

## *In situ* Polymerization of Nylon-Cellulose Nano Composite

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### Abstract

Polymeric Nano composite has been strongly studied due to the improvement achieved when a little amount of Nano sized particles are added to the polymer matrix. This is primarily due to large surface area which increased the interaction between the nanoparticles and the polymer. There are different routes for preparation of the polymer Nano composite with Nano fillers it can be melt compound, *in situ* polymerization and the solvent method. The *in situ* method was found to be best method due to that the nanoparticle is introduced directly to the monomer and it allowed for few minutes to disperse well to the monomer before the initiator is added to start polymerization. The *in situ* method gives control over the particle size and morphology. The present studies investigate the surface morphology and thermal properties of nylon when the cellulose Nano-whiskers of different content was added into nylon monomer. SEM for surface studies, TGA for thermal stabilities and FTIR for chemical properties were studied. TGA results reveal that nylon thermal properties changes with addition of Nano crystals compared to pure nylon.

**Keywords:** *In situ* polymerization; Cellulose; Composites

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### Introduction

Polymer Nano composite is composed of polymer material and filler component in which is at least one dimension (<100 nm). Polymeric reinforced composite properties are strongly affected by the size, shape and degree of material filler adhesion; Nano composite can be prepared by melting compound, *in situ* polymerization and solvent method [1-4]. Dispersion of the nanoparticles to the monomer interface is a critical step due to the fact that it determines the mechanical properties of the produced Nano composite. It is well known that poor dispersion of nanoparticle will affect the mechanical properties Nano composite [5]. Poor dispersion can be avoided by Nano composite prepared by *in situ* method because with *in situ* polymerisation the filler solution is added directly into the monomer allowing it for few minutes to dispersed well as the results its gives a better control to size and morphology of the Nano composite produced [2,4].

Polymeric Nano composite can be obtained by using natural fibers and inorganic fillers. Natural fibers are mostly used as replacement for synthetic fibers in automotive due to the various reasons including environmental friendliness and

inexpensiveness. Mostly used natural fiber is cellulose due its properties like strength, stiffness and high performance [5]. In fact, cellulose nanocrystals are mostly used as fillers reinforcement material due to primarily higher modulus and availability [6]. The nanoparticles are generally in cooperated in different polymers for preparing new materials with better properties than pristine counterparts. However, very little information is known about reinforcement of nylon by cellulose, particularly sourced from biomass.

Nylon is aliphatic or semi-aromatic polyamides which can be processed into fibres, films or different shapes depending on desired applications. Like any other polymers, nylon could be reinforced with different fillers including cellulose to vary some properties. In order to study the nylon/NCC composite different concentrations of NCC could be used expecting good results and improvements on the thermal, mechanical and morphology. Material science in ceramics and polymers they frequently use the word Nano composite. Nano composite has unique properties which led to studies about limitations and tethering polymers which has grown the interest to the science field for material development in order to study the formation, structures and dynamic of polymer Nano composite interface.

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## Literature Review

### Polymers and nano composite

Polymer is made by macromolecules in which consists of small molecular units that are repeated over and over again to form along chain and are held by covalent bonds. Monomer is a small molecular unit. Nylon, polyvinyl chloride and polystyrene are examples of polymers and are synthetic polymers [2,3]. Polymers are normally synthesized by one of two ways can be addition or step – growth pathway. Addition polymerisation the polymer is formed by monomers connected together by addition reaction. Step growth the monomers link together and grows into dimers, trimer so forth. Condensation pathway the condensation polymerisation the polymer is formed by monomers connected with the release of the side product such as HCl and water. One of the examples of condensation pathway is the polymerization of a diacid and diamine to make nylon 6 and producing water as a by-product.

Both thermoplastic and thermosetting have limited application in automobile, electrical, electronics, packaging textile and household applications due to mechanical properties [7]. In order to overcome that they were reinforced mostly with inorganic Nano fillers for a desired Nano composite material. This has brought increased interest in the applications of thermoplastics. Polymeric reinforced composite properties are strongly affected by the size, shape and degree of material filler adhesion; Nano composite can be prepared by melting compound, *in situ* polymerization and solvent method. Melt blending and *in situ* polymerization are mostly used to synthesize polymer Nano composite. Melt blending method the molten thermoplastic is blended with the nanofiller in order to elevate the polymer-nanofiller contacts. For a solution blending suitable solvents are used to disperse nanofillers followed by dissolving the polymer in the same solvent and mixing the two at room temperature. The Nano composite is collected by precipitating or casting a film [4,8]. In an *in situ* polymerization, a filler solution is dispersed directly into a monomer before an initiator is added for polymerization.

