

Investigation of Mechanical Properties of Nanocellulose Reinforced Synthetic Polymer Composite

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ABSTRACT: In Sri Lanka, a considerable percentage of agricultural waste such as rice straw and sugarcane bagasse is discharged to the environment without a commercial use and forms a huge organic environmental pollution. Therefore, the agricultural wastes can be used to extract cellulose and indirectly apply an additional value to the abundant priceless wastes. Nanocellulose is a cellulosic material which has at least one dimension in the nanometre range and has a potential for polymer reinforcement. Based on their structure nanocellulose extracted from plant species are categorised into two; nanofibrillated cellulose (NFC) and nanocrystalline cellulose (NCC). The present paper discussed the surface modification of NFC using Silane coupling agent (Si-69) and fabrication of silylated NFC reinforced polypropylene (PP) composites with different loadings of NFC from 0-5 wt. % by adding 0.5 wt. % per sample. The mechanical properties of the composite samples were compared with respect to neat PP and Scanning electron microscope (SEM), Fourier-transform infrared spectroscopy, X-ray diffraction, mechanical tests (tensile strength, percentage elongation at break, impact strength and hardness), percentage water absorption and melt flow index (MFI) were used to characterize the developed composites. The experimental results emphasize the wide improvement of mechanical properties with extremely narrow reduction of water absorption and processability of silylated NFC based PP than pure PP. The 3.5% silylated NFC reinforced PP composite indicated the highest improvement in mechanical properties such as hardness, tensile and impact strength, a 7.4%, 12.6%, and 86.1% higher than the neat PP, respectively.

Keywords: Agricultural waste, nanocomposite, nanofibrillated cellulose, polypropylene, rice straw

INTRODUCTION

Frequently, natural fibres are used to reinforce with synthetic polymer composite due to the abundance, economic benefits and biodegradable properties (Samarasekara et al., 2018a; Samarasekara et al., 2018b; Samarasekara et al., 2014). Cellulose is the most commonly available, polymeric substance occurring in plant species and can be easily extracted by using agricultural waste materials such as sugar cane burgesses, rice straws and also from wood waste. (Nanayakkara et al., 2018; Nanayakkara et al., 2017; Kahawita and Samarasekara, 2016). Plant cell wall contains lamella structure of cellulose microfibrils and after separation

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of matrix materials (mainly hemicellulose and lignin); it is possible to isolate cellulose fibres in nanometre range.

Nanocellulose contains many favorable features than natural cellulose; such as distinctive tensile strength, high stiffness and Young's modulus with lightweight (Dufresne 2013; Kalia et al., 2009). In respect to nanocrystalline cellulose (NCC), nanofibrillated cellulose (NFC) consists of a bundle of long chains, flexible cellulose molecules with high aspect ratio. Average diameter is in between 10-100 nm and average length extends 100 nm to several micrometres (Rastogi and Samyn, 2015). NFC is also well known as nanofibrillar cellulose, cellulose nanofibril and cellulose nanofibre (Khalil et al., 2014). Naturally, NFC has three-dimensional "Spaghetti" like structure consists of alternating crystalline and amorphous regions (Lee et al., 2014) and as a result of that NFC can form an entangled network structure and it would lead to increase the storage modulus. Therefore, production of NFC reinforced Polypropylene (PP) composite could improve the performance of the material than pure PP. However, NFC is a hydrophilic material and PP is hydrophobic. Therefore, a proper surface modification is needed to improve the compatibility between the matrix and the reinforcement. Additionally, the modification should not harm the natural structure of the cellulose and should improve or maintain the qualities of NFC.

The surface modification processes can be classified as chemical and physical methods (Wu et al., 2016). Most of the time hydrophobicity of nanocellulose is improved by the chemical treatments due to the formation of a stable surface after modification. There are different chemical methods; however, the most common surface modification method is the addition of a coupling agent. There are more than forty coupling agents used in the industry and among them silylation is the most common coupling methods used to combine NFC and nonpolar matrices. Generally, silylation is the attachment of the silyl group ($-\text{SiR}_3$) to host molecular surface by removing hydrogen atoms bonded to a heteroatom such as $-\text{OH}$, $=\text{NH}$, $-\text{SH}$. Therefore, silylation process converts the hydrophilic surface of NFC into hydrophobic by attaching silyl groups to the $-\text{OH}$ groups in the cellulose at elevated temperature with the presence of water (Hubbe et al., 2008). A wide variety of reagents are available with silyl groups and the present study used Si-69 as a silylating agent.

