International Journal of Science and Research (IJSR)
ISSN: 2319-7064
SJIF (2021): 7.86

# Comparative Analysis of the Thermal Behavior of Nylon-6 Composites Reinforced with Functionalized and Non-Functionalized Silica

**Savita Meena**

Department of Chemistry, M.S.J. Government P.G. College, Bharatpur 321001, Rajasthan, India
Corresponding author Email: *savita.iitd[at]gmail.com*
ORCID iD: https://orcid.org/0000-0003-1238-7946

**Abstract:** ***This work presents a systematic evaluation of surface-functionalized silica as reinforcing filler in Nylon-6 composites. Both non-functionalized and 3-aminopropyltrimethoxysilane (APTMS at loadings of 1-4 wt%) functionalized silica particles were incorporated into a Nylon-6 matrix through melt compounding. The comparative effects of both fillers on crystallization and thermal behaviour were analysed using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The incorporation of silica resulted in a slight enhancement in crystallization behavior, with the onset crystallization temperature (Tc, onset) exceeding 196 °C for both non-functionalized and APTMS-functionalized silica filled composites. These results indicate that both fillers function as effective nucleating agents, facilitating earlier crystallization of the polymer matrix. All Nylon-6/APTMS-functionalized silica composites show increased char yields, ranging from 1.52% to 2.48%. Nylon-6/APTMS-functionalized silica composite (NS4) shows the highest char yield (2.48%), suggesting a stronger protective effect at higher filler content. The present study demonstrates the potential of APTMS-functionalized silica for the development of high-performance Nylon-6 composites intended for advanced engineering applications.***

**Keywords:** Nylon-6, fumed silica, melt-compounding, TGA, DSC

## 1. Introduction

Polymer composites have garnered significant attention as advanced materials offering superior thermal, mechanical, and barrier properties compared to conventional polymers [1,2]. Among them, Nylon-6 (polycaprolactam) is a widely used engineering thermoplastic known for its strength, wear resistance, and chemical stability [3]. However, its relatively limited thermal stability and susceptibility to moisture absorption restrict its broader application in demanding environments. To address these limitations, the incorporation of nanoscale fillers, particularly silica, has been extensively explored as an effective reinforcement strategy.

Nylon-6/silica composites integrate the semicrystalline nature and mechanical robustness of Nylon-6 with the high surface area and reinforcing potential of silica particles [4]. The inclusion of silica has been shown to enhance stiffness, strength, and tribological performance, thereby extending the applicability of these materials in automotive, aerospace, and industrial sectors where lightweight and durable components are required [5]. Despite these advantages, non-functionalized hydrophilic silica exhibits poor compatibility and dispersion within the hydrophobic Nylon-6 matrix, compromise the expected property enhancements. To overcome these challenges, surface functionalization of silica has emerged as a key approach to improve interfacial adhesion and dispersion within polymer matrix [6].

Among various functionalization approaches, the use of organofunctional silanes, particularly 3-aminopropyltrimethoxysilane (APTMS), are highly effective coupling agents that react with hydroxyl groups on the silica surface through condensation reactions while simultaneously interacting with polymer chains. This dual functionality reduces surface energy, prevents particle agglomeration and strengthens filler-matrix interfacial interactions thereby improving composite performance [7]. Various processing techniques, including in situ polymerization [6], melt blending [8] and compression moldings [9] are commonly used to incorporate silica into Nylon-6 matrix. Composites containing APTMS-functionalized silica have demonstrated superior tensile strength, impact resistance, and flexibility, especially at optimized filler loadings. Dynamic mechanical analysis often reveals a lower glass transition temperature (Tg), attributed to the formation of a more flexible interfacial region between the filler and polymer matrix, that enhances chain mobility [10].

In this context, the development of surface-functionalized fillers is crucial for advancing next-generation polymer composites with enhanced processability, mechanical integrity and thermal stability [11]. Accordingly, present study systematically examines the influence of non-functionalized and APTMS-functionalized fumed silica on the crystallization behavior and thermal properties of Nylon-6/silica-based composites. This work provides a comparative analysis of their reinforcing efficiency and highlights their potential contribution to the development of high performance, durable and multifunctional materials in advanced engineering applications.