Dispersion of the nanoparticles to the monomer interface is a critical step due to that it determines the mechanical properties of the produced Nano composite therefore poor dispersion of nanoparticle will affect the mechanical properties Nano composite [4]. Poor dispersion can be avoided by Nano composite prepared by *in situ* method for Nano composite produced. Polymer Nano composite benefits over pure material are robust, being eco-friendly and can be re-usable [3]. Composites materials have been identified as measure substitutes over conventional materials including metals, metal alloys, wood ceramics and polymers [8]. Composites materials developed today are categorized based on their reinforcement and matrix. Reinforcement types used there are particle reinforced composites, fiber reinforced composites and structural composites. With Polymer- matrix composites are prepared by mixing polymers with inorganic filler materials such as reinforcing fibers (e.g. glass, carbon, aramid, etc) and particulate solids (talc, carbon black, calcium carbonates, mica).

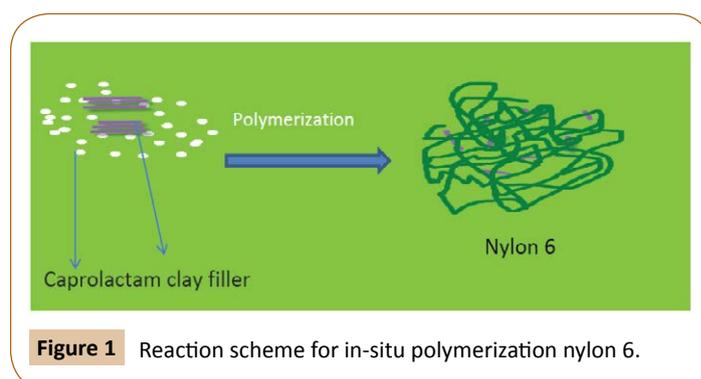
Such composite exhibit physical properties synergistically derived from both the organic and inorganic components e.g. they show superior mechanical properties and higher heat deflection temperature compared to the pristine polymers while maintaining processibility. It is important to develop composite system based on the application [8]. The fillers have three kinds, nanoparticles which comprise of particles having all three dimensions in nanometres range e.g. semiconductor and colloidal dispersion of polymers, two dimensional nanofiller wherein two dimension of the filler are in nanometres scale- cellulose whiskers and nanotubes are the examples and nanofiller corresponds to the case in which there is only one dimension on a nano level-layered silicates or clays which are platelet shaped.

The work presented in this dissertation is focused on polymer Nano composite incorporated with nanofiller having two dimensions cellulose whiskers. To enhance the polymer properties performance the fillers with micrometre range dimensions are widely used to form composites. The properties of the composites alter depending on filler loading, shape and size. For fibres, fillers having larger aspect ratio can improve the properties of polymers.

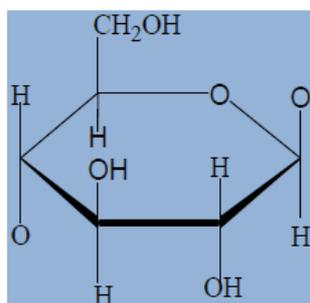
There are three possible structures polymer Nano composite can be made: phase separated micro composite, intercalated Nano composite and exfoliated Nano composite. The structures formation depends on the nature of components used including polymer matrix, clay and organic cation. Polymer Nano composites are having wider applications. In 1980 Toyota Company was the first company to develop and commercialize polymer/clay Nano composite (**Figure 1**). They used nylon 6 as the matrix phase and montmorillonite as the clay filler for a timing belt cover in one of their car models which became the first commercial polymer Nano composite. Application of polymer Nano composite using different polymer matrices and nanofillers are based on their improved mechanical properties (tensile strength and young's modulus), improved heat by 30°C stability and enhanced barrier to water.

### Cellulose

Cellulose is a natural polymer and polysaccharide which is having  $\beta$ -1, 4-linked anhydro-D-glucose units. The strong hydrogen bonds are established by the presence of the hydroxyl (-OH) groups (**Figure 2**) in the cellulose structure. Cellulose main sources are wood, cotton, hemp, flax, sisal, sugarcane bagasse,



**Figure 1** Reaction scheme for in-situ polymerization nylon 6.



**Figure 2** Shows Cellulose Structure.

corn cob, cassava bagasse, banana rachis, soy hulls and rice husk [9-11].

