



Article Evaluation of Mechanical and Thermal Properties of Polypropylene-Based Nanocomposites Reinforced with Silica Nanofillers via Melt Processing Followed by Injection Molding

Mantsha Hennie Erna Seshweni¹, Mamookho Elizabeth Makhatha¹, Orebotse Joseph Botlhoko², Babatunde Abiodun Obadele³, Vijeesh Vijayan⁴, Dundesh S. Chiniwar⁵, Pawan Kumar^{1,*}, and Vishwanatha H. M. ^{6,*}

- ¹ 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
- ² Centre for Nanostructures and Advanced Materials, DSI-CSIR Nanotechnology Innovation Centre, Council for Scientific and Industrial Research, P.O. Box 395, Pretoria 0001, South Africa; obothoko@csir.co.za
- ³ Department of Chemical, Materials and Metallurgical Engineering, Botswana International University of Science and Technology, Private Bag 16, Palapye 10071, Botswana; obadele4@gmail.com
- ⁴ Nitte (Deemed to be University), NMAM Institute of Technology (NMAMIT), Department of Mechanical Engineering, Nitte 574110, India; vijeeshv@nitte.edu.in
- ⁵ Department of Mechatronics, Manipal Institute of Technology, Manipal, Manipal Academy of Higher Education, Manipal 576104, India
- ⁶ Department of Mechanical and Industrial Engineering, Manipal Institute of Technology, Manipal, Manipal Academy of Higher Education, Manipal 576104, India
- * Correspondence: pkumar@uj.ac.za (P.K.); vishwanatha.hm@manipal.edu (V.H.M.)

Abstract: Polymer nanocomposites have been of great interest to packaging, energy, molding, and transportation industries due to several favorable properties including a higher resistance to stress and cracking even under flexed conditions, and also a chemical resistance to water, acids, and alkalis. The current work disseminates the studies on the mechanical and thermal properties of the polypropylene HHR102 polymer reinforced with nano dispersoids of silicon dioxide at varied weight fractions. The nanocomposites, fabricated via melt processing followed by injection molding, were tested for tensile strength, % elongation, tensile modulus, and impact toughness. Further, the samples were also subjected to dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA) to determine the dynamic storage modulus and thermal stability. The addition of nano-silica in polypropylene HHR102 resulted in enhanced ductility and well-balanced tensile modulus; however, the tensile strength and impact toughness were found to be decreased. On the other hand, the storage modulus was significantly increased for all nano-silica (NS)-containing polypropylene HHR102 matrices. With the increased nano-silica content, the storage modulus was optimal. Further, with the lower weight loss of 30% and 50%, the thermal stability of the increased silica content PP nanocomposites was much affected. However, it improved at a weight loss of 30% for the lower silica content PP nanocomposite (PP-1%NS). The imbibition was found to increase with the increase in NS. The increase in imbibition is attributed to the micro-voids generated during ageing. These micro-voids act as channels for water absorption. Further, the degree of crystallinity of the nanocomposites was decreased as a result of inhibition by the nano-particles on the regular packing of polymer molecules. The structure-property correlations were explicated based on the achieved mechanical properties.

Keywords: polypropylene; nanocomposite; ductility; thermal stability; thermogravimetric analysis; thermomechanical; climate; pollution; transportation



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1. Introduction

The automotive industry's ongoing desire for the development of durable, lightweight automobiles with enhanced fuel efficiency and decreased greenhouse gas emissions has gained increased attention. The development of durable lightweight automobiles with fuel efficiency is also in line with the continuous demand for a clean environment (climate disruption by air pollution). The automotive industry has made remarkable improvements in the type of material employed for a specific application or targeted function to achieve a durable lightweight material [1]. Specific attention has been given to polypropylene (PP) due to its cost-effectiveness, recyclability, high strength, good physical properties, chemically resistant characteristics, and outstanding processability, which allow for filler incorporation and property improvement [2,3]. Also, PP is characterized by a density of about 0.905 g/cm^2 , which can contribute to fuel reduction in automobiles. It is well known that every 10% reduction in automobile weight results in a 5% to 7% fuel consumption [4]. As a result, PP has found applications in automotive bumpers and other lightweight automotive components [5,6]. Unfortunately, the low flexibility and insufficient thermomechanical properties of PP have limited its wide application. Therefore, considerable work has been done on PP-based composites. Naskar et al. [7] highlighted that the fundamental understanding of the structure-property relationship between polymer matrix and reinforcing agents is critical to simultaneously improve the stiffness and impact strength. Processing thermoplastic polymers repeatedly to make products is possible, though it might result in material deterioration [8]. Polymer preparation involves high temperatures irrespective of the fabrication route. Hence, it is important to understand the decomposition temperature of the filler to achieve the improvement required in the nanocomposite.

