

Thermomechanical Properties of Ductile Nano Silica Polymer Nanocomposite

Mantsha ErnaSeshweni¹, Orebotse Joseph Botlhoko², and Mamookho Elizabeth Makhatha³

Abstract—Herein, polypropylene (PP) nanocomposites containing dual fillers such as 3% nano silica (NS) and 10% treated sisal fiber (TSF) were prepared via melt extrusion with added functionalities to simultaneously improve the thermomechanical and ductility of the PP-based material. Also, for potential 3D-printing filament construction for automotive application and recyclability. This is probably due to an increase in the stiffness of the PP matrix due to the reinforcing effect imparted by the dual filler particles that allow a greater degree of stress transfer at the interface and restriction on molecular chains motion. The results showed that the addition of NS/TSF into PP matrix improved its thermomechanical properties, and elongation at break from 28% to maximum increase of 639% with well-balanced tensile modulus and strength. Most importantly, the PP-based nanocomposite material was reprocessed to produce 3D-printing filaments. The outcomes of this research hold immense potential for advancing the field of manufacturing, offering a novel dual filler nanocomposite with enhanced thermomechanical properties, improved ductility, and recycling characteristics.

Keywords—Ductility, thermomechanical properties, polypropylene nanocomposites, filaments.

I. INTRODUCTION

The critical issue of automotive industry in the development of complex, durable lightweight vehicles with fuel efficiency standards has attracted increasing attention owing to the continuous demand for clean environment (climate disruption, air and noise pollution). The exclusive shift towards advance 3D printing manufacturing technology can play a critical role in expanding or solving the manufacturing industry production problems such as complexity and waste generation, using recycling strategy. Herein, the most important part prior to the actual printing process is the development of homogenous filaments in terms of thickness and length. Compared to traditional industrial polymer composite, materials such as polymer nanocomposites have greater specific durability and lightweight properties due to nanoparticles critical densities and larger specific surface area advances. In this rational, specific attention has been given to polypropylene (PP) to improve its properties due to its dominance in automotive industry and

other applications. However, reinforcing PP matrix requires evenly microfiller or nanofiller distribution, dispersion, and excellent particle-polymer chain interaction for improved performance [1]. Natural reinforcements have been discovered to constitute better reinforcing properties in most polymers for the design application of automotive components. Also, fiber reinforcements embedded in polymer matrix demonstrated potential mechanical properties improvement in many studies. However, strongly polarized hydroxyl groups in natural fibers result in poor mechanical interlocking adhesion of the polar hydrophilic reinforcement with a non-polar hydrophobic polymer matrix, compromising composite performance [2],[3]. This is due to the amorphous material, such as lignin and hemicellulose, which inhibits these hydroxyl groups from reacting with the matrix. In this rational, physical and/or chemical treatment of the fiber is then applied with the aim of enhancing fiber-polymer composite interfacial bonding and properties [3],[4].

On the other hand, previous studies have investigated on the incorporation of nanoparticles to improve the mechanical thermal, and thermochemical properties of the matrix phase. Because of the homogeneous and uniform dispersion of nanoparticles, as well as their inherent large specific surface area, the contact surface between nanoparticles and the PP matrix can be considerably increased, thus increasing martial properties. In addition, nanoparticle reinforcement seems to constitute stiffness improvement with cost reduction at low reinforcement content as compared to the traditional reinforcement agent such as glass fibers, carbon fibers, and other [5],[6].

Herein, silicon dioxide (SiO₂) or nano-silica (NS) is an inorganic nanomaterial with high specific strength, toughness and good stability at high temperature has remarkable results of modifying and toughening polymers [7],[8]. It is well-known that the NS nanoparticles exhibits excellent size, shape, particle-matrix interface adhesion or chemical interaction via OH bonds with PP, thus potential to effectively improve the mechanical, and thermomechanical properties of PP matrix [7],[9]. Moreover, NS is usually used as nucleating agent and

Mantsha Erna Seshweni¹ is 1Department of Engineering Metallurgy, Faculty of Engineering and the Built Environment, University of Johannesburg, John Orr Building, DFC, 25 Louisa St, Doornfontein, Johannesburg 2028, South Africa

Orebotse Joseph Botlhoko² is was with Council for Scientific and Industrial Research Council (CSIR) Chemical Cluster, Nanostructured and Advanced Materials, Pretoria 001, South Africa;

Mamookho Elizabeth Makhatha³ is with the Department of Engineering Metallurgy, Faculty of Engineering and the Built Environment, University of Johannesburg, John Orr Building, DFC, 25 Louisa St, Doornfontein, Johannesburg 2028, South Africa

clarifying agent, that is, to promote the crystallization of polymeric materials.

