GVU Journal of Research and Development Vol. 1, Number 2, August 2024 ISSN: 3045-5145

Graft Copolymerisation of Acrylamide on Nanocrystalline Cellulose from Agricultural Waste

Moses O. Onigbinde & Gift E. Edison
Chemical Sciences Department
Glorious Vision University (Formerly Samuel Adegboyega University)
Ogwa, Edo State, Nigeria
monigbinde@gmail.com

DOI: https://doi.org/10.5281/zenodo.14035635

Abstract

Nanocrystalline cellulose (NCC) is a promising renewable biomaterial that can be used as reinforcing component in high performance nano composite and as absorbent polymer. In this study, graft copolymerisation of acrylamide onto nanocrystalline cellulose gotten from plantain peel (PP) and orange mesocarp (OM) was done. The raw samples were subjected to alkali pretreatment method followed by bleaching process to extract the cellulose. Thereafter, the extracted cellulose was hydrolysed with 50% sulfuric acid at 30^0C for 2hours to obtain the NCC. Graft polymerisation of acrylamide onto the NCC in heterogeneous medium was initiated with ceric ammonium nitrate. The grafting conditions were 30^0C at a time interval of 2hours, ratio of monomer to NCC 3:1 and an initiator concentration of 0.020M. OM gave a higher NCC yield of 23.50% while PP gave a yield of 5.01%. The % polymerisation and % grafting for OM were 55.6 and 45.7 and for PP 10 and 3.2 respectively. The oil sorption analysis shows an improvement in the property of the grafted NCC compared with the raw OM and PP. This work has explored the surface modification and application of NCC using graft copolymerisation giving better understanding on this emerging nanomaterial.

Keywords: Graft Copolymerisation, Nanocrystalline Cellulose, Agricultural Waste

Introduction

Cellulose (Latin: rich in small cells) is a biopolymer found in plant cells such as wood, cotton and other plant materials. It is the richest polymer in nature. Cotton has the utmost cellulose content of plant with above 90% cellulose compared to wood that is about 40-50% (Eichhorn *et al* 2010). The cellulose polymer $(C_6H_{10}O_5)_n$ is a linear homopolysaccharide comprising of D- an hydro glucopyranose unit (AGU) linked together by β-1-4glycosidic linkaages (Fortunati *et al* 2013; Ukkund *et al* 2018). This cellulose is one of the most vital components of agricultural waste, allowed to rot away un-utilised in the environment.

In the recent times, the application of cellulose in nanotechnology has gained substantial interest in both academia and the industry (Wohlhauser *et al* 2018). According to Oxford dictionary, nanotechnology the science of developing and making extremely small, but powerful machine, is defined as the understanding of control of matter at least one dimension measuring 1 to 100nm by mechanical treatment or chemical modification (Gupta *et al* 2013). Nanocrystalline cellulose, nanocellulose, nanocrystals, wiskers, nanofibrils or nanofibers are terms use when a cellulose fiber crystal has at least one dimension within the nanometer size range.

Nanocrystalline celluloce (NCC) is one of the newest renewable nanomaterial researches has shown to pave way in many dissimilar applications of diverse products such as in personal care, food and pharmaceutical, paper and fiber products, biofuel, building materials for insulations and sprays, coating, packaging, composites in reinforcing polymers and conductive materials reinforcement, capacitors, super absorbent polymers and in oil recovery as fracturing fluid (Ukkund *et al* 2018). The appropriate incorporation of NCC in an assortment of functional nanomaterials with excellent properties, or appreciably improved physical, chemical and biological properties as well as electrical properties is very essential to man daily needs.

NCC are commonly obtained from cellulosic materials using mechanical and chemical techniques. Ultrasonication, microfluidisation, high-pressure homogenisation, high-speed blending, cryocrushing and blending are examples of mechanical techniques while chemical techniques include acid hydrolysis and enzymatic hydrolysis (Magagula *et al* 2022). However, due to ease of use, relatively high yield and short preparation time chemical techniques are usually employed. And generally using chemical technique, NCC are obtained by acid hydrolysis using strong acids like sulphuric acid which selectively degrade the amorphous region of the cellulose fiber leaving the crystalline region intact (Wohlhauser *et al* 2018).