Petroleum derivatives of synthetic polymers are widely available in the market due to simple, highly available and cost-effectiveness. When considering the world plastic market, more than 60% of the thermoplastic requirement is fulfilled by polyolefin. Therefore, polypropylene becomes second only to polyethylene and consists of many advanced characteristics including excellence water and chemical resistance, low toxicity, and inexpensiveness. However, polypropylene has a moderate amount of mechanical properties. Therefore, the durability of the final product becomes low. To overcome the obstacles, scientists are dominantly focusing on the production and development of natural fibre reinforced polymer composites (Egodage et al., 2017; Samarasekara and Jayasuriya, 2014; Gunapala and Samarasekara, 2013). Therefore, this research is focused on the production and development of surface modified NFC reinforced PP composite with enhanced mechanical properties. The fabricated nano-composite material can be used for different engineering applications including packaging, construction, aerospace and automotive.

METHODOLOGY

Surface Modification of NFC

Si-69 (Bis [3-(triethoxysilyl)propyl] tetrasulfide) was used as the silane agent for the surface modification of NFC. 50 g of NFC was mixed with a 1:10 weight ratio of 85% ethanol and the mixture was sonicated for 40 minutes. Separately, 30 wt. % Si-69 and the same amount of ethanol were added to another beaker and placed 10 min for the hydrolysis process. After that, the two separate mixtures were added together and again sonicated for 40 minutes. Then, the solution was heated to 70 °C for 2 hours and the concentrated solution was transferred to a flat ceramic plate for oven drying at 70 °C. Ultimately, surface modified or silylated NFC was collected after the complete evaporation of ethanol (Rajapaksha et al., 2017).

Composite Fabrication

Surface modified NFC was mixed with a homopolymer of polypropylene with different loadings of NFC through melt processing method. Initially, polypropylene was added to internal mixing machine. The mixing process was done for 5 min at 180 °C (Banbury type rotors, speed – 65 rpm). Then surface modified NFC was added to the system and the sample was further mixed at the same temperature for another 3 min. After that, the samples were compressed to produce temporary plates and the prepared batch samples were separately moulded at 180 °C for 8 min, with 0.5 Ton/inch pressure. Ultimately, the samples were allowed to air cool and the sheets were separated.

RESULTS AND DISCUSSION

Analysis of Surface Modified NFC

Morphology

SEM image of pure NFC (Figure 1a) revealed long, three-dimensional fibres and most of the fibres were within the nanometre range. The surface modified NFC (Figure 1b) was contained smoothly covered layers around the fibres. However, there was some coagulation identified after the silylation process.