As an attempt to improve the fundamental properties of PP-based material, we have carefully observed that the thermomechanical properties and ductility effects of fiber/PP composite can be further improved by the incorporation of NS nanoparticles into the PP matrix. And the same material can be recycled and used to produce filaments for potential 3D-printed automotive prototypes. Therefore, the major objective of this study is to leverage on the potential chemical interaction between NS and PP matrix for the improvement of thermomechanical properties and ductility/flexibility capabilities of PP reinforced with treated sisal fiber (TSF). The development of dual filler NS-TSF reinforced PP nanocomposites via industrially favorable melt processing techniques have great merits (see Fig. 1).

II. EXPERIMENTAL

A. Materials

Polypropylene (PP), a commercial homopolymer (HHR102) grade in the form of pellets was received from Sasol, South Africa. Characteristic parameters according to the supplier information are as follows: MFR = 2.0 g/10min, density = 0.905 g.cm⁻³ with melting temperature = 168 °C. The sisal fiber leaves were collected from an old local farm in Limpopo, South Africa. Firstly, sisal fiber leaves were dried, and manually cut into ±15 mm length using a scissor. Then washed with distilled water, and oven-dried at 100 °C for 3 h. Commercial silicon dioxide (SiO₂) in the form of white powder (spherical, porous) with a size of 5-20 nm particles was supplied by Sigma-Aldrich Solutions.

B. Sisal fiber surface treatment

About 5 g of sisal fiber was soaked for an hour in the alkali solution (40 g sodium hydroxide (NaOH) pellets in 100 ml of distilled water) at room temperature. The sisal fiber was then drained and placed in an oven for 4 h at 100 °C, then the treated sisal fiber was denoted as TSF.

C. Processing of the PP matrix and nanocomposites.

Neat PP, TSF/PP and NS-TSF/PP nanocomposites were prepared via melt mixing technique in a co-rotating twin-screw extruder (Thermo Electron [Karlsruhe] GmbH, D-76227 Karlsruhe, Germany; L/D = 40; diameter = 11 mm) (see Fig. 1). The speed of the screw together with its feed rate were 77.7580 rpm and 3.9789 kg/h, respectively. The different temperatures zones for the extruder were set at 120, 150, 160, 170, 180, 180, 180, 180, 180, and 180 °C (die). All the components were dry mixed in a plastic bag before melt-mixing. Importantly, the PP pellets, TSF/PP, and NS-TSF/PP were premixed in the respective weight percentage; 100%, 10%/90%, and 3%-10%/87% and denoted as neat PP, 10%TSF, and 3%NS-10%TSF, respectively. The extruded materials were cooled using in tap water in a water bath, pelletized, and oven-dried at 60 °C for a period of 12 h.

Neat PP and nanocomposites samples were then placed into injection moulding machine (ENGEL e-mac50) of a 500 kN

clamping force for specimens production (see Fig. 1). The injection moulding machine was set at 195, 190, 180, and 180 °C. The metering, specific back pressure, injection pressure, and injection speed were set at 28 to 59 mm range, 100 bar, 290 to 550 bar range, and 100 mm.s⁻¹. Prior to analysis, samples were annealed at 60 °C for 16 h under a vacuum oven.

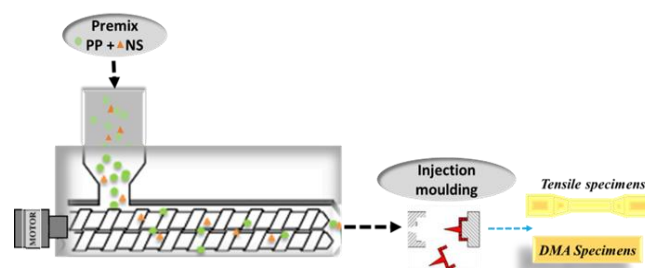


Fig. 1 Schematic illustration of PP and nanocomposites melt processing.