Reinforcing PP requires an even distribution, infiltration, and dispersion of the reinforcement to adhere to the PP chains to avoid weak interfacial interactions or poor adhesion between the nanoparticles and the PP matrices. Thus, the chosen mixing process must be able to disperse the particles homogeneously to yield optimum results.

Nanoparticle reinforcement seems to achieve stiffness improvement at low reinforcement content as compared to reinforcement with fibers, such as glass and carbon [7]. This is due to the higher surface area to volume ratio, which offers stronger interfacial interaction in the matrix. Nanoparticles have the potential to agglomerate due to inter-particle interactions, disturbing the uniform dispersion and affecting the tensile modulus, thus preventing the material from achieving certain applications, such as semi-structural automobile parts (hoods, doors, and fenders). However, the material can still maintain its strength.

Silicon-di-oxide or nano-silica (NS) is an inorganic chemical product with high specific strength, high toughness, and high thermal stability, and it has demonstrated outstanding results in modifying and toughening polymer matrices [9,10]. It is well known that the NS particle size, particle/matrix interface adhesion, particle loading, particle shape, and geometry all contribute to the effective improvement of the mechanical properties and heat resistance [11]. Among other properties, NS is usually used as a clarifier or nucleating agent to promote the crystallization of a semi-crystalline polymer matrix. Thus, it contributes to the initiation of the crystallization at elevated temperature profiles [12]. Kumar et al. [13] highlighted that the amalgamation of the filler with a decrease in size from smaller to nanoscale improves the filler–resin interfacial adhesion. The particle size is of great effect with good dispersion abilities, acting as a bridge for the nanoparticle–matrix interaction.

Polypropylene (PP) thermoplastic is often reinforced with nanoparticles or fibers to increase composite properties such as strength and thermal expansion, as well as to reduce mold shrinkage. The dispersion of fillers and interfacial properties between the filler and a polymer can be improved further using a surface modification protocol [11]. Grafting or modifying reinforcement and/or using compatibilizers on the matrix for improving the applications of nanocomposites has been proven feasible by researchers such as Yuan et al. [8]. Polyolefin chains were grafted onto silica particles with a modification of a multi-step process, activating the surface of the NS with PP chains at a low grafted chain amount. Bala et al. [14] investigated NS reinforcement in PP-modified asphalt for pavement

application. The effect was revealed through an improvement of the fatigue properties when NS was combined with the thermoplastic polymer. The study mentioned the benefits of NS, specifically its large surface area, its ability to disperse well, its strong absorption, great stability, and excellent chemical purity.

Designing nanocomposites is associated with adhesion, debonding, and filler homogeneity dispersion challenges [15]. However, efficiency in unmodified surfaces still attracts research attention. Ponnusamy et al. [16] studied fiber-reinforced epoxy composites with varying weight concentrations of NS particles; however, surface modification was not performed using NS. Yeasmin et al. [17] reported inherent Si-OH groups on silica particles which envisage reactivity towards an epoxide ring-opening reaction and forming an Si-O-C linkage with a restricted molecular mobility of the resin, better adhesion, and increased interface area without the presence of any other catalyst or promoter [18,19]. On the other hand, it was reported that an agglomeration of unmodified silica can be dispersed when embedded in the polymer matrix [20]. Other studies also highlighted that the effectiveness of the reinforcement is mainly governed by the controlled dispersion of nanofillers, as well as their interfacial interaction with the matrix [21]. Also, Liu et al. [22] reported that the surface of silica nanoparticles is covered with abundant hydroxyl groups, thereby enhancing the potential for chemical modification. Moreover, through their work, Awad and Khalaf [23] suggested a greater possibility for chemical interaction between the PP and nano-silica layers; this was attributed to the increasing intensity of the hydroxyl group (absorbance peak) with increased nano-silica load. Herein, the possible particle–polymer matrix interface adhesion or chemical interaction is more likely to be governed by the hydroxyl group pathway, thus having the potential to effectively improve the mechanical and thermomechanical properties of the PP matrix.