Hemicellulose and lignin are other major components found in natural fibers with cellulose. Cellulose has great features over other fibers such as the biodegradability [12], coupled with the low cost, high specific strength and lighter weight than glass and this has led to the extensive development of studies in order to produce green materials [13]. The cellulose properties led to cellulose to be used as filler or reinforcement material.

When compared with inorganic reinforcements, derived cellulose nanomaterials have great benefits such as renewability and low density, highly specific strength, high aspect ratio, good mechanical properties, low thermal expansion, low toxicity, and hydroxyl groups (-OH) [5,14]. Cellulose nanomaterials are isolated and extracted differently. One can be isolated by acid and other by mechanical procedure in which as a result producing nanomaterial having different morphologies. The characteristics are a consequence of the cellulose source and extraction method used. The commonly used cellulose are microcrystalline cellulose (MCC), micro fibrillated cellulose (MFC), nano fibrillated (NFC), cellulose nanocrystals (CNC). There are several approaches to isolate nanoparticles including mechanical with acid extraction producing nano crystals (CNC's) and with mechanical producing nano fibrils (CNFs). CNCs are crystalline in nature and have wide applications due to the nano size having equal or less than 100 nm and are needle-like cellulose particles [15]. Cellulose nanoparticles are widely used as fillers in the polymer Nano composite due to an improvement in performance. Intermolecular forces of the cellulose molecule are in charge for certain firmness of the unit chains. The intramolecular hydrogen bonding formed between hydroxyl groups and oxygen's of the adjoining ring molecules alleviates the connection and that results in the linear configuration of the cellulose. Cellulose source and material extraction method are factors responsible for variation crystallinity degree of cellulose [15].

## Nylon

Nylon is synthetic, aliphatic or semi-aromatic polyamides. It can be melt-processed into fibers, films or different desirable shapes [7]. Polyamide fiber, originated from a diamine and a dicarboxylic acid, there are a very large number amide group (-CO-NH-) - provides hydrogen bonding between polyamide chains, giving nylon high strength at elevated temperatures, toughness at

low temperatures, combined with its other properties, such as stiffness, wear and abrasion resistance, low friction coefficient and good chemical resistance [16]. These properties have made nylons the strongest of all man-made fibers in common use. Nylons are very important in the thermoplastic industry they offer good mechanical and thermal properties. The features are very useful because they determine the applications of the fiber produced [7]. Nylon can be used as standalone or composites. What is more attracting about it is an ease to clean, quickly dries and rigidity. The composites of nylon are mostly applied in the automobile industry. There are different types of nylon, which differ with monomer, for commercial purposes such as nylon 6, 11, 12, 6/6, 6/10, 6/12, etc. The popular nylons used are nylon 6 and nylon 6/6 in which is used in textile industry. The polymer can be also used in coating of metal objects, molding and tubing extrusion.

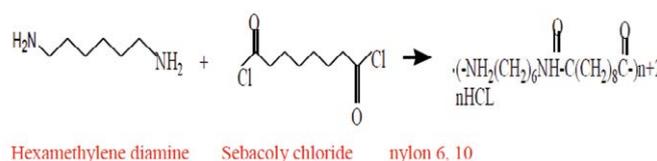
Nylon 6/10 shown in **Figure 3** is a polyamide made by amine molecules which has group {-NH<sub>2</sub>} at each end and acid chloride having {-COCl} group at each end as well. The diamine and the diacid chloride link together at the end-on-end to form chain. This reaction the polymerisation is called interfacial polymerisation because the monomers are two immiscible liquids which forms a layer and comes to contact at the interface. Nylon 6, 10 is given by number of carbon atoms present in diamine monomer and number of carbons in the diacid chloride. Six carbons come from diamine and ten comes from diacid chloride produced. Nylons are some of the most important fibers produced commercially. With nylons the intermolecular force hydrogen bonding is the most important. The nitrogen-bonded hydrogen's of one nylon chain will hydrogen bond very strong with carbonyl oxygen's of another nylon chain.