D. Processing of the 3D printing filaments.

For 3D printing filaments preparation, neat PP and 3-10% NS/TSF nanocomposites samples were pulverized, pre-mixed at 50%/50% ratio and re-extruded to produce the 3D printing filaments for future 3D printing complex parts of automotive, thus recycling.

III. CHARACTERIZATION

Fourier Transform Infrared Spectrometry (FTIR) analysis were performed using the Thermo scientific Smart spectrometer at room temperature, in the operational spectral range of 4000 - 400 cm⁻¹ and 16 scans with 4 cm⁻¹ spectral resolution (following KBr protocols).

Dynamic mechanical analysis (DMA): The dynamic storage modulus (E'), loss modulus (E''), and tan delta of the specimen were measured at a temperature function (-40 to 120 °C) and at 2 °C min⁻¹ heating rate in the dual cantilever bending mode. Samples were measured at a constant frequency of 10 Hz and 0.02% strain amplitude.

Tensile tester: Tensile test measurements were conducted using an Instron 5966 tester (Instron Engineering Corporation, USA) with a load cell of 10 kN, based on ASTM 638D standards. The tests were performed on dog-bone-shaped injection-moulded, under tension mode at a single strain rate of 5 mm.min⁻¹ and room temperature. The average of six sample measurements were reported for each sample.

Thermogravimetric analysis (TGA): Thermal stability analysis for samples was conducted on TGA TA Instruments to. Analysis were carried out in a nitrogen atmosphere with a flow of 20 mL.min⁻¹. In measuring degradation of the samples with temperature, samples were heated at room temperature to 900 °C at heating rate of 10 °C.min⁻¹. A weight reduction as a result of the increase in temperature was observed for each sample. Experiments were performed at least three times for every sample, results were then reported according to the most representative.

IV. RESULTS AND DISCUSSION

A. Fourier-Transform Infrared Spectroscopy Analysis

Fig. 2 shows the FTIR spectra, which described how chemical treatment helps to produce reactive hydroxyl groups within the material constituents that can participate in fiber-polymer matrix adhesion. The alkali treatment has the potential to effectively reveal the removal of the amorphous material. The TSF is characterized by the intense broader peak at 3223 cm^{-1} which indicate the -OH stretching vibration absorption, attributed to the hydroxyl groups of cellulose and hemicellulose. Moreover, TSF is characterized by a well-defined peak at 1646 cm^{-1} which indicated an absorption of carbonyl group in lignin [10],[11]. Also, the observed peak at 1018 cm^{-1} of TSF is attributed to the stretching vibration (C-O) of lignin. On the other hand, NS is characterized by broader band of 3382 cm^{-1} which indicate the stretching of vibrations from the hydroxyl group for filler-polymer interaction/dispersion via hydrogen bonding. Moreover, characterized by intense broad peak at 1063 cm^{-1} due to Si-O-Si asymmetry. Also, shows the symmetry peaks of Si-O-Si at 960 cm^{-1} and 799 cm^{-1} attributed to the stretching of vibrations [12],[13].