The principle behind this research is regenerating agricultural by–products which are composed of cellulose in the plant cell walls that can be useful to the environment. The principal functional group in pure cellulose is hydroxyl (-OH), making cellulose a polyol with primary and secondary alcohol functional groups (CH_2OH,-CHOH). The numerous hydroxyl groups of cellulose in cellulosic materials (agricultural waste) can be partly or entirely modified by reacting with various chemicals to create a wide range of end yield referred to as ‘cellulose derivatives.’ The derivative such as cellulose nitrates, acetates, xanthates, ethers, nanocellulose, rayon and cellophane have far reaching industrial applications (Dong *et al* 2013).

When trying to modify either physical or chemical properties of polymers, graft copolymerisation is one of the most frequently used method. In this process, the side chain is joined to the main polymer backbone or substrate by covalent bond to form a copolymer with branched structure. The products obtain from cellulose can be readily made to possess any number of required properties due to the modification made by grafting. In graft copolymerisation involving nanocrystalline cellulose, the active hydroxyl groups of the NCC can react directly with the functional group of the graft or initially with small molecular monomers before its polymerisation through chain growth to form modified products (Wang *et al* 2021). In the work of Lee *et al* acrylamide was grafted to the surface of nanocellulose using benzophenone as the initiator to improve the dispersion ability of the grafted nanocellulose while Morandi *et al* with ethyl bromo isobutyrate as the initiator grafted polyphenylene on nanocellulose yielding a product which showed chiral nematic structure and strong adsorption for 1,2,4-trichlorobenzene (Wang *et al* 2021).

This research work was carried out to study the extraction of nanocrystalline cellulose prepared from agriculture waste; orange mesocarp and plantain peel, by acid hydrolysis. The function of the mineral acid hydrolysis is to generate cellulose nanocrystals by emancipation of crystalline region from semi crystalline cellulose fiber. This work further explores the surface modification and application of NCC using graft copolymerisation.

Materials and Method

Samples Preparation

Orange (*C. sinensis*) was obtained from Ore in Ondo State while plantain was obtained from Ogwa in Edo State. To generate orange mesocarp from the oranges, the epicarp and endocarp were peeled. The orange mesocarp was first sundried and oven dried before grinding. The pulverised mesocarp was then sieved and packaged for further use. For the plantain, the bark was removed washed, cut into pieces and oven dried before grinding. Then, the pulverised plantain peel was sieved and packaged for further use.

Extraction of Cellulose

After sample preparation, 40 gram of cellulose powder from each sample was weighed and digested with 2% w/v sodium hydroxide l00^{0}C for 30 minutes and then washed with distilled water and filtered. The filtered material was mixed with 17.5% w/v sodium hydroxide at 80^{0}C for 1hour. After the extensive washing with distilled water, it was filtered and the residue mixed with 150ml of 3.5% w/v sodium hypochlorite at 80^{0}C for 20 minutes. Then later washed and filtered. The procedure was finalised by drying the residue at 60^{0}C for 6hours.

Preparation of Nanocrystallline Cellulose

The extracted cellulose was subjected to the hydrolytic action of 50% sulphuric acid. The acid hydrolysis was done for 8hours at room temperature with constant stirring. This was done to prevent charring of the cellulose material by acid. The product obtained was washed to a pH of 7. After washing, the product was then dried before packaging for further use.

Sample Characterisation

The ash content, moisture content, cellulose, hemicellulose, lignin and other physicochemical properties of the raw sample, obtained nanocrystalline cellulose and grafted nanocrystalline cellulose were determined using standard methods (Abdel-Halim, 2014).