Much research on polymer nanocomposites has been focused on modified nanoparticles/fillers, the incorporation of larger amounts of the ideal filler, or leveraging the synergetic effects of dual filler systems to improve polymer matrix properties. Among the various modified strategies, the modification of hydrophobic organic clay (9% mica) with cetyltrimethylammonium bromide has shown an enhanced modulus and thermal stability of the PP matrix [3]. PP nanocomposites containing dual filler systems based on MgFeAl-layered double hydroxide (2.5%, 5%, and 7.5% LDH) cause catalytic degradation effects during melt processing [24]. Importantly, the incorporation of silica waste into the PP matrix resulted in a gradual increase in the tensile modulus and tensile strength with an unfortunate decrease of elongation at break (from 8.9% to 6.35% for the PP/10%silica waste composite) [12]. In this rationale, it is vital that the fundamental concept and inherent properties of nano-scale particles with a low content (\leq 3% filler loading) are evaluated in the context of the tailored mechanical, thermal, and thermomechanical properties of PP nanocomposites. The fundamentals of the degree of crystallinity and catalytic degradation during melt processing are studied to reveal the effects of mechanical property response and water adsorption. Herein, we report on the facile fabrication and evaluation of low-content NS incorporation (1%, 2%, and 3%) into PP nanocomposite materials with lightweight, flexible characteristics, and improved thermomechanical properties for automotive applications.

2. Materials and Methodology

The PP employed herein is a homopolymer (HHR102) of a commercial grade in the form of pellets, with the following properties: melt flow index (MFR) of 2 g /10 min, density of 0.905 g/cm³, and melting temperature (T_m) of 168 °C. Silicon dioxide (SiO₂) or NS nanopowder (spherical and porous, Sigma-Adrich, South Africa), having a size range of 5–20 nm and molecular weight of 60.08 g/mol, was used.

Prior to processing, the NS nanopowder and PP pellets were pre-mixed and placed in a co-rotating twin-screw extruder (Thermo Electron, Karlsruhe, Germany) for the production of PP nanocomposites of L/D = 40, diameter = 11 mm, and containing 1%, 2%, and 3% NS nanoparticles, via melt processing. The feeding zone temperature was set to 120 °C, and

the temperatures of the rest of the extrusion process zones including the die were set to 150 °C, 160 °C, 170 °C, and 180 °C (die). The feed rate and screw speed were maintained at 4 kg/h and 78 rpm, respectively. Subsequently, the extruded samples were collected through the water bath, pelletized, and dried in an oven at 60 °C for 12 h.

Later, the resulting samples were injection-molded into different specimens using an injection molding machine (ENGEL e-mac50, ENGEL AUSTRIA GmbH). The different zone profile temperatures of the injection molding machine were set to 195 °C, 190 °C, 180 °C, and 180 °C, respectively, while the metering, specific back pressure, injection pressure, and injection speed were set in the range of 28–59 mm, 100 bar, 290–550 bar, and 100 mm/s, respectively. Prior to characterization, the samples were placed in a zip-lock bag for polymer chain relaxation and storage. The composition of the fabricated nanocomposite materials is shown in Table 1. Before mechanical and thermal analysis, the samples were annealed at 60 °C for 16 h in a vacuum oven.

Table 1. Nanocomposite material composition.

Neat PP (wt.%)	NS (wt.%) Batch 1
100	0
99	1
98	2
97	3

The tensile properties of the fabricated samples were characterized using a universal testing machine (Instron 5966, Instron Engineering Corp., Norwood, MA, USA), considering ASTM 638D standards [25]. The tests were performed on dog-bone-shaped injection-molded samples in tension mode, at a single strain rate of 5 mm/min and at room temperature.

The impact strength was determined using a Charpy impact testing instrument (CEAST 9050 Motorized, Instron Engineering Corp., Norwood, MA, USA). Rectangular bar-shaped injection molded PP-based samples (length = 80 mm, width = 10 mm, and thickness = 4 mm) were used. The samples for the Charpy impact test were notched one-sided, with a notch root radius of 0.25 mm at a depth of 2 mm. The notched Charpy impact strength was then measured at room temperature, with a 3.7 m/s drop velocity and a 7.5 J impact energy.