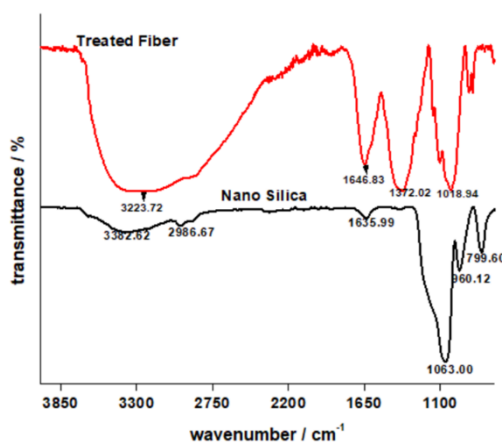


Fig. 2 FTIR spectra of TSF and NS

B. Thermomechanical properties of neat PP and nanocomposites.

Fig. 3 display storage modulus and tan delta of neat PP and reinforced PP as a function of temperature, where the PP-based nanocomposites were subjected to periodic stress employing dynamic mechanical test. The incorporation of 10% TSF into the PP matrix slightly improved the storage modulus of the material, this suggests an improvement in the stiffness of the polymer matrix due to the polymer chain restriction in the segmental motion. It is clear that the introduction of dual filler system, reinforcement agents (3% NS particles together with 10% TSF) offers a significant increase in the storage modulus of neat PP matrix (Fig. 3(a)). This is probably due to an increase in the stiffness of the PP matrix with the reinforcing effect imparted by the NS particles that allowed a greater degree of stress transfer at the interface. The storage modulus of the PP-based nanocomposites was prominent for dual filler system, due to the filler particles reinforcing effect and stronger restriction

on molecular chains motion as result of the synergistic effects of two fillers with different morphology and structure supplemental activities. This behavior is primarily attributed to improved interfacial adhesion between the filler particles and the matrices [9]. With the increasing temperature, it can be observed that the storage modulus decreases for all samples. The observation is generally due to the molecular mobility increase on polymer chains [14]. In brief, this behavior indicates the limited chain mobility of polymer matrix at lower temperatures and some sort of unrestricted chain mobility at high temperature profile. However, the interactions generated by the presence of TSF and NS/TSF particles compensated for the modulus rate of fall in the nanocomposites system.

The damping properties of the material give the balance between the viscous phase and elastic phase in a polymeric structure. In the present investigation, the measurement of tan delta as a function of temperature is represented in Fig. 3(b). The addition of both fillers did not shift the glass transition temperature peak toward high temperature profile in relation to that of neat PP. The magnitude of the tan delta peak is observed to increase for 10% TSF and 3-10% NS/TSF samples in comparison to neat PP. Importantly, the damping peak in dual filler system (3-10% NS/TSF sample) showed a slight decreased magnitude of tan delta in comparison to 10% TSF sample. This is because the NS particles carry an extent of stress and allow only a part of it to strain the interface. Therefore, this behavior suggests that less energy dissipation will occur in the PP matrix with a stronger interface characteristic. While the material with high magnitude of the damping peak will tend to dissipate more energy.

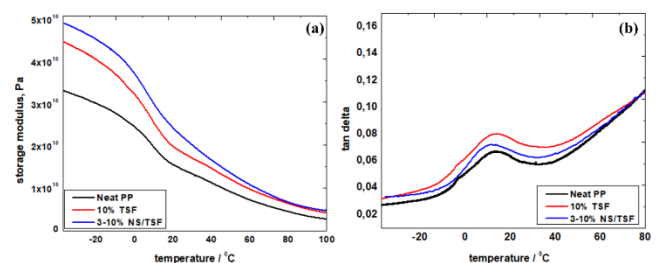


Fig. 3 Storage modulus (a) tan delta (b) of neat PP and nanocomposites.

C. Mechanical properties of neat PP and nanocomposites.

This section explores the potential of dual filler system in improving mechanical properties, particularly the flexibility characteristics of neat PP, which is inherently light and characterized by high tensile modulus. Fig. 4 and Table I below indicate dramatic improvement of elongation at break (Fig. 4(d)), with well-balance of tensile modulus (Fig. 4(b)) and tensile strength Fig. 4(c)) upon the incorporation of 3-10% NS/TSF particles into the neat PP matrix. According to Wu et al. [15], NS surface properties and their level of dispersion has the ability to influence the physical cross-linking effect. This suggests that the stress could accumulate in the physical cross-linking region compared to the polymer matrix regions. Importantly, the elongation at break behavior shows a

significant increment which reached the instrument limit (about 640%) for dual filler nanocomposites (3-10% NS/TSF). This demonstrates the effectiveness of the addition of NS particles towards the formation of ductile and tough PP-based nanocomposites. The role of the NS particles promoted the elastic nature of PP-based material. Also, the stress-strain (Fig. 4(a)) display the maximum amount of tensile stress PP-based materials can withstand prior deformation. This shows that the load transfer depends on the interaction behavior of the polymer and the filler. Generally, the fillers constitute stiffness properties, hence the potential to improve the modulus properties, while deformation depends on the filler-polymer adhesion phenomena [9]. Therefore, well-balance of tensile modulus and tensile strength is possibly due to the synergistic effects of relatively low NS (3%) particles and 10% TSF incorporation as well as the degree of dispersion [16]. The slight elongation at break increase based on the 10% TSF is due to the enthalpic interaction between the fiber and the polymer matrix.