Results and Discussion

Table 1: Physicochemical Parameters for the Raw Agricultural Waste

Parameters	Raw OM	Raw PP
Form	Powder	Powder

Colour	Yellowish white	Light brown
Ph	3.03	6.39
Tapped density	1.40	0.80
Solubility	Insoluble in water and ethanol	Insoluble in water and ethanol

The physicochemical parameters of the raw orange mesocarp and plantain peel were as presented in table 1. Both sample used were in powdery form. Orange mesocarp was slightly acidic while plantain peel was neutral. However, plantain peel has a lower density than orange mesocarp indicating that Also, both samples were insoluble in water and ethanol.

Table 2: Chemical Composition of the Sample

Constituent	**OM**	**PP**
Ash	0.26	0.65
Moisture	11.0%	16.5%
Lignin	8.78	14.71
Hemicellulose	14.06	21.53
Cellulose	27.94	35.87

The knowledge of compositional parameters of any agricultural waste intended to be used for NCC preparation or grafting is very important; this is because this determination established the suitability of the material for intended use. Table 1 shows the various composition of OM and PP. The cellulose % however was seen to be relatively low in OM and high in PP. The cellulose percentage yields were comparable to what obtained in literatures. Orji *et al* (2015) using soda pulping got cellulose percentage yield of 8%.

Table 3: Percentage Yield of NCC from the Samples

Sample	**PP**	**OM**
% yield	23.50	5.01

The extraction process was done on a dry basis. As presented in table 3, plantain peel cellulose gave a percentage yield of 23.50% Nano- crystalline cellulose, which was higher than that obtained from orange mesocarp cellulose (5.01%). The poor yield of OM cellulose is assumed to be due to the nature of its fibre and the concentration of the sulphuric acid (SA) used. So, they easily got destroyed. From literature, if the concentration of SA is less than 50 wt. % then micro-scale particles are isolated. On the other hand, if the concentration of SA is higher than 63 wt. % the cellulose completely dissolved and as a result instead of nano-crystalline the amorphous particles are formed with decreased yield. In the range of the acid concentration from 55 to 61 wt. %, a low decrystallisation of the initial cellulose is taken place that contributes to forming of rod-like nano crystalline cellulose particles. These optimal conditions in combination with the high-power permit obtaining the rod-like nanocrystalline cellulose particles with increased yield (70-75%) (Michael, 2012).

Table 4: Physicochemical and Grafting Parameters of Grafted Nanocrystalline Cellulose

Parameters	Grafted NCC from OM	Grafted NCC from PP
Form	Powder	Powder
Colour	White	Dark brown
Ph	4.39	5.26
Solubility	Insoluble in water and ethanol	Insoluble in water and ethanol
Polymerisation %	55.60	10.00
Graft %	45.70	3.20

Table 4 captures both the physicochemical and grafting parameters of the grafted NCC from the two agricultural waste examined. The physicochemical parameters reveal that products from both samples were in powdery form. Orange mesocarp grafted NCC was whitish with a pH of 4.39 while plantain peel grafted NCC was dark brownish with a pH of 5.26. Also, both grafted NCC were insoluble in water and ethanol. For the grafting parameters, orange mesocarp grafted NCC has polymerisation and grafting percentages of 55.60 and 45.70 respectively while plantain peel grafted NCC has polymerisation and grafting percentages of 10.00 and 3.20 respectively. The grafting parameters were high in orange mesocarp showing that the grafing was more effective in orange mesocarp NCC than plantain peel.

Table 5: Oil Sorption Analysis of the Samples

Samples	Raw	NCC	Grafted NCC
OM	63.97	56.31	76.25
SCB	68.33	71.39	74.21
PP	47.21	71.28	74.26

From the results of the analysis carried out as shown in table 4, it is clear that sorption capacity of the samples increased from the raw sample to Nano crystalline cellulose and the grafted samples for all the samples considered. The oil sorption value is important in several applications. For instance, in ink and coating formulation or in oil spillage water treatment where it give an indication of the amount of oil that can be absorbed by the particles. Oil adsorption values are strongly affected by the particle size surface area and surface chemistry of the particle it represent the minimum weight of oil required to coat each particles and to fill the weight between them (Landry *et al* 2015). The result confirms the possibility of applying the NCC produced in the application where oil sorption is relevant.