These hydrogen bonds make crystals of nylon very strong, because they hold the nylon chain together very tightly as the results making fiber to be stronger. The nylon is crystalline product at a given sample in a solid form. There is in the amorphous phase, the combination of crystalline and strongly associated amorphous phases is what makes nylon thermoplastic so tough. Nylon Nano composite are prepared by *in situ* polymerisation, the filler is added to the monomer and dispersed by ultrasonification in order to allow gain growth aggregation of nano particles to the monomer before polymerisation starts. This adds the advantage to the nylon Nano composite nylons.

## Materials and Methods

### Chemicals

The sugar bagasse was obtained at Empangeni (KwaZulu Natal), South Africa. Sodium hydroxide (NaOH) low chloride for analysis



**Figure 3** Reaction scheme for synthesis of nylon 6, 10.

and Sodium Sulphite (NaS) were bought from Merck South Africa. Sodium chlorite (NaClO<sub>2</sub>), Hexamethylene Diamine (98%) and Sebacyl chloride were purchased from Spectro chem and Sulphuric Acid (98%) was purchased from Merck South Africa.

### Preparation of cellulose

Sugar bagasse was washed with boiling water four times for one hour with changing of water replacing with fresh one in order to remove unwanted dirty stuffs. The sugar-bagasse was then further treated with 2% NaOH solution, 0.7% NaClO<sub>2</sub> (which has acetic acid in order to gain pH4 solution) and 1% NaS respectively for one hour. Each treatment was repeated four times accompanying with repeated wash using deionised water to remove excess chemicals and to gain neutral pH 6-7. Schematic diagram (Figure 4) of the extracted cellulose from sugar-bagasse is shown below.

### Preparation of cellulose nano whiskers

Cellulose obtained from sugar-bagasse after NaS treatment was hydrolysed using 50% Sulphuric acid concentration under strong agitate of mechanical stirrer at under the ice bath for 30 min. The hydrolysis was stopped by adding 500 ml of deionized. The suspensions were centrifuged at 4400 r.p.m. for 30 min and dialyzed using membrane in water for 5 days until the pH was 6-7. The suspension was dispersed by ultrasonification for 5 min and stored in the refrigerator for further use. Different methods were reported for the extraction cellulose from sugarcane bagasse [6] (Figure 5).

### Synthesis of nylon

Hexamethylene diamine of about 1 g was dissolved in 25 ml of water in a 250 ml beaker. Solution of Sebacyl chloride (1 g) and Hexane of 25 ml was made in a separate beaker. Hexane/Sebacyl chloride solution was added onto hexamethylene solution using a glass rod to pour down with a film formation at the interface. The thread was drawn out of the interface firstly by tweezers, slowly was winded (Figure 6) up into the glass rod. After all the polymer (nylon) collected. Nylon was washed thoroughly with water and it was let too dry in air.

### Synthesis of nylon-cellulose nano composite

Hexamethylene diamine of about 1 g was dissolved in 25 ml of water in a 250 ml beaker. Cellulose whiskers (1%, 3% and 5%) were added *in situ* in the Hexamethylene diamine/H<sub>2</sub>O and were

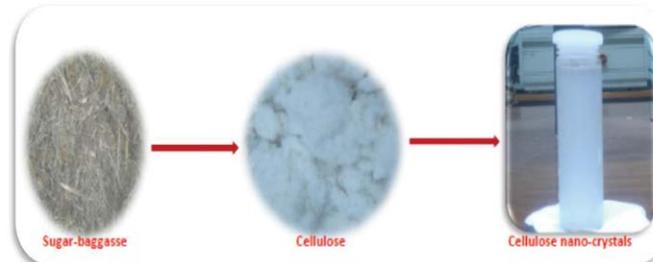


Figure 5 Schematic showing sugar bagasse transformation to nanocrystals.



Figure 6 Schematic representation for the nylon of how was collected.

allowed to disperse in the monomer solution for 10 min using ultrasonification. Quickly solution of Sebacyl chloride (1 g) and Hexane of 25 ml was made in a separate beaker. Hexane/Sebacyl chloride solution was added onto Hexamethylene solution for polymerization, using a glass rod to pour down with a film formation at the interface. The thread was drawn out of the interface firstly by tweezers, slowly and was winded up into the glass rod. After all the polymer (nylon) collected, nylon was washed thoroughly with water and it was let too dry in air (Figure 7).

## Characterisation Methods

### Morphology and surface studies

**Scanning electron microscopy (SEM):** Samples for analysis were prepared and used to characterize the crystal structure and distribution of nylon Nano composite.