## 2. Experimental

### 2.1 Materials and their Properties

An injection-molding grade Nylon-6 (Gujlon M28 RC) with a melt flow index (MFI) of 28 g/10 min at 230 °C was procured from Gujarat State Fertilizers & Chemicals Limited (GSFC), Gujarat, India. Nylon-6 is a semicrystalline engineering thermoplastic widely recognized for its excellent mechanical strength, thermal resistance, chemical stability,

and high crystallinity, making it suitable for a broad range of industrial applications. Hydrophilic fumed silica (HDK N-20) was utilized as the nanoscale reinforcing filler. The material consisted of white, odorless particles with an average particle size in the range of 100-500 nm, high specific surface area, and high purity. The silica exhibited a pH range of 3-4.5 and was insoluble in water, with high melting and boiling temperatures of approximately 1700 °C and 2230 °C, respectively. APTMS-functionalized silica was synthesized according to the procedure reported in our previous publication [12].

### 2.2 Measurements and Characterization

Compounding of all composites was performed using a Thermo Fisher Scientific PRISM EUROLAB 16 co-rotating twin-screw extruder equipped with a 16 mm screw diameter and a length-to-diameter (L/D) ratio of 40:1.

Differential scanning calorimetry (DSC) was carried out on a TA instrument, DSC Q200 at a heating rate of 10 °C/min. under $N_2$ atmosphere using aluminium crucibles. The DSC measurement recorded glass transition temperature (Tg), crystallization temperature (Tc), melting temperature (Tm). Apparent enthalpies of fusion were calculated from the area of the endothermic peak. The weight percent crystallinity of Nylon 6 was calculated using following equation:

$$\% \text{ Crystallinity} = \frac{\Delta H_{f1}}{\Delta H_{f2} \times w} \times 100$$

Where $\Delta H_{f1}$ represents the measured heat of fusion of the sample, $\Delta H_{f2}$ corresponds to the heat of fusion of 100% crystalline Nylon-6 (182 $Jg^{-1}$) and w is weight fraction of Nylon-6 present in the composite [13].

Thermogravimetric analysis (TGA) was performed using a PerkinElmer Pyris 6 thermogravimetric analyzer. The measurements were conducted over a temperature range of 50-600 °C under a $N_2$ atmosphere at a constant heating rate of 20 °C/min. The thermal degradation behavior and stability of the prepared composites were assessed by determining characteristic degradation parameters, including the onset degradation temperature (Tonset), maximum degradation temperature (Tmax), and end decomposition temperature (Td). In TGA, the residual weight fraction of the sample is registered as a function of temperature or time under a controlled heating rate.

### 2.3 Composition of Nylon-6/silica and Nylon-6/APTMS-functionalized silica composites

A series of Nylon-6/silica composite formulations were prepared to investigate the effect of varying concentrations of non-functionalized and APTMS-functionalized silica on the thermal properties of the Nylon-6 matrix.

**Table 1:** Composition of Nylon-6 with silica and APTMS-functionalized Silica

| *S. No.* | Compositions | Nylon-6 (wt%) | Fumed silica (wt%) | APTMS (wt%) |
|---|---|---|---|---|
| 1 | NY | 100 | 00 | 00 |
| 2 | NS | 99.5 | 0.5% | 00 |
| 3 | NS1 | 99.5 | 0.5% | 1% |
| 4 | NS2 | 99.5 | 0.5% | 2% |
| 5 | NS4 | 99.5 | 0.5% | 4% |

### 2.4 Compounding of Nylon-6 with silica

Nylon-6 was used as the matrix material, while both non-functionalized and APTMS-functionalized silica were incorporated as reinforcing fillers at varying loadings ranging from 1 to 4 wt%. The composites were fabricated through melt compounding, wherein the twin-screw extrusion process enabled uniform dispersion of silica particles within the Nylon-6 matrix. Processing was performed within a temperature range of 220-260 °C under optimized extrusion conditions to ensure efficient mixing and homogeneous filler distribution. In addition, the effect of the silane coupling agent, APTMS was investigated by varying its concentration from 1 to 4 wt% relative to the silica content in order to enhance interfacial adhesion between the polymer matrix and filler particles. The extruded molten strands were subsequently quenched in a two meters long water bath and granulated at ambient temperature. The obtained granules were then dried in a vacuum oven at 80 °C to remove residual moisture prior to further characterization and processing.

