubbles and result in surface defects. The cast films were removed from the casting plates and dried in a vacuum oven at 60°C for 4 h to remove residual solvent. The average thickness of the film was about 0.08–0.10 mm.

2.3.3 Preparation of Nonwoven Nanofibril Mats. The nonwoven mats of cellulose fibers and nanofibrils were formed by filtering the water-nanocellulose slurry. For the nanocellulose, special membrane filter (Polyethersulfone, 0.1 μm) was used for mat formation of fibrils was used for drying and forming the mat. The slurry was agitated during the filtering process to distribute the nanocellulose evenly on the mesh. The nanocellulose formed mat could easily be peeled off from the mesh after drying due to strong hydrogen bonds. The thickness of the fiber mat was adjusted by altering the cellulose concentrations on the water–nanocellulose slurry. The thickness of the mats varied between 0.05–0.2 μm.

2.3.4. Nanocomposite Preparation. The composite materials were prepared by the film-stacking method. In this method, the PU films and non woven nanocellulose mats were stacked and compression moulded. The temperature (150–200°C), pressure (10000–20000 kPa) and compression time (1–4 min) were varied to find the optimum composite properties. The compression moulding conditions were optimized to 175°C at 10000 kPa for 1 min and 30 s. The final composites, containing 1, 2 and 4 wt% nanocellulose, were termed PU-NC(1%), PU-NC(2%), and PU-NC(4%) respectively.

2.4 Characterization

2.4.1 X-Ray Diffraction (XRD). Wide-angle X-ray diffraction data were collected using a Rigaku 200B X-ray diffractometer (40 kV, 40 mA) equipped with Cu Kα radiation (λ = 0.1541 nm) Patterns were recorded by monitoring diffractions from 1.5° to 30°. The scan speed was 2°/min.

2.4.2 Environmental Scanning Electron Microscopy (ESEM) Analysis. Philips XL30 FEG ESEM was also used to observe the morphology of dried nano film with an accelerating voltage of 30 kV. The nanofibers were analyzed using water suspension of the nanofibers. A drop of suspension of nanofibers was kept onto a carbon film and left to dry in a silica gel ambient for 12 h followed by coating with platinum using the sputtering techniques. The film was sputter-coated with platinum using a Baltec SCD050 sputter coater for enhanced conductivity.

2.4.3 Transmission Electron Microscopy (TEM) Analysis. Transmission electron micrographs of cellulose nanofibres were taken with a Philips CM 30 transmission electron microscope with an acceleration voltage of 75 kV. Nanowhiskers were deposited from an aqueous dilute dispersion on a microgrid covered with a thin carbon film (~200 nm). The deposited nanowhiskers were subsequently stained with a 2% uranyl acetate solution to enhance the microscopic resolution. For analysis of the nanocomposites, the samples were first prepared by placing PU/nanocellulose into epoxy capsules, and the epoxy was cured at 70°C for 24 h in a vacuum oven. Then the cured epoxies containing PU/nanocellulose were then trimmed in a Leica Ultracut EM UC6 ultramicrotome with freshly cleaved glass knives to obtain into 80–100 nm thickness. A carbon layer of 3 nm thickness was deposited on these slices on 200 mesh copper nets for TEM observation.

2.4.4 Scanning Force Microscopy (SFM) Analysis. Cellulose nanofibrils were observed using atomic force microscopy, NanoScope IVa, Multimode SPM (Veeco Inc. Santa Barbara, USA), in tapping mode. Calibration was performed by scanning a calibration grid with precisely known dimensions. All scans were performed in air with commercial Si Nanoprobes SPM tips with a resonance frequency of about 300–330 kHz. A free amplitude (A_0) of about 20 nm and a set-point ratio (r_{sp}) between 0.4 and 0.6 were used. r_{sp} is the ratio between the setpoint amplitude (A_{sp}) and A_0. Image processing including flattening was made. The images were obtained simultaneously in tapping mode at the fundamental resonance frequency of the cantilever with a scan rate of 0.5 line/s using a j-type scanner. The free oscillating amplitude was 3.0 V, while the set point amplitude was chosen individually for each sample. For the sample images were scanned on at least five different fibers. Usually two different areas of each fiber were investigated. Only one representative image of sample is shown. Samples of cellulose nanofibril for characterization were prepared by pipetting a 0.12 g/l aqueous whisker suspension was allowed to dry on a freshly cleaved mica surface. The sample was allowed to dry in room temperature overnight.