Conclusion

The outcome of the research work has established the possibility of preparing Nanocrystalline cellulose (NCC) from plantain peel (PP) and orange mesocarp (OM) which is less utilised agricultural waste. Also, it was established that this Nanocrystalline cellulose can be grafted with a vinyl monomer (acrylamide) under a heterogeneous medium with a ceric ammonium nitrate redox initiation mechanism. More importantly, the acid hydrolysis for the NCC synthesis gave a relatively higher yield of 23.50% for OM in comparism to PP with a yield of 5.01%. For the percentage polymerisation 55.6% was gotten for OM and 10% for PP. The oil sorption capacity determination has confirmed that the properties of the grafted nanocrystalline cellulose has been improved upon compared to the ungrafted material. With further work to enhance the properties of the grafted nano cellulose material and product characterisation, it is hoped that novel biomaterial suitable for various industrial applications would have been discovered.

References

Abdel-Halim, E. S. (2014). Chemical modification of cellulose extracted from Sugarcane Bagasse: Preparation of Hydroxyethyl Cellulose. *Arabian Journal of Chemistry,* 7, 362–371.

Dong H., Snyder J.F., Tran D.T. & Leadore, J. L. (2013). Hydrogel, aerogel and film of cellulose Nanofibrils functionalised with silver nanoparticles. *Carbohydr. Poly*, 95, 760-767.

Eichhorn, S.J., Dufrensne, A., Aranguren M., Marcovich N.e., Capadona, J.R. & Rowan S.J. (2010). Environmental friendly method for the extraction of coir fiber and isolation of nanofiber. *Carbohydrate Polymers,* 92. 1477-1483.

Fortunate, E., Puglia, D., Monti, M., Peponi, L., Santulli, C., Kenny, J. M. & Torre, L. (2013). Extraction of cellulose nanocrystals from phormium tenax fibres. *J. Polym. Environ,* 21, 319-328.

Gupta, V.K. & Ali, I. (2013). Water treatment for inorganic pollutants by absorption Technology. *Environmental Water,* 4, 29-91.

Magagula, L. P., Masemola, C. M., Ballim, M. A., Tetana Z. N., Moloto N. & Linganiso E. C. (2022). Lignocellulosic biomass waste-derived cellulose nanocrystals and carbon nanomaterials: A review. *International Journal of Molecular Sciences,* 23, 4310.

Orji, J. I., Akpa P. A. & Adikwu, M. U. (2015). Physicochemical properties of co-precipitate of plantain peel cellulose and gelatin. *Journal of Pharmaceutics and Drug Delivery Resources,* 4(4), 33-45.

Ramsden, J.J. (2005). What is nano tecghnology? *Nanotechnology Perceptions,* 1, 3-17.

Ukkund, S. F., Taqui, S. E., Mayya, D. S. & Prasad, P. (2018). Nanocrystalline cellulose from agricultural waste: An overview. *International Journal of Nanoparticles*, 10(4), 284-297.

Wang, X., Wang, N., Baoming X., Wang, Y., Lang, J., Lu, J., Chen, G. & Zhang, H. (2021). Comparative study on different modified preparation methods of cellulose nanocrystalline. *Polymers,* 13, 3417.

Wohlhauser, S., Delepierre, G., Labet, M., Morandi, G., Thielemans, W., Welder C. & Zoppe, J. O. (2018). Grafting polymers from cellulose nanocrystals: synthesis, properties and applications. *Macromolecules,* 51, 6157-6189.

Yi, V.N.W., Hvey., N.C., Peng, T.Y., Xian, O.Z. & Hoong, S.S. (2021). Isolation of cellulose derived from orange peel and its application in biodegradable films. *Cellulose Chemistry and Technology*, S.S (3-4), 311-324.

Zaib, S. & Igbal, J. (2019). Nanotechnology: Applications, techniques, approaches and the adrananut in toxicology and environmental impact of engineered nanomaterials. In: Importance and applications of nanotechnology. Med Docs Publishers LLC refer to the ability to engineer materials precisely at the scale of nanometers.