## 3. Result and Discussion

### 3.1 Differential scanning calorimetry (DSC)

The prepared Nylon-6 and its silica-based composites were characterized using DSC analysis to evaluate their thermal transitions and crystallization behavior. The samples were first heated from 30 to 270 °C and maintained at 270 °C for 1 min in order to remove the residual thermal stresses from the samples developed during processing. The samples were subsequently cooled from 270 to 30 °C and then reheated from 30 to 260 °C, followed by uncontrolled cooling.

DSC analysis revealed that the melting temperature (Tm) remained nearly constant at approximately 223 °C for all compositions, indicating that the incorporation of silica had no significant effect on the crystalline phase of the Nylon-6 matrix. This observation suggests that the presence of fumed silica did not substantially disturb the crystalline packing or crystal perfection of the Nylon-6 chains [6,14]. However, composites containing APTMS-functionalized silica exhibited a slight decrease in the onset melting temperature with increasing concentration of the coupling agent. This behavior may be attributed to enhanced interfacial interactions between the functionalized silica surface and the Nylon-6 matrix arising from improved chemical compatibility introduced by the coupling agent [15].

The enthalpy of crystallization (ΔH) decreased from 62.11 $Jg^{-1}$ for neat Nylon-6 to values ranging between 55.69 and 58.86 $Jg^{-1}$ for the composites containing APTMS-functionalized silica. This reduction in crystallization enthalpy suggests a slight decrease in crystal perfection and crystalline content due to the incorporation of silica particles within the Nylon-6 matrix [13]. In contrast, the crystallization temperature (Tc) of Nylon-6/silica composites showed a noticeable increase compared to neat Nylon-6. The observed increase in Tc indicates that the silica particles, particularly APTMS-functionalized silica, acted as effective heterogeneous nucleating agents, thereby promoting crystallization during the cooling process [14]. The degree of

crystallinity exhibited a similar trend, with neat Nylon-6 showing a value of 32%. A marginal increase was observed for the Nylon-6/silica composite (32.9%), whereas the APTMS-functionalized silica composites displayed slightly lower crystallinity values ranging from 29.62% to 31.05%. This reduction suggests that surface functionalization of silica may restrict polymer chain mobility at the interface, thereby slightly hindering crystal formation within the Nylon-6 matrix. These results are summarized in **Table 2** and **Figure 1-2**.

Overall, the incorporation of silica fillers showed negligible influence on the melting behavior of Nylon-6 matrix. However, their effect on crystallization behavior was relatively limited. These findings indicate that although silica may act as a heterogeneous nucleating agent, it does not fundamentally alter the underlying crystallization mechanism of the polymer matrix [6].

**Table 2:** Thermal (DSC) properties of neat Nylon-6, Nylon-6/silica and Nylon-6/APTMS-functionalized silica composites

| Properties | Nylon-6 | Nylon-6/Silica composite | Nylon-6/APTMS-functionalized silica composite | | |
|---|---|---|---|---|---|
| | NY | NS | NS1 | NS2 | NS4 |
| Tm onset (°C) | 217.83 | 212.80 | 212.79 | 210.06 | 213.09 |
| Tm (°C) (Melting temp.) | 223.04 | 223.86 | 223.84 | 223.39 | 223.54 |
| ΔH (°C) (Enthalpy of crystallization) | 62.11 | 61.91 | 58.86 | 55.69 | 58.39 |
| Tc (°C) (Crystallization temp.) | 192.19 | 192.81 | 192.81 | 192.64 | 192.81 |
| Tc onset (°C) | 194.95 | 196.51 | 196.51 | 196.36 | 196.46 |
| % Crystallinity | 32.0 | 32.90 | 31.10 | 29.62 | 31.05 |