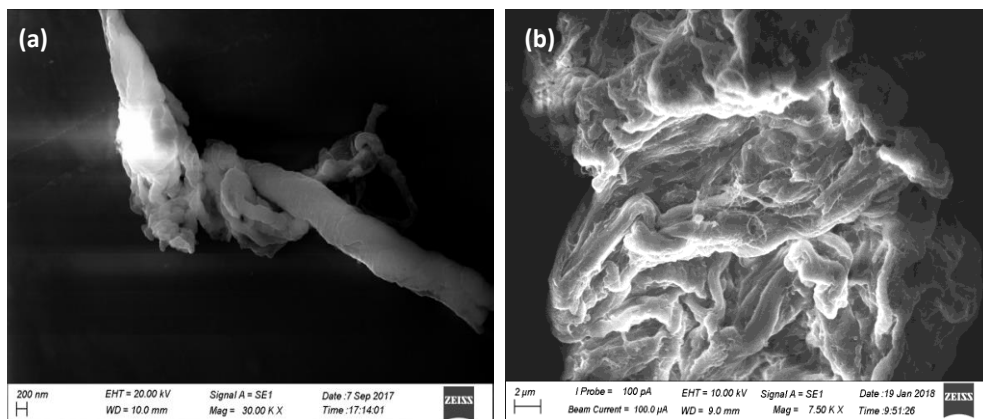


Figure 1. SEM image of (a) pure and (b) silylated NFC

FTIR

Notable FTIR band of in 3420 cm^{-1} of pure NFC spectrum explains the O-H stretching vibrations of cellulose (Figure 2). The peak at 2917 cm^{-1} demonstrates C-H stretching vibrations and the band also shifted to high values from 2900 cm^{-1} which can be further proved the amorphous structure of nanocellulose. The region in between $800\text{--}1200\text{ cm}^{-1}$ is the fingerprint region for cellulose. Both primary and secondary alcoholic C-O stretching vibrations in cellulose indicated in the peaks of 1114 cm^{-1} and 1163 cm^{-1} , respectively. In addition, the absorption band at 897 cm^{-1} and 1058 cm^{-1} assigned to C-O-C stretching at glycosidic linkages and within pyranose ring, respectively (Fan et al., 2012).

After normalizing two spectra, the huge reduction of O-H band was identified in the surface modified NFC graph. Except that, there are four new peaks were observed. The absorption bands are in around 788 cm^{-1} and 670 cm^{-1} , respectively correspond to the Si-C and Si-O-Si symmetric stretching. Based on the past studies shoulder peaks at 964 cm^{-1} and 1242 cm^{-1} are the characteristic peaks for Si-O-C bond (Britcher et al., 1995). Therefore, it confirms the reaction between the hydrolyzed silane and the nanocellulose.

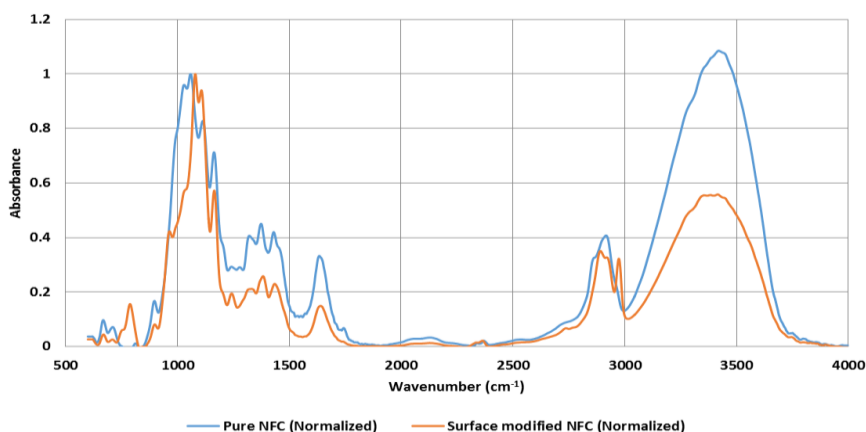


Figure 2. Normalized FTIR graphs of pure and silylated NFC

XRD

The native cellulose (cellulose *I*) has two different crystal structures; I_α and I_β and differ mainly in the packing arrangement of their hydrogen-bonded sheets. Cellulose I_α contains triclinic unit cell and cellulose I_β has a monoclinic unit cell (Poletto et al., 2013). According to the XRD pattern of pure NFC (Figure 3), there are four peaks can be identified in the 2θ values of 14.906° , 16.683° , 23.013° and 34.577° . These peaks extremely match with the literature values of I_β monoclinic structure (Santmarti and Lee, 2018). Therefore, the results proved that pure NFC sample contains I_β crystal structure and instrumental analysis was completely equal to the native cellulose with monoclinic unit cell structure.

