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Rheological, Morphological, and Crystallization Behavior of Nylon-6 Nanocomposites Reinforced with Modified and Unmodified Silica

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Abstract: ***Nanoscale silica and 3-aminopropyltrimethoxysilane (APTMS)-modified silica were incorporated into the Nylon-6 matrix through melt compounding to evaluate their influence on morphology, crystallization behavior, and rheological properties. Wide-angle X-ray diffraction (WAXD) analysis revealed that Nylon-6/APTMS-modified silica composites (NS1 1 wt% and NS4 4 wt% APTMS-treated silica) retained the α-phase peaks of Nylon-6 with reduced intensity and peak broadening after silica incorporation, indicating disrupted chain packing and reduced crystallinity from 45% (Nylon-6) to 38% (NS1) and 32% (NS4) due to restricted polymer chain mobility. Transmission electron microscopy (TEM) confirmed partial agglomeration of silica particles within the Nylon-6 matrix. Rheological studies showed an increase in equilibrium torque during melt processing, indicating stronger interfacial interactions in composites containing APTMS-modified silica compared to those with unmodified silica. modified composites, NS4 (4 wt% APTMS-modified silica) exhibited the lowest shear viscosity across the studied shear rate range, showing lower viscosity than pure Nylon-6 at both 100 s^{-1} (65 Pa·s vs. 72 Pa·s) and 1800 s^{-1} (47 Pa·s vs. 50 Pa·s). The results demonstrate that APTMS surface modification significantly enhances the structural and functional properties of Nylon-6/silica composites.***

Keywords: Nylon-6, Nanocomposites, Rheological behavior, TEM, WAXD

1. Introduction

Nylon-6/silica nanocomposites have attracted considerable attention for high-performance engineering applications, particularly in the automotive and aerospace industries, due to their enhanced mechanical, thermal, and tribological properties compared to pure Nylon-6 [1-4]. The incorporation of nanoscale silica particles into the Nylon-6 matrix produces hybrid materials with improved stiffness, strength, thermal stability, and wear resistance [5-7]. These nanocomposites are commonly fabricated through techniques such as in situ polymerization, melt blending, and compression molding, where silica nanoparticles are dispersed either during polymerization or within the polymer melt [8-11].

Among various reinforcing fillers, fumed silica has proven particularly effective in tailoring the rheological behavior of polymer systems because of its high surface area and ability to interact strongly with polymer chains [12]. Uniformly dispersed silica nanoparticles can significantly enhance the structural integrity and performance of Nylon-6 composites by promoting strong interfacial interactions within the polymer matrix [13]. However, the hydrophilic nature of fumed silica often results in poor dispersion, particle agglomeration, and weak interfacial compatibility with the relatively hydrophobic Nylon-6 matrix, thereby limiting the overall improvement in composite properties [14].

To overcome these challenges, surface modification of silica nanoparticles has emerged as an important strategy for improving filler–matrix compatibility [15]. Surface-modification of silica not only enhances nanoparticle dispersion and reduces agglomeration but also introduces reactive functional groups capable of forming stronger interfacial interactions with the polymer matrix [16]. In particular, 3-aminopropyltrimethoxysilane (APTMS) has been widely employed as a silane coupling agent due to its effectiveness in improving the interfacial adhesion between silica and Nylon-6 [17]. Previous studies have demonstrated that APTMS-modified silica can significantly improve tensile strength, impact resistance, and elongation at break, especially at moderate filler concentrations [18]. Furthermore, dynamic mechanical studies have reported a reduction in glass transition temperature (Tg), which is attributed to the formation of a flexible interfacial region that facilitates polymer chain mobility [19].

The development of surface-modified fillers is therefore essential for advancing the design of high-performance polymer nanocomposites with improved processability, thermal stability, and mechanical properties [20]. Although numerous studies have investigated the individual effects of modified and unmodified silica nanoparticles, direct comparative analyses of their influence on the morphological, crystallization, and rheological behavior of Nylon-6 matrices remain limited [21].