### Chemical analysis

**FT-IR spectra:** The spectra of cellulose, nylon and nylon/CNC composite and were obtained using FTIR-ATR Perkin- Elmer. All samples were scanned over a range of 400 to 4000 per 100 samples scan.

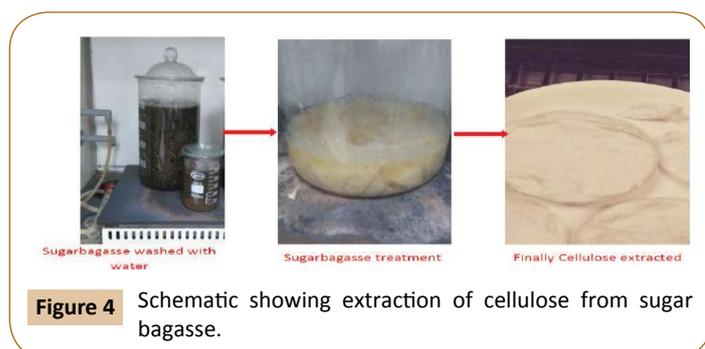
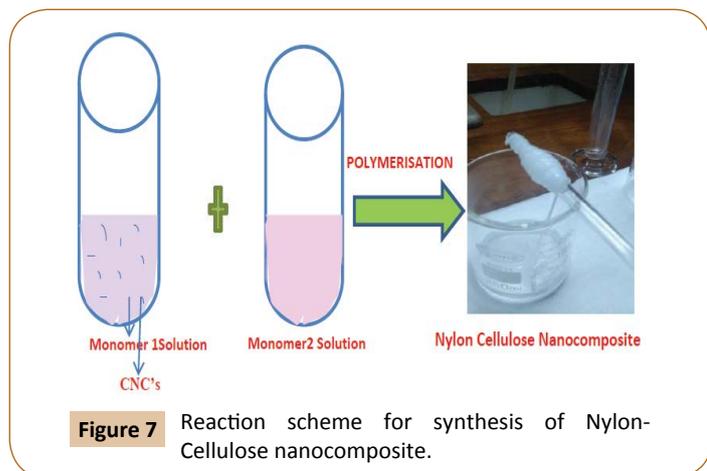


Figure 4 Schematic showing extraction of cellulose from sugar bagasse.



**Figure 7** Reaction scheme for synthesis of Nylon-Cellulose nanocomposite.

**Thermal analysis:** Thermal gravimetric analysis of the cellulose, nylon and nylon-cellulose Nano composite samples (0.15 mg) were done with a Perkin Elmer (TGA) with heating rate of 30°C/min up to 600°C in Nitrogen gas environment.

**Water absorption:** Samples for analysis were prepared by immersing samples in a beaker containing distilled water at room temperature for different times and compared the initial weight with final weights after soaking and were recorded. Water absorption percentage was calculated by using formula:

$$\text{Water Absorption \%} = \frac{W_f - W_i}{W_i} \times 100$$

$W_f$  as the final weight of the sample after soaking and  $W_i$  before the sample was immersed in water.

## Results and Discussion

### Scanning electron microscopy (SEM)

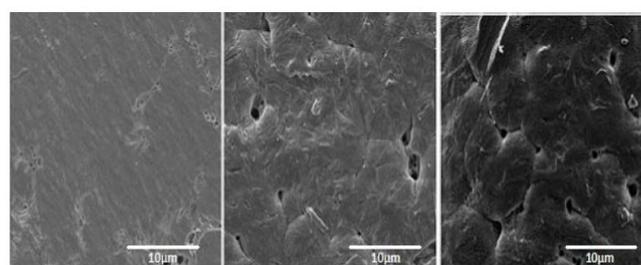
**Figure 8** shows the SEM microscopy images of the investigated samples. The image of the nylon-5% Nano composite shows the agglomerated (**Figure 8c**) cellulose which is the higher content in this study. This generally would probably results in poorer overall properties of the system. Nylon-1% and nylon-3%, however shows better dispersion of the cellulose in the nylon matrix which is clearly evidenced by small holes within the nylon matrix.