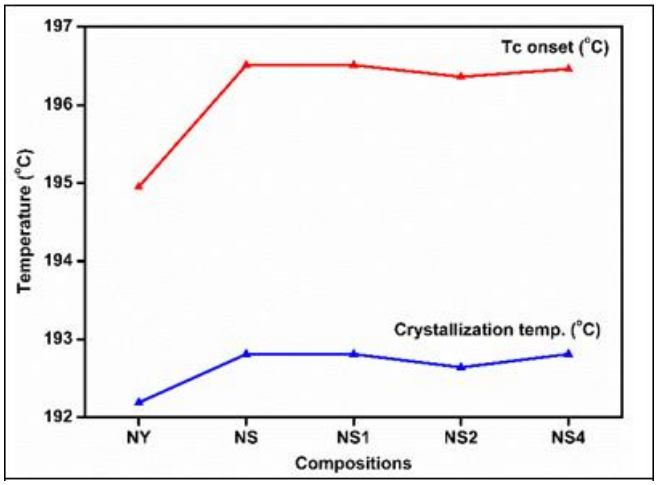


**Figure 1:** Crystallization temperature curves of neat Nylon-6, Nylon-6/silica and Nylon-6/APTMS-functionalized silica-based composites

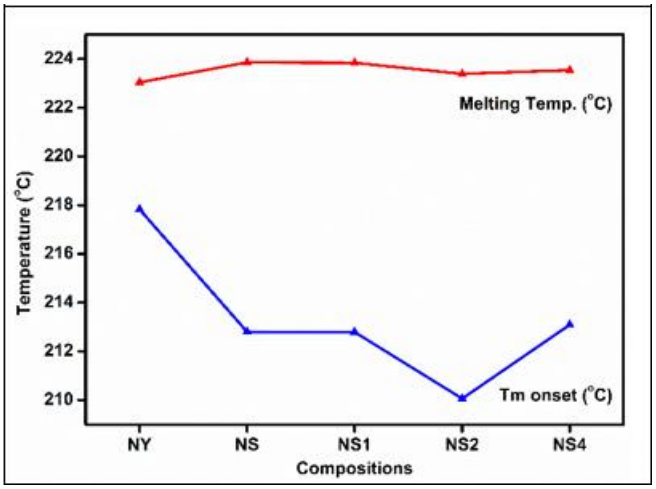


**Figure 2:** Melting temperature curves of neat Nylon-6, Nylon-6/silica and Nylon-6/APTMS-functionalized silica-based composites

### 3.2 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was carried out to evaluate the thermal degradation behavior of neat Nylon-6 and its silica-based composites, and their corresponding results are summarized in **Table 3** and **Figure 3**. Neat Nylon-6 exhibited an onset degradation temperature (Ti) of 439.89 °C, whereas the Nylon-6/silica composite (NS) and Nylon-6/APTMS-functionalized silica composites (NS1-NS4) showed slightly lower Ti values in the range of 429.81-432.42 °C. Similarly, the end decomposition temperature (Td) decreased from 481.09 °C for neat Nylon-6 to approximately 472-474 °C for the silica-filled composites. The temperature corresponding to the maximum degradation rate, represented by the inflection point temperature, also shifted from 466.71 °C for neat Nylon-6 to 457.91-460.72 °C for the composites.

Among all the investigated samples, the Nylon-6 composite containing silica functionalized with 4 wt% APTMS exhibited the lowest thermal stability, with an onset degradation temperature of 430.29 °C and end decomposition temperature of 472.52 °C. The Nylon-6/APTMS-functionalized silica composites exhibited lower thermal degradation temperatures compared to neat Nylon-6, indicating a decrease in thermal stability after surface modification of the filler [14]. Furthermore, the reduction in thermal stability became more pronounced with increasing coupling agent concentration in the silica. Composites containing higher amounts of APTMS-functionalized silica, particularly the NS4 formulation, degraded at comparatively lower temperatures. The observed reduction in thermal stability can be attributed to the incorporation of surface-functionalized silica and silane functional groups, which may alter the degradation behavior of the Nylon-6 matrix through changes in interfacial interactions and polymer chain mobility [4].