In this study, Nylon-6/silica nanocomposites containing both unmodified silica and APTMS-modified silica were prepared through melt compounding to systematically evaluate their effects on composite morphology, crystallinity, and rheological properties. The work aims to provide a comprehensive understanding of how silica surface modification influences filler dispersion, interfacial interactions, and the overall performance of Nylon-6 nanocomposites. The findings are expected to contribute to the development of next-generation Nylon-6-based materials with enhanced structural and functional characteristics for advanced engineering applications.

2. Experimental

2.1 Materials and reagents

All reagents and solvents utilized in this study were purified and dried according to standard laboratory procedures [22]. Injection molding grade Nylon-6 (Gujlon M28 RC, MFI 28 g/10 min at 230 °C) was procured from Gujarat State Fertilizers and Chemical Ltd., Gujarat, India. Hydrophilic fumed silica (HDK N-20) with particle size ranging from 100–500 nm was used as the filler material. 3-Aminopropyltrimethoxysilane (APTMS) has a molecular weight of 179.29 g/mol and a density of 1.027 g/mL was obtained from Sigma-Aldrich, Germany, and used as a silane coupling agent.

2.2 Compounding of Nylon-6 with silica and APTMS-modified silica

Nylon-6/silica nanocomposites with varying concentrations of fumed silica and APTMS-modified silica were prepared to investigate their morphology, rheological properties, and crystallization behavior (**Table 1**). The composites were fabricated by melt blending of Nylon-6 with 0.5 wt% silica and APTMS loadings of 1 wt% and 4 wt% using a Thermo Fisher PRISM EUROLAB 16 twin-screw extruder (16 mm diameter, 40:1 L/D ratio) at 220–260 °C. The extruded strands were subsequently water-quenched, pelletized, and vacuum dried at 80 °C prior to characterization. The detailed preparation procedure for these composites has been reported in my previously published work [23,24].

Table 1: Nylon-6/silica and Nylon-6/APTMS-modified Silica composites

Materials	Compositions			
	NY	NS	NS1	NS4
Nylon-6 (wt%)	100	99.5	99.5	99.5
Fumed silica (wt%)	00	0.5	0.5	0.5
APTMS (wt%)	00	00	1	2

2.3 Characterization of Nylon-6 nanocomposites

Rheological properties of Nylon-6/silica nanocomposites were measured by Rosand advanced capillary rheometer Model RH7. Capillary rheometer is a technique, where Nylon-6, Nylon-6/Silica and Nylon-6/APTMS-Modified silica nanocomposites were dried at 80 ºC for overnight under vacuum, then extruded through a die of specified dimension and the pressure drop across the die recorded. Processing temperature of instrument was 260 °C and shear rate range was set 100 to 2000 s^{-1}.

Transmission electron microscopy (TEM) studies were performed on an instrument, JEOL-2100 (Japan), attached with LaB6 filament operating at an accelerating voltage of 200 kV. Sepiolite was dispersed in ethanol by ultrasonication, and a drop was infused on a 200-mesh copper net for the TEM study. The nanocomposite samples were prepared using Leica Ultracut UCT microtome. Ultrathin sections of injection molded bars were cryogenically cut in the flow direction by a glass knife of 45° cutting edge.

Wide-angle X-ray diffraction (WAXD) measurements of compounded Nylon-6, silica and Nylon-6/APTM-modified silica nanocomposites were performed on PANalytical X'Pert PRO X-ray diffractometer of using Ni filtered Cu Kα (1.54 Å wavelength) radiation. Diffractogram of all samples were recorded at identical setting of the instrument and at the top of the samples. Radial scans of intensity (I) vs. diffraction angle were recorded in the range 10° to 35° of 2θ at the rate of 3° per minute.