To study the thermal stability of the injection-molded samples, thermogravimetric analysis (TGA) was carried out on a TG analyzer (TGA Q500, TA Instruments, DE, USA). The analyses were conducted under a nitrogen atmosphere with a flow of 20 mL/min, and about 10 mg of samples was heated from room temperature to 900 °C at a rate of 10 °C/min.

Water diffusion tests were performed on the rectangular bar-shaped samples (length = 80 mm, 10 mm in width = 10 mm, and thickness = 4 mm). The samples were immersed in water in different containers for 3, 6, 9, 12, and 15 days. The weight of the samples was measured before and after immersion. The water absorption percentage of each sample was calculated using Equation 1 [26].

water absorption % =
$$\frac{w_w - w_d}{w_d} * 100$$
 (1)

where w_w and w_d describe the wet and dry weights, respectively.

To examine the thermal properties, particularly the crystallization and melting temperature of the PP-based material, differential scanning calorimetry (DSC) tests were performed using a DSC 8500, PerkinElmer instrument.

Approximately 15 mg of a sample was subjected to a temperature range from -25 to 180 °C under a nitrogen atmosphere. The samples were exposed to heating and cooling at a rate of 10 °C/min in three consecutive scans: heating, cooling, and heating. Three independent runs were conducted for each sample. The initial heating scan was used to

remove the sample's thermal history, while the cooling scan determined the crystallization temperature (T_c), and the second heating scan determined the melting temperature (T_m) together with the melting enthalpy (ΔH_m). The degree of crystallinity (χ_c) for the PP-based material was calculated using Equation 2.

$$\% Crystallinity = \frac{\Delta H_m}{\Delta H^0 m} * 100$$
⁽²⁾

where ΔH_m is the sample's melting heat and ΔH^0_m is the fusion heat of a completely (100%) crystalline PP, which is considered to be 198 J·g⁻¹.

3. Results and Discussion

3.1. Mechanical Properties of the Neat PP and PP-NS Nanocomposites

The effects of the weight fraction of NS on the mechanical properties of the nanocomposites are presented in Figure 1. The stress-strain behavior shown in Figure 1a displays the maximum amount of tensile stress a material can withstand prior to deformation. Overall, tensile strength decreased with the incorporation of NS nanoparticles into the PP matrix. However, the PP-based nanocomposite containing 3% NS reinforcement shows maximum tensile strength at 42.6 MPa, followed by PP/1% NS and PP/2% NS at 41.8 MPa and 41.4 MPa, respectively. The sight improvement observed from PP/3%NS nanocomposites is slightly lower to that of the neat PP (42.6 MPa and 45.5 MPa). Importantly, a well-balanced tensile modulus is observed for all PP-NS nanocomposites compared to that of the neat PP (Figure 1b). Generally, the load transfer is dependent on the interaction behavior between the polymer and the filler and, according to Mirjalili [11], fillers promote phenomenal stiffness abilities; therefore, their ability to improve or maintain the modulus of materials depends on their degree of interaction with the polymer matrix. Also, the great interfacial bonding between the reinforcement agent and the polymer matrix can enable load transfer and resists composite failure, such as fracture. Due to this reason, an increased tensile strength may be expected. Clearly, in our case, the neat PP shows better tensile strength results as compared to reinforced PP nanocomposites. This behavior could be due to many factors such as the incompatibility characteristic between the polar and nonpolar nature of NS and the polymer, or the degree of filler dispersion into the polymer matrix [27]. Low load transfer capacity in the nanocomposite could lead to stress being concentrated at certain points; this is the case according to Wu et al. [20], who found that the surface properties and level of dispersion of the NS can produce a physical cross-linking effect, whereby stress accumulates in the physical cross-linking regions rather than in the polymer matrix regions. Also, such mechanical behavior suggests that the incorporation of NS particles caused the catalytic degradation of the PP-NS nanocomposites during melt processing at elevated temperature (See Section 2), and eventually this caused the decrease in tensile strength. Naseem et al. [24] reported a significant decrease in mechanical properties of MgFeAl(5)-LDH/PP nanocomposites due to the enhanced PP degradation resulting from Fe during melt processing.