**Table 3:** Thermal (TGA) properties of neat Nylon-6, Nylon-6/silica and Nylon-6/APTMS-functionalized silica composites

| Properties | Nylon-6 | Nylon-6/Silica composite | Nylon-6/APTMS-functionalized silica composite | | |
|---|---|---|---|---|---|
| | NY | NS | NS1 | NS2 | NS4 |
| Ti onset (°C) | 439.89 | 432.42 | 429.81 | 432.26 | 430.29 |
| Td (°C) End temp. | 481.09 | 473.00 | 473.24 | 474.64 | 472.52 |
| Inflection point (°C) | 466.71 | 457.91 | 458.87 | 460.72 | 457.97 |
| Char yield (%) | 1.32 | 1.36 | 1.53 | 1.52 | 2.48 |

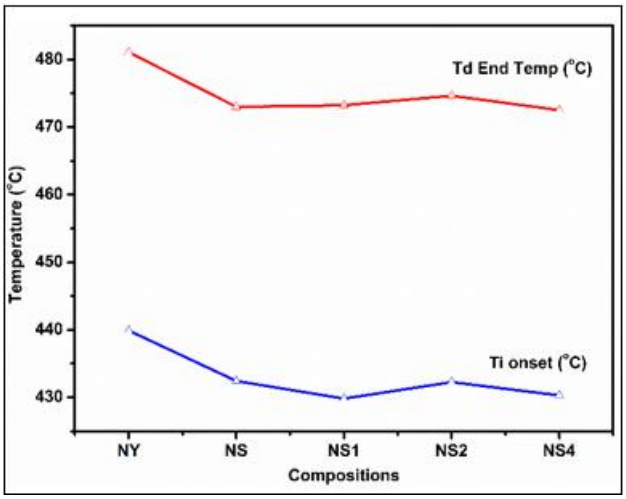


**Figure 3:** Degradation temperature curves of neat Nylon-6, Nylon-6/silica and Nylon-6/APTMS-functionalized silica-based composites

This behavior is also likely associated with the presence of organic groups introduced by the silane coupling agent, which possess lower thermal resistance and decompose earlier during thermal degradation [16]. The char yield of the composites was observed to be slightly higher than that of neat Nylon-6. Neat Nylon-6 exhibited a char yield of 1.32%, whereas the Nylon-6/silica composite showed a marginal increase to 1.36%. In the case of the APTMS-functionalized silica composites (NS1-NS4), the char yield further increased, ranging from 1.52% to 2.48%. The increase in char yield with APTMS-functionalized silica indicates enhanced thermal residue formation, suggesting improved thermal stability and potential flame-retardant properties due to the filler-matrix interactions [17].

## 4. Conclusion

In this study, Nylon-6/silica composites were successfully fabricated via melt blending using both non-functionalized and APTMS-functionalized silica. The fumed silica was effectively surface-functionalized with APTMS, which acted as a coupling agent to improve compatibility and interfacial adhesion with the Nylon-6 matrix. TGA experiments revealed that the composites exhibited a slightly earlier degradation onset compared to neat Nylon-6. The incorporation of APTMS-functionalized silica resulted in a reduction in the onset decomposition temperature, while simultaneously promoting increased char residue formation, with values ranging from 1.52% to 2.48%. Among all formulations, the NS4 composite showed the highest char yield, indicating enhanced thermal stability at elevated temperatures and improved thermal protection due to stronger filler-matrix interactions. DSC results showed that both functionalized and non-functionalized silica had a negligible influence on the melting temperature and overall crystallization behavior of Nylon-6, although a slight nucleating effect was observed in the presence of silica. APTMS-functionalized silica led to a marginal decrease in crystallinity; however, the overall thermal characteristics of the polymer matrix remained largely unaffected. This suggests improved polymer-filler interactions without compromising the inherent thermal stability of Nylon-6.

Collectively, these findings demonstrate that surface-functionalized silica effectively enhances interfacial bonding within the composite system while maintaining desirable thermal performance. Such improvements may contribute to enhanced flame-retardant behavior and thermal protection in Nylon-6-based composite materials.

**Acknowledgements**

The author gratefully acknowledges Indian Institute of Technology Delhi, India for providing financial and technical support throughout the M.Tech. program. The successful completion of this research work would not have been possible without the resources, facilities, and academic environment provided by the institute.

The author also wishes to express sincere thanks and deep appreciation to Prof. Josemon Jacob, Department of Materials Science and Engineering (DMSE), IIT Delhi, India for his invaluable guidance, insightful suggestions, and continuous support during the course of this research. His mentorship and motivation played a significant role in the successful completion of this work.