3. Result and Discussion

3.1 Rheological behavior

The rheological behavior of Nylon-6 and its silica-filled nanocomposites was evaluated by measuring the shear viscosity as a function of shear rate, and the results are presented in **Table 2** and **Figure 1**. All samples exhibited a decrease in shear viscosity with increasing shear rate, indicating typical shear-thinning (pseudoplastic) behavior of polymeric systems [25,26]. This behavior is attributed to the progressive orientation and disentanglement of polymer chains under applied shear.

The incorporation of unmodified silica into the Nylon-6 matrix (NS) resulted in a significant increase in shear viscosity over the entire shear rate range compared to pure Nylon-6. At a shear rate of 100 s^{-1}, the viscosity increased from 72 Pa·s for pure Nylon-6 to 99 Pa·s for the NS nanocomposite. Similarly, at 1800 s^{-1}, the viscosity of the NS nanocomposite remained higher (71 Pa·s) than that of pure Nylon-6 (50 Pa·s). The increased viscosity can be attributed to the strong hydrogen bonding interactions between the hydroxyl (-OH) groups present on the silica surface and the amide groups of Nylon-6 [1,2]. These interactions restrict the mobility of polymer chains and reduce the free volume within the matrix, thereby increasing resistance to flow. Consequently, the presence of unmodified silica adversely affects melt flow behavior and processability [27].

In contrast, nanocomposites containing APTMS-modified silica (NS1 and NS4) exhibited comparatively lower viscosities than the unmodified silica nanocomposite. Surface modification of silica with APTMS replaces a significant portion of the surface hydroxyl groups with organosilane moieties, thereby reducing strong filler–polymer hydrogen bonding interactions. The organic propyl chains of APTMS improve compatibility between the silica particles and the Nylon-6 matrix, leading to improved filler dispersion and reduced particle agglomeration [15]. Among the APTMS-modified nanocomposites, the NS4 sample containing silica treated with 4 wt% APTMS showed the lowest shear viscosity throughout the studied shear rate range. At 100 s^{-1}, the viscosity of NS4 was 65 Pa·s, which was even lower than that of pure Nylon-6 (72 Pa·s). A similar trend was observed at higher shear rates, where NS4 exhibited a viscosity of 47 Pa·s at 1800 s^{-1} compared to 50 Pa·s for pure Nylon-6. The pronounced reduction in viscosity indicates that higher APTMS loading effectively weakens interfacial hydrogen bonding and facilitates easier chain movement under shear [3]. Furthermore, the improved dispersion of modified silica particles may contribute to

reduced filler–filler interactions and enhanced network disentanglement during flow.

Overall, the rheological results demonstrate that surface modification of silica using APTMS significantly influences the melt flow behavior of Nylon-6 nanocomposites. While unmodified silica increases viscosity and limits processability due to strong interfacial interactions, APTMS-modified silica, particularly at higher loading (4 wt%), improves filler–matrix compatibility and reduces shear viscosity, thereby enhancing the processing characteristics of the composites.

Table 2: Shear rate vs. shear viscosity of Nylon-6 and its nanocomposites

Shear Rate (s^{-1})	Shear viscosity (Pa·s)			
	Nylon	NS	NS1	NS4
100	72	99	92	65
500	70	94	65	63
600	66	89	62	58
900	64	85	58	56
1200	61	81	55	52
1500	55	76	51	49
1800	50	71	49	47

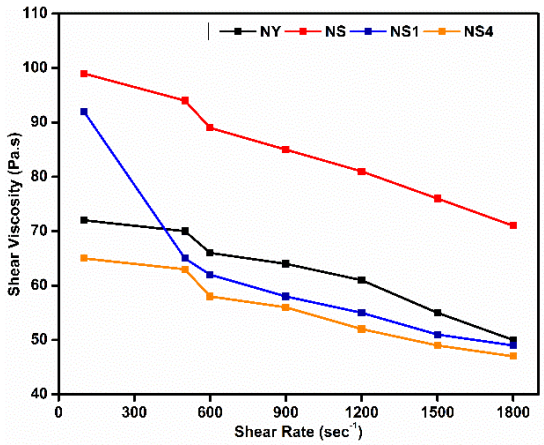

Figure 1: Change of viscosity with shear rate for Nylon-6, Nylon-6/silica and Nylon-6/APTMS-modified silica nanocomposites