After surface modification of NFC, all peak intensities of surface modified NFC were reduced in respect to pure NFC. Most importantly, the characteristic I_β monoclinic structure peak intensity (23°) was reduced after the surface modification process. In addition, the instrumental value of crystallinity was turned down from 74.5% to 70.2%. The reduction of crystalline percentage may be happened due to the addition of silane coupling agents to crystalline regions of NFC. During the modification process, large silane groups replaced the small -OH groups present in the NFC surface. Due to the addition of large groups to the surface, the distance

between molecules in the main chain would increase (Sheltami et al., 2015). Therefore, the separation could be effected to the reduction of the crystalline percentage of NFC after the surface modification.

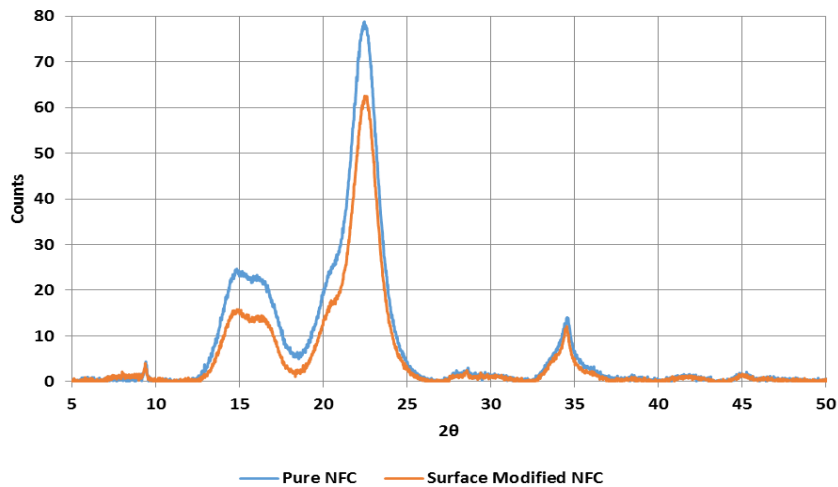


Figure 3. Normalized XRD patterns of pure and silylated NFC

Mechanical Properties of Fabricated Composites

Tensile Strength

In reference to the tensile strength of pure PP (24.7 MPa), all the composite samples have demonstrated increased values and the 3.5% NFC composite achieved the maximum amount of 27.8 MPa (Figure 4). However, the samples beyond the addition of 3.5% NFC displayed a reduction of tensile strength.

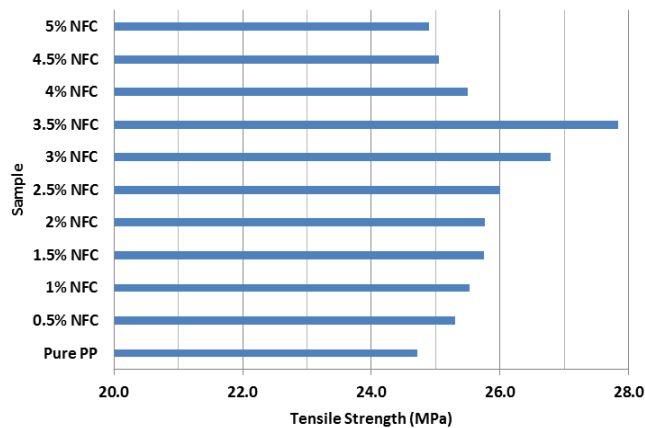


Figure 4. The tensile strength of pure PP & surface modified NFC-PP composites

The results proved the better adhesion between NFC and polypropylene matrix. Therefore, the surface modification of NFC, replace $-OH$ groups in the NFC surface by adding hydrophobic silane groups. If the attachment is more powerful, NFC is acting as reinforcement to PP matrix and performs better than the pure PP. Therefore, the results strongly imply that the surface

modifier or Si-69 is acting as a compatibilizer and improve the compatibility between hydrophilic reinforcement and the hydrophobic matrix up to the addition of 3.5% of NFC. Then, the tensile strength of higher reinforcement composites (4% to 5%) indicated a slight decrement probably due to the agglomeration of NFC as a result of the reduction of hydrophobic silane groups in the surface.