## References

[1] S.K.S. Hossain, M.E. Hoque, 9 - Polymer nanocomposite materials in energy storage: Properties and applications, in: M. Jawaid, M.M. Khan (Eds.), Polymer-based Nanocomposites for Energy and Environmental Applications, Woodhead Publishing, pp. 239-282, 2018.

[2] R.K. Bharadwaj, "Modeling the Barrier Properties of Polymer-Layered Silicate Nanocomposites," Macromolecules, 34, 9189-9192, 2001.

[3] M.M. Hasan, Y. Zhou, H. Mahfuz, S. Jeelani, "Effect of $SiO_2$ nanoparticle on thermal and tensile behavior of nylon-6," Materials Science and Engineering: A, 429, 181-188, 2006.

[4] H. Mahfuz, M. Hasan, V. Dhanak, G. Beamson, J. Stewart, V. Rangari, X. Wei, V. Khabashesku, S. Jeelani, "Reinforcement of nylon 6 with functionalized silica nanoparticles for enhanced tensile strength and modulus," Nanotechnology, 19, 445702, 2008.

[5] M. García, G. van Vliet, M.G.J. ten Cate, F. Chávez, B. Norder, B. Kooi, W.E. van Zyl, H. Verweij, D.H.A.

Blank, "Large-scale extrusion processing and characterization of hybrid nylon-6/$SiO_2$ nanocomposites," Polymors for Advanced Technologies, 15, 164-172, 2004.
[6] L. Zhang, Y. Xiong, E. Ou, Z. Chen, Y. Xiong, W. Xu, "Preparation and properties of nylon 6/carboxylic silica nanocomposites via *in situ* polymerization," Journal of Applied Polymer Science, 122, 1316-1324, 2011.
[7] D.V. Okhrimenko, A. Budi, M. Ceccato, M. Cárdenas, D.B. Johansson, D. Lybye, K. Bechgaard, M.P. Andersson, S.L.S. Stipp, "Hydrolytic Stability of 3-Aminopropylsilane Coupling Agent on Silica and Silicate Surfaces at Elevated Temperatures," ACS Applied Materials & Interfaces 9, 8344-8353, 2017.
[8] J.W. Cho, D.R. Paul, "Nylon 6 nanocomposites by melt compounding," Polymer, 42, 1083-1094, 2001.
[9] M. García, M. De Rooij, L. Winnubst, W.E. van Zyl, H. Verweij, "Friction and wear studies on nylon-6/$SiO_2$ nanocomposites," Journal of Applied Polymer Science, 92, 1855-1862, 2004.
[10] J. Parameswaranpillai, N. Hameed, T. Kurian, Y. Yu, Nanocomposite Materials: Synthesis, Properties and Applications, CRC Press, Boca Raton, 2016.
[11] S. Krishnaswamy, L. Tinsley, V. Marchante, S. Addepalli, Z. Huang, H. Abhyankar, "Effect of extrusion and compression moulding on the thermal properties of nylon-6/silica aerogel composites," Journal of Thermoplastic Composite Materials, 31, 992-1009, 2018.
[12] S. Meena, "Enhancing Surface Properties of Fumed Silica via APTMS Functionalization: A Comprehensive Characterization Study," International Journal of Science and Research (IJSR), 11, 1416-1421, 2022.
[13] B. Wunderlich, Thermal Analysis of Polymeric Materials, Springer Berlin, Heidelberg, 2005.
[14] M. García, J. García-Turiel, B. Norder, F. Chavez, B.J. Kooi, W.E. van Zyl, H. Verweij, D.H.A. Blank, "Polyamide-6/Silica Nanocomposites," Advance Engineering Materials, 6, 724-729, 2004.
[15] D. Li, Q. Liu, L. Yu, X. Li, Z. Zhang, "Correlation between interfacial interactions and mechanical properties of PA-6 doped with surface-capped nano-silica," Applied Surface Science, 255, 7871-7877, 2009.
[16] B.D. Queiroz, V.L.P. Janzantti, J.D. Ambrósio, "Effects of 3-APTMS-Modified Nano-SiO2 on the Mechanical Properties and Crystallization Behavior of Polyamide-6," Materials Science Forum, 869, 314-319, 2016.
[17] N.K. Yan, Thermal degradation properties of nylon-6/ clay nanocomposites (Doctoral dissartation), 2007.