The introduction of NS nanoparticles increased the elasticity of PP (Figure 1d). The elongation-at-break properties relied more on the presence of the reinforcement than on the matrix, meaning that the properties of the nanocomposite could significantly change with the addition of the nanomaterial to its structure. This concurs with the observed results (Table 2, Figure 1d), where the incorporation of NS particles into the PP matrix dramatically increased the elongation at break from 28.5% (neat PP) to 641% (PP-NS nanocomposites). Importantly, the reported elongation value of about 641% is the Instron 5966 instrumental limit. This means that the PP-NS nanocomposites material could still stretch even more if this was not the instrument limit.



Figure 1. Tensile properties of the neat PP and PP-NS nanocomposites: (**a**) stress versus strain curves, (**b**) variation in modulus, (**c**) variation in tensile strength, and (**d**) variation in elongation at break.

Material -	Tensile Modulus (MPa)		Tensile Strength (MPa)		Elongation at Break (%)	
	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.
Neat PP	1351.0	± 115.5	45.5	5 ± 0.6	28.5	6 ± 6.8
1% NS	1248.5	\pm 110.2	41.8	3 ± 1.5	641.0	0 ± 0.2
2% NS	1236.6 ± 43.8		41.4 ± 0.8		641.1 ± 0.1	
3% NS	1356.0	0 ± 89.9	42.6	5 ± 1.1	641.7	1 ± 0.3

Table 2. Tensile properties of neat PP and PP-NS nanocomposites.

Figure 2 presents the impact strength of the neat PP compared with the reinforced PP nanocomposites. The neat PP displays higher impact properties than the reinforced PP with the increase in %NS nanopowder in the polymer. The decrease in the impact strength upon adding NS is attributed to the inherent polar and non-polar characteristics of the reinforcing agents and polymer matrix. Fundamentally, this will result in a low tenacity to absorb mechanical energy under impact loading before fracturing. A similar trend in the incorporation of oil palm fiber-silica into the PP matrix was reported by Rozi et al. [5]. This behavior confirms the catalytic degradation of the PP-based nanocomposites, which was demonstrated by the tensile properties deterioration shown by the stress–strain results in Figure 1. However, according to Adediran et al. [28], the material's resistance characteristics are governed to some extent by the applied strain rate and structural change.



Figure 2. Impact strength of the neat PP and PP-NS nanocomposites.

3.2. Dynamic Mechanical Analysis (DMA) of the Neat PP and PP-NS Nanocomposites

Figure 3 shows the storage modulus and damping factor (tan delta) of the neat PP and reinforced PP as a function of temperature. The addition of the reinforcement agents tended to increase the stiffness properties of the neat PP. The increment is attributed to the enhanced adhesion. Strong interfacial adhesion has the potential to allow the filler-polymer stress transfer phenomenon, thereby improving the storage modulus properties [11]. Figure 3a shows the variation in storage modules with varying %NS (1–3%) in the PP. The addition of 1–3% NS results in a significant increase in the storage modulus of the neat PP matrix. The storage modulus in the PP-based nanocomposites was prominent by the addition of 3 wt.% NS. This enhancement is due to the reinforcing effect of the filler particles and stronger restrictions on the movement of molecules. This confirms the extent to which the PP nanocomposite material can withstand the amount of deformation or strain as observed in Figure 1a. Such improvements depend on the adhesion of the reinforcement agent with the polymer matrix. However, with the increase in temperature, the storage modulus is observed to decrease for the neat PP and reinforced PP nanocomposites. This is due to the increased molecular mobility of the polymer chains [29]. Interestingly, at any given temperature, it is observed that the storage modulus in 3% NS-reinforced PP is higher as compared to 1% NS and 2% NS additions.



Figure 3. Variation in (**a**) storage modulus and (**b**) tan delta of the neat PP and PP-NS nanocomposites with temperature.