Percentage Elongation at Break

Compared to pure PP, the addition of NFC to PP matrix, reduce the percentage elongation at break (Figure 5). The results suggest that increment of NFC amount in the PP matrix causes a reduction of ductility or an improvement of brittleness of composites. The outcome explains the strong interfacial bonding between the reinforcement and matrix. Therefore, the silane modification could create rigid interphase between the NFC and PP.

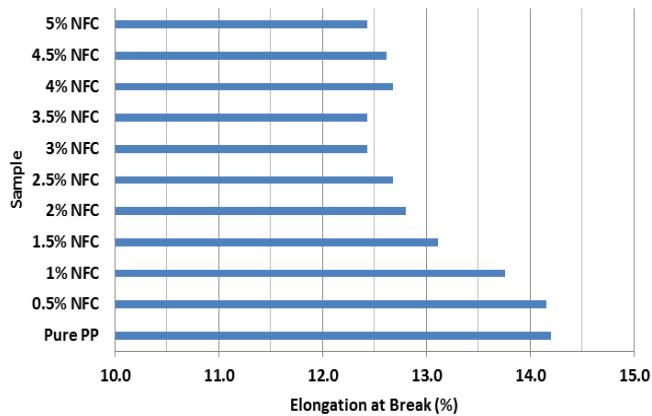


Figure 5. Percentage Elongation at break of pure PP & surface modified NFC-PP composites

Impact Strength

Based on the test results of Impact strength (Figure 6), all 10 composites were significantly improved in relation to the addition of NFC percentage than the pure PP sample (2.16 kJ/m²).

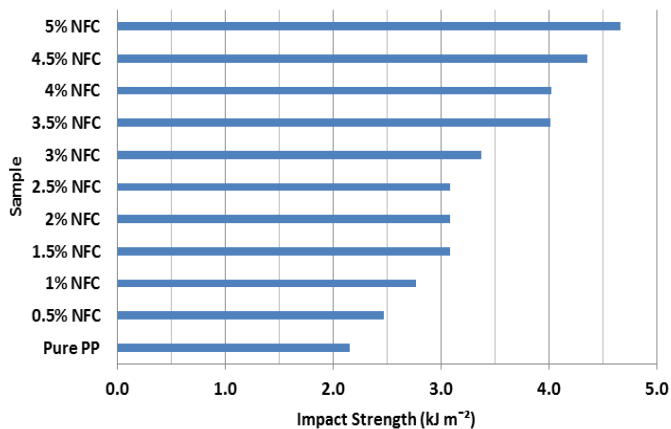


Figure 6. The impact strength of pure PP & surface modified NFC-PP composites

The maximum achieved value (4.67 kJ/m^2) is approximately two times higher than the pure PP. The results clearly verified that Si-69 is acting as a perfect compatibilizer and better load transferring material between matrix and fiber.

Hardness

All average hardness values of composites are higher than the pure PP (Figure 7). Addition of surface modified NFC to PP matrix increase the hardness up to 3.5% of NFC loading and after that, a slight reduction was observed. Initially, the hardness value increased with an increase in modified NFC content due to the better interaction between NFC and PP matrix. However, a slight reduction of hardness at higher NFC loadings was observed. Beyond 3.5 wt. % of NFC incorporation may lead to improve the agglomeration in the PP matrix and become difficult to achieve a homogeneous dispersion. In addition, surface modified NFC also sensitive for water molecules and may form microcavities during the processing. Other than that, 3.5 wt. % may be the maximum percentage of fiber volume fraction which interacts with the matrix.

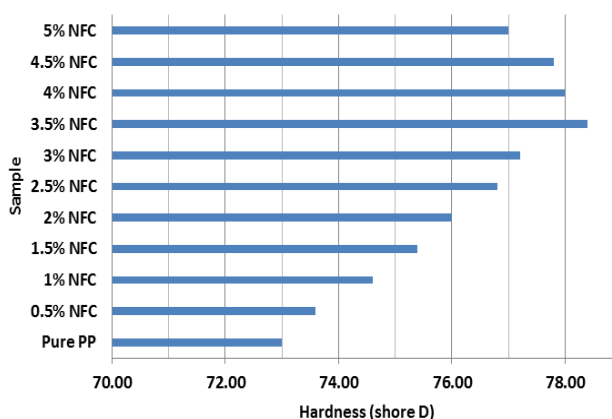


Figure 2. The hardness of pure PP and surface modified NFC-PP composites

Percentage Water Absorption

Water absorption amount of pure PP and surface modified NFC was shown in Figure 8.