### Chemical analysis (FTIR)

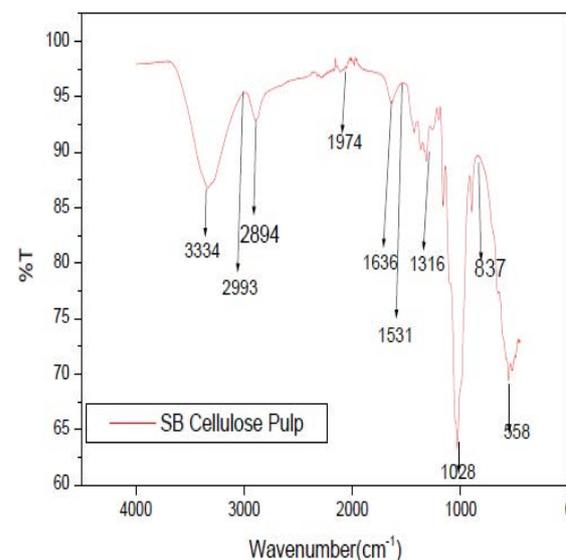
The main difference in respect to functional groups in the sugarcane bagasse may be observed on the FTIR spectrum presented in **Figure 9**. It is seen in **Figure 9** that the intense spectral bands at 3334  $\text{cm}^{-1}$  is associated with -OH stretching, which is the intramolecular Hydrogen bonds for cellulose. The band at 2894-2993  $\text{cm}^{-1}$  is attributed to the C-H stretching. The band for the absorption of Water is observed at 1636  $\text{cm}^{-1}$ . Spectral bands at 1531 and 1316  $\text{cm}^{-1}$  are associated with aromatic ring present in lignin and  $\text{CH}_2$  bending vibration [6]. The weak intensity stretching and deformation at 1028  $\text{cm}^{-1}$  is associated with C-O band. The important cellulose chemical spectral bands are 3334 and 2993  $\text{cm}^{-1}$  which confirms cellulose material. Similar spectrum was already observed, who investigated the sugarcane bagasse pulping and bleaching: Thermal and chemical characterization. The main differences in FTIR spectra can be seen in **Table 1**. This

table summarizes higher bands observed in the FTIR spectrum of sugarcane bagasse and their assignments to chemical group vibrations and molecules.

The chemical composition of nylon and nylon Nano composites are shown in **Figure 10**. Nylon is made from Carboxylic acid and amine therefore spectral bands peak at 3302, 2986, 2924, and 1636  $\text{cm}^{-1}$  are significant bands and are intense. The band at 3302  $\text{cm}^{-1}$  is associated with amine (N-H stretch). Nylon Nano composites were also having band 3302  $\text{cm}^{-1}$  but their band is broad due to the present of OH group from cellulose



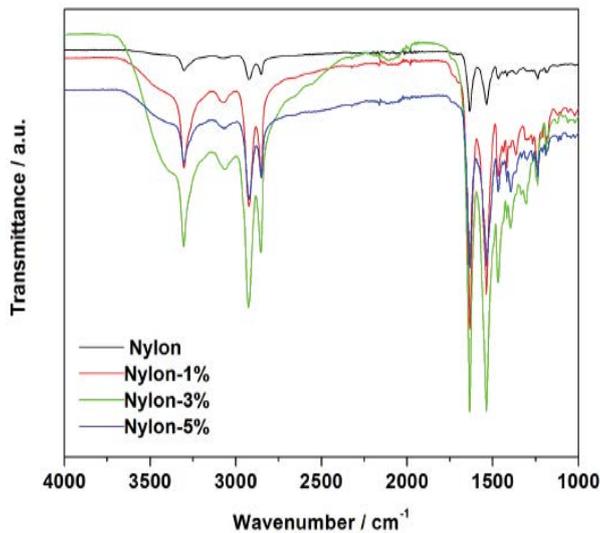
**Figure 8** SEM pictures of a) nylon-1% b) nylon-3% c) nylon-6%.



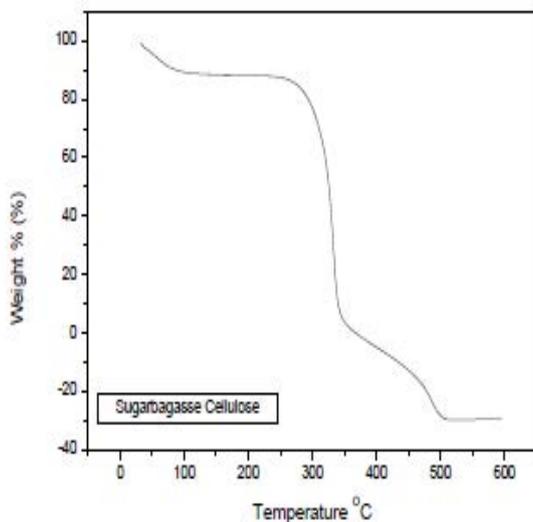
**Figure 9** The FTIR of cellulose extracted from sugarcane bagasse.