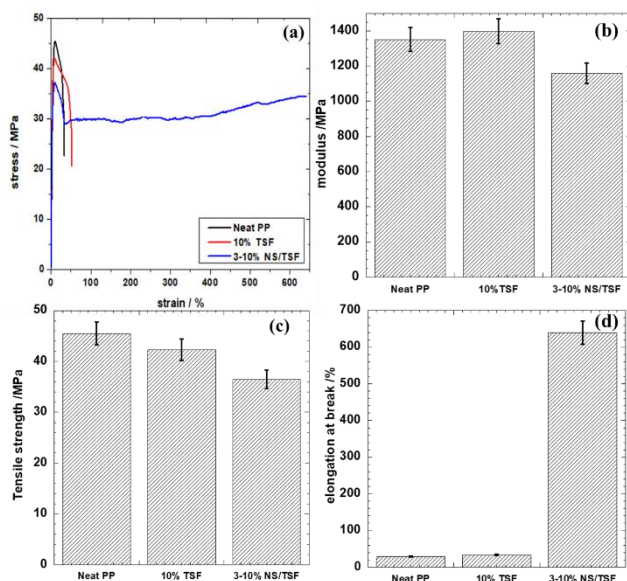


Fig. 4 Tensile stress-strain (a) modulus (b) tensile strength (c) elongation-at-break (d) of neat PP and nanocomposites.

D. Thermal stability of neat PP and nanocomposite

Thermal analysis plays a significant role in understanding the thermal behavior and stability of polymeric material. Herein, TGA allows for a comprehensive analysis of the thermal properties of neat PP and nanocomposites, by providing insights into their thermal stability and potential degradation under elevated temperatures (see Fig. 5). These analyses are vital for polymeric materials with potential automotive application. The presented TGA thermographs in Fig. 5 reveal that the onset of degradation in 10% TSF nanocomposite occurs at slightly higher temperatures compared to neat PP matrix. While the onset of degradation in 3-10% NS/TSF nanocomposite occurs at notably lower temperatures compared to neat PP matrix.

The overall observation suggests that the incorporation of NS particles in the composites does not really improve the thermal

stability of the material. One possible explanation for this behavior could be related to the presence of Si atoms bonded to oxygen atoms in NS chemical structure. The lack of thermal stability improvement in the dually reinforced nanocomposites, present limited restriction on by the reinforcement agents [9]. Consequently, the lower thermal degradation in NS/TSF nanocomposites, could not making them not suitable for applications where about 350 °C temperature resistance is required but this indicate that the material is not suitable to be used as heat barrier in more than 450 °C such as neat PP [17].

TABLE I
TENSILE PROPERTIES

Sample ID	Tensile modulus (MPa)	Tensile Strength (MPa)	Elongation at break (%)
Neat PP	1350.1 ±115.5	45.5 ±0.6	28.5 ±6.8
10% 10% TSF	1398.2 ±71.5	42.3 ±0.5	33.3 ±8.2
10% 3%-10% NS/TSF	1159.4 ±45.5	36.46 ±0.93	639.1 ±5.1

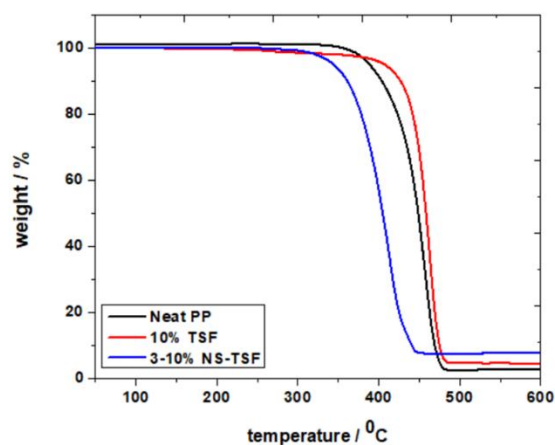


Fig. 5 Thermal stability of neat PP and nanocomposites.