2.4.5 Mechanical Test. The mechanical properties of the films were measured on a Universal Materials Testing Machine from Instron, U.S.A., equipped with a 500 N load cell. The tensile test was performed at 23°C with a gauge length of 40 mm and crosshead speed of 100 mm/min. Samples were cut into rectangular strip with dimension of $80 \times 5 \times t$ mm^3, where t, the thickness, varied from 0.18 mm to 0.25 mm. For each sample, five strips were tested. Young's modulus was determined from the slope of initial low strain region. Toughness was defined as work to fracture and was calculated as the area under the stress–strain curves.

3. Results and Discussion

The morphological investigation of the structural changes occurred during different treatment procedures were done by environmental scanning electron microscopy and Transmission electron microscopy. The different structural changes occurred in raw, steam exploded, bleached and acid treated sludge fibers are shown in Fig. 2(a–d). The micrographs prove for the well separation of the micro cellulose fibrils from the raw sludge fibers when the primary sludge undergoes steam treatment. The steam treatment facilitates the dissolution of non-cellulosic components present in the primary sludge fibres. The dissolution of these components during the steam explosion process allows the embedded micro fibrils having the diameter less than 5 μm to break up from the raw sludge.

The further purification of steam treated sludge fibers by bleaching also assist to increase the separation of thin microfibrils having the diameter less than 2 μm from the fiber surface. These fibers also observed to have few nanofibrils detached from the microfibril structures. The TEM micrograph of steam coupled acid treated sludge fibres proves separation the well individualized nanofibrils having the diameter less than 100 nm.

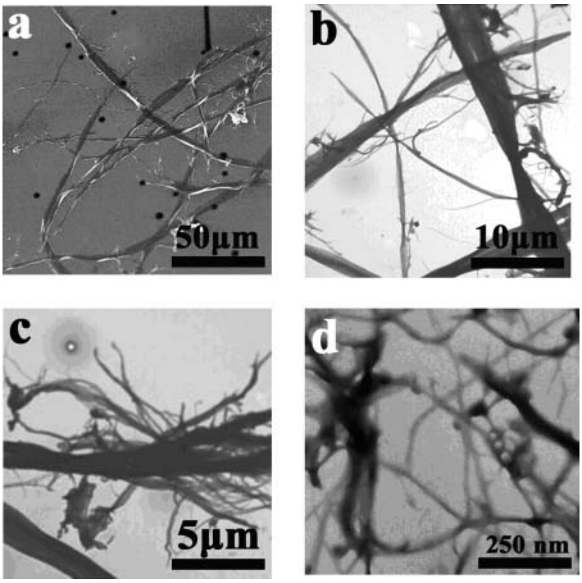

Figure 2. (a) SEM micrographs of raw sludge fibres; (b) TEM micrographs of steam exploded sludge fibres; (c) TEM micrographs of bleached sludge fibres; (d) TEM image of acid treated sludge fibres.

The micrographs prove that the helicoidal structure of cellulose is maintained during all treatment processes. The micrographs also shows an increase in tendency of fibrillation of sludge fibers when it undergoes steam explosion, bleaching and further acid coupled steam treatment.