**Table 1:** Infrared main transition for Sugarcane Bagasse.

Wavenumber ( $\text{cm}^{-1}$ )	Vibration	Source
3300	O-H linked shearing	Polysaccharides
2885	C-H symmetrical stretching	Polysaccharides
1732	C=O unconjugated stretching	Xylans
1650-1630	OH (water)	Water
1335	C-O aromatic ring	Cellulose
1162	C-O-C asymmetrical stretching	Cellulose
670	C-OH out-of-plane bending	Cellulose



**Figure 10** The FTIR spectra of nylon and its sugarcane bagasse composites.



**Figure 11** The TGA spectra of sugarcane bagasse cellulose.

nanowhiskers. Bands associated with CH group were also noted to be the same as for pure nylon and strong spectral band at  $1636\text{ cm}^{-1}$  is associated with C=O group.

### Thermal stability (TGA)

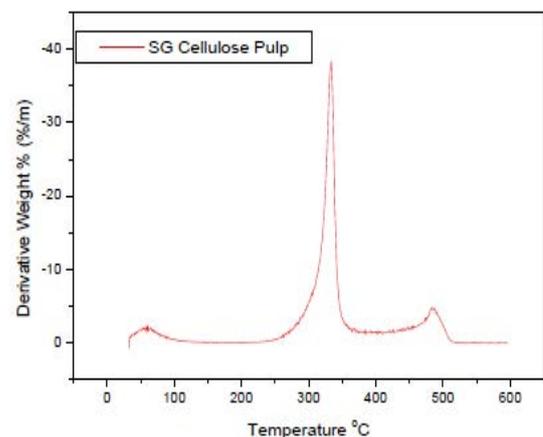
The TGA and DTG graphs of pure cellulose are shown in **Figure 11**. Pure cellulose presents two decomposition phases as it shown by **Figure 11**. The first around  $300\text{ }^{\circ}\text{C}$  corresponds to the degradation temperature and the second one corresponds to complete temperature decomposition. Similar results were obtained by Mulinari and colleagues when studying the sugarcane bagasse cellulose/HDPE composites obtained by extrusion. There is a clear mass loss also from the TGA and DTG graphs around  $\sim 30$  to  $100\text{ }^{\circ}\text{C}$  due to water molecule. There is also an apparent last step

from TGA curve around  $480\text{ }^{\circ}\text{C}$  which may be attributed to the presence of lignin (**Table 2**).

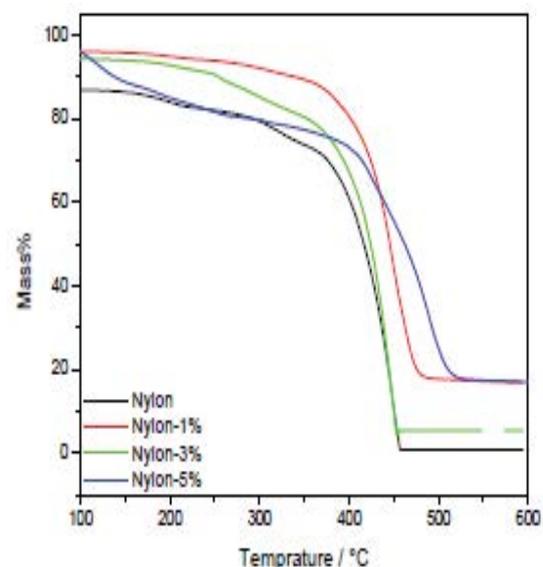
**Figures 12-14** represent the TGA as well as the DTG graphs of pristine nylon and its cellulose composites. It is seen in **Figure 12** that the addition of cellulose improves the thermal stability of the neat nylon. For an example, at  $T_{50\%}$  1% and 3% of the filler shows 7% as well as 11% increase from the neat nylon respectively.