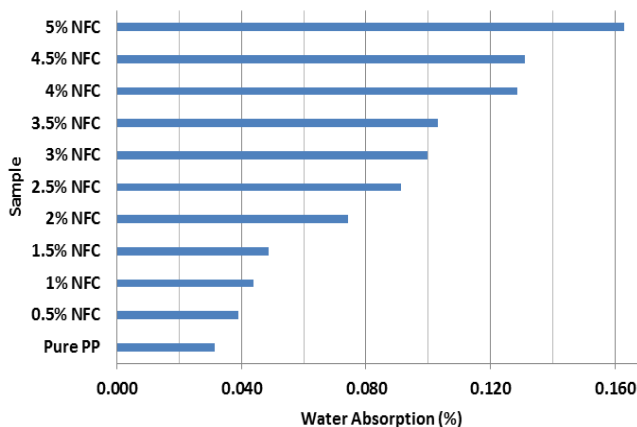


Figure 3. Water absorption percentage of pure PP & surface modified NFC-PP composites

Out of the 11 samples, pure PP has the lowest level of water absorption (0.03%) due to the hydrophobic nature of the material. The hydrophilic characteristic of NFC was reduced by the replacement of $-OH$ from silane groups. Practically, 100% of replacement could not be achieved and the surface modified NFC contains some water favorable $-OH$ groups. Therefore, the addition of modified NFC to pure PP leads to improve the water absorption.

Melt Flow Index

According to the Figure 9, the increment of surface modified NFC amount in the composite gradually lead to reduce the MFI values. The test was carried at 230 °C under 2.16 kg. The melting points of pure PP and surface modified NFC are 165 °C and 310 °C, respectively. Therefore, it can be assumed that at 230 °C, pure PP is completely in the melting state and NFC is in the solid phase. Therefore, NFC contains strong internal bonds with respect to matrix PP molecules. As a result of that, NFC slightly improves the viscosity of the composites and reduces the MFI value. However, the variation between MFI values of pure PP and composites is low. Therefore, the addition of NFC to pure PP does not generate a significant change in the processing of the material.

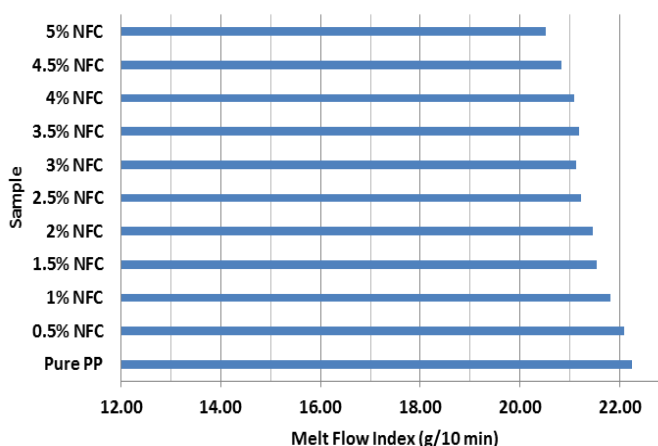


Figure 4. Melt flow index of pure PP and surface modified NFC-PP composites

CONCLUSIONS

The experimental results emphasize a wide improvement of mechanical properties with extremely narrow reduction of water absorption of silylated NFC based PP than the pure PP. The best mechanical properties were given by the 3.5% silylated NFC reinforced PP composite and hardness, tensile and impact strength values are respectively 7.4%, 12.6%, and 86.1% higher than the pure PP. Therefore, 3.5 wt. % of Si-69 surface modified NFC can be taken as the optimum level of reinforcement for PP matrix. This developed agricultural waste based product can be used for various applications to create a green environment..

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