The primary sludge nanofiber suspension obtained after the acid coupled steam treatment was analyzed to determine diameters using AFM. The AFM image (Fig. 3) shows the surface of air-dried sludge nanofiber. It is seen that the fibers are indeed nanosized, and the diameter of nanofibers is within the range 5–20 nm. The well interconnected network of nanofibers can also be seen from the AFM image. The acid correlated steam treatment method has been used to produce cellulose nanofibrils, essentially with the diameter in the nanometer range and with lengths ranging to several micrometers.

The AFM image shows continuous nanofibers with a uniform diameter of approximately 12 nm, forming an extremely fine network, which is observed as a significant outcome of the technique adopted for the nanofibril extraction. Thicker fibrils in the agglomerated form were not observed in the scanned areas. The width of isolated sludge fibers in this study corresponds to the nano rage, indicating that the adopted steam coupled acid treatment method extracts the nanofibrils without breaking the interconnected fiber structure. This cross-linked fibril structure of the extracted sludge fibers helps to offer maximum reinforcement in the polymeric matrices for nanocomposite applications.

The morphological investigation of the prepared Polyurethane-Nanocellulose (PU-NC) nanocomposite films were done to analyse the structure of the nanofibrils after the composite fabrication. The microtomed TEM image of PU-NC with nanocellulose loading of 2% is shown in Fig. 4. The sludge nanofibrils with the diameter below 20 nm are observed to be completely dispersed in the polyurethane matrix without any large agglomeration. The cellulose nanofibrils in the nanocomposite seem to be concentrated in certain areas. The TEM shows that the fibril structure is completely preserved in the developed nanocomposite.

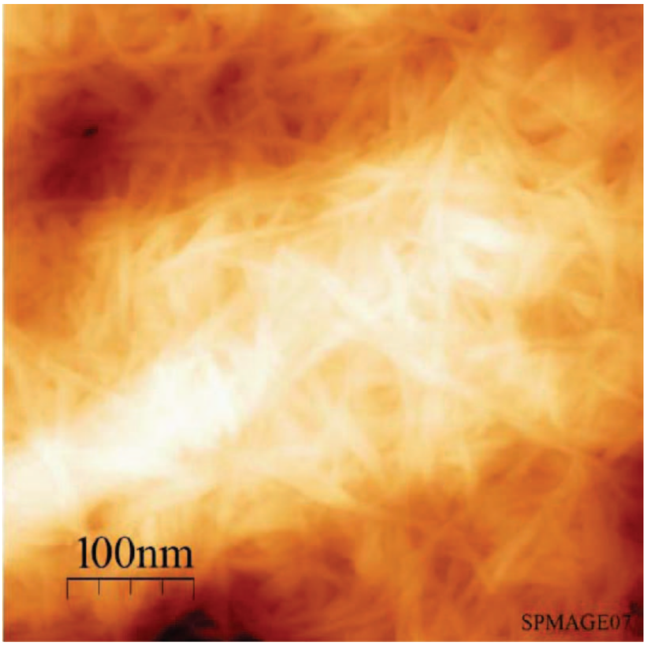

Figure 3. AFM micrographs of acid treated sludge fiber.

The XRD analysis of the isolated nanocellulose and nanocellulose reinforced PU composites were made to determine the crystalline nature of nanocellulose and its nanocomposite. From the XRD spectra shown in Fig. 5, 2θ angle at 22.7° corresponds to the (200) reflection of cellulose I [25]. This peak is clearly visible in the PU-NC nanocomposite even though the cellulose content is low (2%). The peak centred at $2\theta = 22.7°$ can be identified in the PU-NC (2%) nanocomposite which proves that the original cellulose I structure is conserved in the nanocomposite.