**Table 2:** Degradation temperatures at 20% and 50% mass for all the investigated samples.

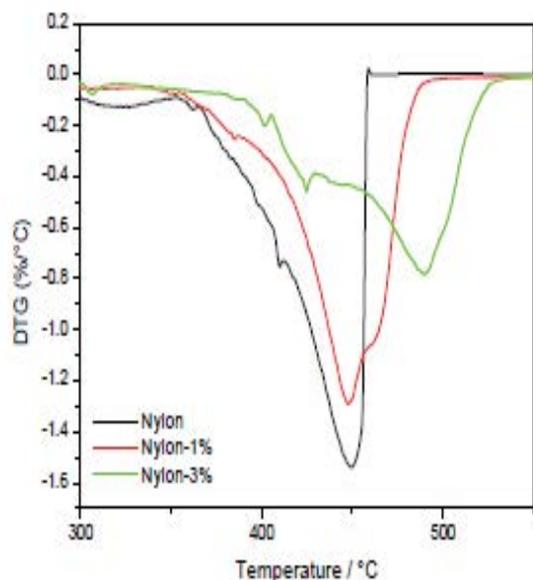
Samples	T20% ( $^{\circ}\text{C}$ )	T50% ( $^{\circ}\text{C}$ )
Nylon	284.3	417
Nylon-1%	407.1	448
Nylon-3%	301	464.9
Nylon-5%	349.7	427



**Figure 12** The DTG graphs of cellulose extracted from sugar bagasse.



**Figure 13** TGA graphs of pristine nylon and its cellulose nanocomposites.



**Figure 14** Represent the DTG of the synthesized nylon and nylon nanocomposite.

This increased stability of the Nano composite compared to neat nylon is due to improved fibre-matrix interaction as it was seen in SEM pictures. This was helpful to impede the heat transfer into the interior of the material and lower the temperature of decomposition. It is well known that the more stable interfacial structure of the smaller particles and the better dispersion in the polymer matrix normally results in better composites properties. The filler in this case normally forms a compact char intumescent char, creating a physical barrier which can reduce the degradation rate. It is also clear from **Figure 13** that the char residues of a better dispersed system (nylon-1% and nylon-3%) than the poorly dispersed nylon-5%. This could be attributed to the fact that a well dispersed system normally forms a compact and stable char which protect the nylon from heat, while an agglomerated system forms an inhomogeneous char which allows the nylon to burn out almost completely. In reality, a char serves as a physical barrier for heat flux from the polymeric surface, as well as a diffusion barrier for gas transport to the flame. It is clear that the contribution of the char can be more important than it is from a simple reduction in combustible gases.

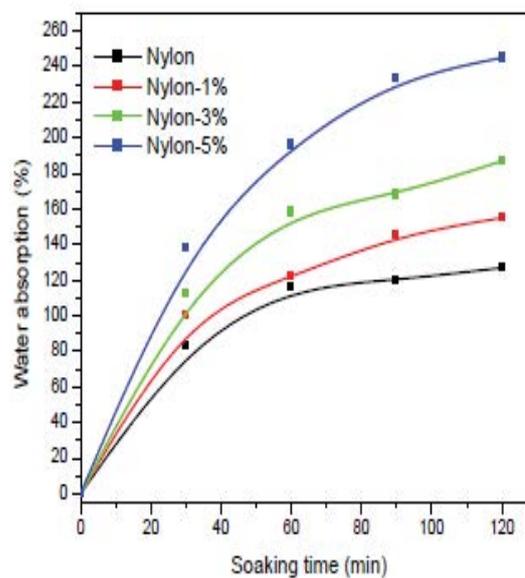
### Water absorption analysis

**Figure 15** shows the percentage of water absorption for neat nylon and its cellulose Nano composites. The discussion of the

results should take into account the influence of intrinsic factors such as the relative amount of fibre in the composites. It is clear that there is a higher water absorption as the content of the fibre is increasing. This is attributed to the hydrophilicity of the fibres in comparison to the nylon polymer.

### Conclusions

The dispersion of nanocrystal into the monomer was done *in situ* was successfully and the results demonstrate that the *in situ* method is the best method owing that nanocrystal are introduced to the monomer before polymerisation commences. Cellulose and nanocellulose crystals were successfully synthesized proven by the FTIR spectrum showing composition and peaks determining cellulose were obtained. Nylon cellulose Nano composite was prepared and characterised using TGA and FTIR. FTIR spectrums were obtained for chemical composition and the bands were true for nylon fiber. TGA using DTG curve shows the relationship of nanocrystals and nylon. The small amount of the nanomaterial has good impact in the fiber. Nylon Fiber shows improvement in the thermal properties with addition of nanocrystals.



**Figure 15** The water absorption graph of nylon and nylon/cellulose nanocomposites.

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