Figure 3b shows the variation in the tan delta of the neat PP and PP-NS nanocomposites with temperature. It is observed that the incorporation of the NS particles led to a slight broadening of the tan delta peak, as well as the enhancement of the glass transition temperature for all the PP-NS nanocomposites as compared to that of the neat PP. This behavior can be attributed to the restriction by the NS particles on the mobility of PP molecular chains at the filer–polymer interface of the matrix [28]. Furthermore, the magnitude of the tan delta peak (peak intensity or height) is observed to slightly increase for the 3%NS-containing PP nanocomposite. The damping peak for the 2%NS-containing PP nanocomposite showed a decreased magnitude of tan delta when compared to that of the neat PP. Such behavior illustrates that the filler particles can only carry an extent of stress and allow a specific magnitude of it to strain the interface. Hence, the energy dissipation occurs in the PP matrix as well as at the interface. However, high energy dissipation generally occurs at the stronger interface while lower energy dissipation occurs at the moderate interface.

In addition, Figure 3b presents the viscous and elastic phase relationships of the neat PP in comparison with the reinforced nanocomposites, observed at different weight fractions of the nanoparticles under the same propagation temperature. However, the neat PP shows a higher tan delta due to the free movement of polymer chains at increasing temperatures, with 1% and 2% NS reinforcements behaving similarly at the same temperatures.

3.3. Thermal Stability of the Neat PP and PP-NS Nanocomposites

Figure 4a shows the TGA and derivative thermal graphs of the neat PP and the nanocomposites reinforced with 1%, 2%, and 3% NS filler. The degradation information of the materials with their respective thermal stability in terms of temperature at varied weight losses of 30 wt.%, 50 wt.%, and 70 wt.%, and maximum degradation temperature (T_{Max}) are presented in Table 3. From Figure 4a and Table 3, it can be found that the incorporation of 1% NS filler into the PP matrix can slightly improve the thermal degradation temperature at 30% weight loss (from 435 to 437 °C). This suggests that NS particles added in low content have the potential to act as a heat barrier in the early stages of degradation. However, above 30 wt.%, no thermal degradation change can be found between the PP-1%NS nanocomposite and the neat PP. An increased NS filler (2% and 3%) addition resulted in a reduction in the inherent thermal stability of the neat PP. The reduction is observed throughout the thermal degradation propagation, 30 wt.%, 50 wt.%, and 70 wt.%, which, according to Mirjalili [11], suggests the inhomogeneous dispersion of the filler. It is expected that the filler incorporation would significantly improve the thermal stability of the neat PP at any stage of temperature application. The thermal degradation or thermal stability improvement processes in polymer nanocomposites are generally due to the adsorption of volatile compounds endowed with nanoparticles on the polymer surface. However, the lack of thermal stability improvement in the reinforced PP-based nanocomposites presented herein suggests the catalytic degradation of the PP-based nanocomposites during melt processing. This behavior is governed by the possible peroxide radical reaction during PP-NS nanocomposite melt processing. Moreover, the reinforcement capability to improve the thermal stability was not possible, specifically at 50% and 70% weight loss, failing to work as a heat barrier in the neat PP [30].



Figure 4. (a) TGA thermal graphs and (b) derivative (DTGA) thermal graphs of the neat PP and PP-NS nanocomposites.

Material	T _{30 wt.%} (°C)	T _{50 wt.%} (°C)	T _{70 wt.%} (°C)	T _{Max} (°C)
Neat PP	435	449	458	458
1% NS	437	448	457	453
2% NS	416	434	447	450

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Table 3. TGA results.

3% NS

Figure 4b and Table 3 present the DTGA graphs and the corresponding data that reveal the maximum degradation temperatures in which the weight loss describes the maximum value. Out of all the materials, the neat PP exhibits a maximum temperature of about 458 °C, reflecting the better thermal stability of the PP-NS nanocomposite material. The maximum degradation temperature of all the PP-NS nanocomposites was lower than that of the neat PP.

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3.4. Water Absorption of the Neat PP and PP-NS Nanocomposites

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Figure 5 presents the water absorption of the neat PP and reinforced PP nanocomposites investigated on varying days. The observed trend is based on the materials' ability to absorb moisture. It can be seen that the moisture absorption changes with increasing days and filler content. The possible reason may be the level of dispersion, as a result of the filler loading that has minimized the tensile stress of nanocomposites against deformation (as observed in Figure 1a), and might have caused micro-voids in the material, which then provided channels for water absorption [31]. It could also possibly be the agglomeration of the nanoparticles residing within the matrix; thus, the tensile properties of the reinforced PP were also affected (as observed in Figure 1c). With the addition of reinforcement NS particles into the polymer structure, water uptake seems to be increasing among the reinforced nanocomposites compared to the neat PP. In addition, the water uptake seems to progress with imbibition time (from day 0 to 15). The filler structure's potential to minimize the weak mechanical properties in a polymer did not have much impact, except for allowing an improved interfacial bond development between the filler and the matrix. Therefore, NS filler reinforcement properties were not improved as expected, as the neat PP was shown to have better properties compared to the reinforced nanocomposites.