E. 3D printing filaments of the re-processed neat PP and nanocomposite

The relatively new and still growing field of 3D-printing has opened up the possibilities to manufacture complex products with high geometrical accuracy, following layer-by-layer construction protocols. Considering that most of the original automotive parts or equipment are manufactured using PP, such as headlight housing [18]. A key aspect of this study was to prepare the PP-based material via injection moulding and test for thermomechanical and other properties. Then, reprocess the same for filament production capabilities. This approach can present environmental sustainability by reducing polymer waste and add value to recycling, circular economy. In this rational, Fig. 6 shows the injection moulded test specimens of neat PP and dual nanocomposite. The successfully melt processed neat PP and dual nanocomposites can be injection moulded into different test specimens and products (Fig. 6 (a)). Thereafter, recycled using the readily available melt processing techniques. Herein, the initially extruded material (neat PP and nanocomposites) were pulverized into small polymer particles (Fig. (b)) prior reprocessing into filaments, thus recycling attributes. The pulverized neat PP and 3-10% NS/TSF nanocomposite were pre-mixed at a ratio of 50/50 then re-

extruded to form 3D-printing filaments (Fig. 6 c and d)) for future prototyping of automotive parts. The filaments were characterized by thicknesses of about 1.7 mm and long enough for continues 3D-printing process.

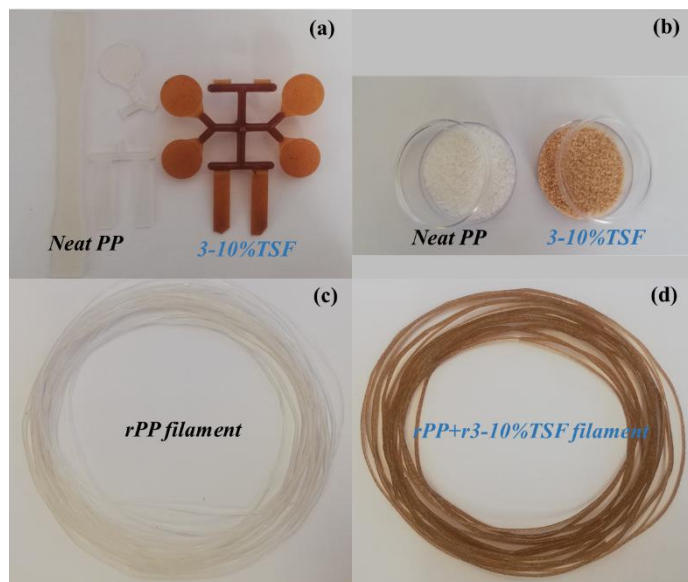


Fig. 6 Injection mould test specimens (a), pulverized polymer material (b), recycled neat PP 3d printing filament (c), recycled neat PP/3-10%NS/TSF (50/50 ratio) 3d printing filament (d).

V.CONCLUSION

In this study, the effects of using TSF only, and dual NS-TSF particles as reinforcement agents on the mechanical, thermal, and thermomechanical properties of PP-based nanocomposites were evaluated. The NS-TSF/PP nanocomposites exhibited dramatic improvement in storage modulus with slight increase of tan delta magnitude and slightly early thermal degradation. The maximum elongation at break of the dual (NS/TSF) nanocomposite system was found to be 639% when compared to the 33% and 28% of TSF nanocomposite and neat PP. The fundamentals and findings presented in this study will pave the way for the development of high-performance NS-TSF/PP nanocomposites with potential for 3D-printing automotive prototypes and value to manufacturing as well as circular economy prospects.

APPENDIX

No appendixes.

ACKNOWLEDGMENT

The authors would like to thank the DSI-CSIR of South Africa for their financial support and further thank the staff of University of Johannesburg. The authors declare no conflicting interests.

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