To examine the effect of nanocellulose as a reinforcing phase in the polyurethane nanocomposites, the classical tensile tests in the nonlinear range were performed. The addition of nanocellulose as the reinforcement in Polyurethane guide to remarkable improvement of tensile and Young's modulus of the nanocomposites as summarized in

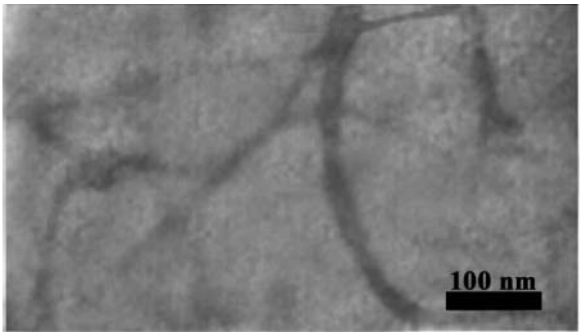

Figure 4. TEM image of polyurethane-cellulose nanocomposite.

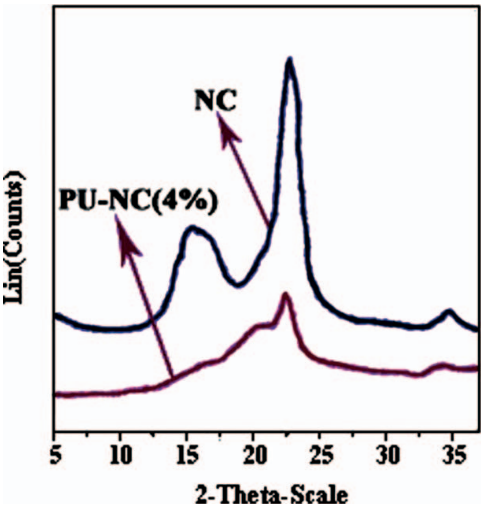

Figure 5. XRD patterns of cellulose and polyurethane-cellulose nanocomposite.

Table 1. Mechanical properties of pure polyurethane and nanocellulose embedded composites

Samples	Tensile Strength (MPa)	Young's modulus (MPa)
PU	17.5 ± 0.6	37.5 ± 0.4
PU-NC(1%)	21.7 ± 2.1	71.3 ± 1.8
PU-NC(2%)	32.4 ± 0.3	108.4 ± 1.5
PU-NC(4%)	45.6 ± 1.4	152.63 ± 1.3

Table 1. The tensile strength of was increased from 17.5 ± 0.6 MPa for pure PU to 21.7 ± 2.1MPa for PU-NC (1%), and further to 32.4 ± 0.3 MPa for PU-NC (2%) which in turn increase to 45.6 ± 1.4 MPa for PU-NC (4%). The Young modulus also shows a sharp increase from pure PU to PU nanocomposite loaded with 4 wt% nanocellulose. A four-fold increase in modulus value is observed for PU-NC(4%) compared to pure PU. These results indicate the strong interaction between nanocellulose and polyurethane matrix offering maximum reinforcement, which significantly increase PU-NC nanocomposites strength.

4. Conclusions

This study highlights the successful isolation of nanofibrils from primary sludge by steam coupled acid treatment. The morphology of the sludge fibers from micro to nano scale were investigated by TEM proves for the successful separation of the well individualized sludge nanofibrils having the diameter less than 100 nm. The AFM analysis also proves the extraction of continuous nanofibers with a uniform diameter of approximately 12 nm, forming an extremely fine network. The TEM micrograph of the nanocomposite shows the sludge nanofibrils with the diameter below 20 nm were observed to be completely dispersed in the polyurethane matrix, preserving the nanofibril structure after composite fabrication.

The XRD analysis confirms that cellulose nanofibril in the prepared nanocomposites preserves the original crystalline structure of cellulose (cellulose I). The mechanical properties of the developed sludge nanocellulose-polyurethane nanocomposite increase directly with the increase in nanocellulose content. The addition of only 4 wt% cellulose nanocrystals, obtained polyurethane nanocomposite with tensile strength of 45.6 ± 1.4 MPa and modulus of 152.63 ± 1.3. The developed nanocellulose and its composites confirmed to be a very versatile material having the wide range of biomedical applications and biotechnological applications.

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