Figure 5. Water absorption of the neat PP and PP-NS nanocomposites.

3.5. Differential Scanning Calorimetry (DSC) of the Neat PP and PP-NS Nanocomposites

DSC was used to determine the crystallization behavior and melting temperature of the neat PP together with its NS-filled nanocomposites. Figure 6 and Table 4 display the parameters associated with the crystallization, melting temperature, and degree of crystallinity (X_c) of the neat PP and PP-based nanocomposites. The thermograms in Figure 6 show less impact or not much variation of the nanofiller towards the melting and crystallization temperature of the neat PP. Temperature plays a major role in the polymer response to heat and cooling, with crystals forming or crosslinks being created. As shown

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in Figure 6 and Table 4, the incorporation of NS particles slightly decreased the crystallization temperature of the neat PP, resulting in a well-balanced melting point. In brief, the crystallization temperature of the 1% NS, 2% NS, and 3% NS nanocomposites decreased by $1.77 \,^{\circ}$ C, $1.22 \,^{\circ}$ C, and $0.45 \,^{\circ}$ C, respectively, compared to that of the neat PP, while the melting temperature for both nanocomposites and neat PP was maintained at 166 $^{\circ}$ C. This can be attributed to the incorporation of non-surface-modified NS particles; hence, no nucleating abilities have been endowed for possible enhancements in crystallization temperature. This behavior confirms the deterioration of tensile strength and the catalytic degradation as the results of a possible peroxide radical reaction during melt processing. Furthermore, the degree of crystallinity decreased with the incorporation of 1%NS and 2%NS content into PP nanocomposites, suggesting well-dispersed NS particles at low content which then restrict the movement of PP chains. The surface modification provides nucleating abilities to NS



nanoparticles, but non-surface-treated NS nanoparticles have little or no influence on the PP-matrix crystallization process [8,32]. Also, it is important to notice the width of the DSC crystallization peak. Since narrow crystallization peaks illustrate the nucleating role of the filler, they facilitate the polymer crystallization [11]. Also, it is important to understand that the broadened melting peaks illustrate a poorer crystallization ability. The neat PP crystallinity shows better properties compared to the nanocomposites as a result of NS preventing the regular packing of the polymer molecules into a highly crystalline form.

Figure 6. DSC curves of the neat PP and PP-NS nanocomposites during (**a**) second heating and (**b**) cooling.

Table 4. The obtained data	from DSC cooling and second	d heating thermograms.
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Material	Mean T _c (°C)	Mean T _m (°C)	Average ΔH_m (J·g ⁻¹)	χ _c (%)
Neat PP	119.78	166.98	90.31	45.61
1% NS	118.01	166.27	87.99	44.44
2% NS	118.56	166.36	87.75	44.32
3% NS	119.33	166.58	100.80	50.91

4. Conclusions

The principal premises of the current research yield the following significant results:

- 1. The ductility (% elongation at break) was significantly improved with the addition of nano-silica, while the tensile strength, modulus, and impact toughness decreased with nano-silica addition as compared to the as-received PP HHR102.
- 2. The storage modulus was optimal when the wt.% of nano-silica was high (3%). The thermal stability was improved at a weight loss of 30%; however, it was unaffected at 50% and 70%, particularly for the PP nanocomposite containing 1 wt.% nano-silica.

- 3. The imbibition was optimal when the nanocomposite weight percentage was lowest. However, a significant increase in water uptake was observed for all samples with imbibition time. It is suggested that the micro-voids generated during ageing provide channels for water absorption, and it progresses with imbibition time.
- 4. The degree of crystallinity of the nanocomposites was slightly decreased as compared to the as-received polypropylene, because the nanoparticles inhibited the regular packing of polymer molecules, thus restricting the movement of PP chains.

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