3.2 Transmission electron microscopy (TEM)

The transmission electron microscopy (TEM) image was used to investigate the dispersion state and morphology of silica nanoparticles within the Nylon-6 matrix. TEM is considered one of the most effective techniques for analyzing the distribution and dispersion behavior of nanoscale fillers in polymer nanocomposites [2]. The silica particles are initially present in the nanometer size range; however, surface modification with the silane coupling agent (APTMS) increases the particle size due to the chemical bonding of silane molecules onto the silica surface [15]. The modified silica particles are observed in the form of small agglomerates with particle sizes in the range of approximately 400–550 nm.

Figure 2 presents the TEM micrograph of the Nylon-6/APTMS-modified silica (NS4) nanocomposite. The darker contrast regions observed in the image correspond to silica-rich domains, while the lighter background represents the Nylon-6 matrix. The micrograph reveals a predominantly uniform dispersion of silica particles with only minor agglomeration, indicating improved interfacial interaction and compatibility between the modified silica and the polymer matrix as a result of APTMS surface treatment. The enhanced dispersion behavior suggests that the silane modification effectively reduced particle–particle interactions and promoted stronger filler–matrix adhesion [28]. The organosilane layer surrounding the silica surface helps prevent severe agglomeration and promotes better filler distribution throughout the matrix.

Furthermore, the nanoscale dispersion observed in the TEM image supports the rheological behavior of the nanocomposites. Improved dispersion and reduced filler agglomeration facilitate better stress transfer and reduce excessive filler network formation, thereby contributing to lower shear viscosity and enhanced processability [3]. The presence of finely dispersed silica domains may also improve the mechanical and thermal properties of the nanocomposites by increasing the effective interfacial area between the filler and polymer matrix [1].

Overall, the TEM analysis confirms that silica nanoparticles were successfully incorporated into the Nylon-6 matrix with relatively good dispersion. Surface modification using APTMS appears to enhance filler distribution and minimize particle agglomeration, which is beneficial for improving the overall performance of Nylon-6/APTMS-modified silica nanocomposite.

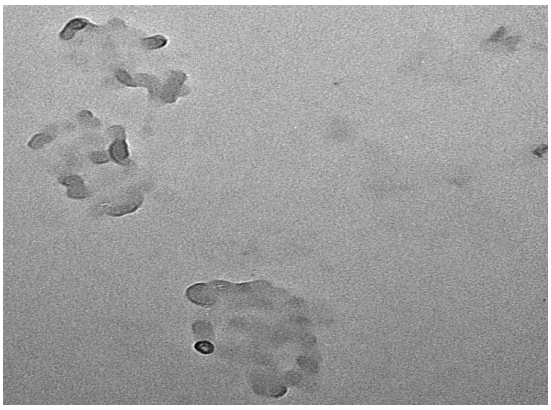

Figure 2: TEM micrograph of Nylon-6/APTMS-modified silica (NS4) composite

3.3 Wide-angle X-ray diffraction (WAXD)

The WAXD patterns of pure Nylon-6, silica, and Nylon-6/APTMS-modified silica nanocomposites (NS1 and NS4) are shown in **Figure 3**. Pure Nylon-6 exhibited characteristic diffraction peaks at $2\theta \approx 21°$ and 24°, corresponding to the α-crystalline phase, confirming its semi-crystalline nature with an estimated crystallinity of approximately 45% [29,30]. In contrast, silica showed a broad diffraction hump around $2\theta = 22–24°$ without any sharp peaks, indicating its predominantly amorphous structure [31].

The diffraction patterns of NS1 and NS4 retained the characteristic α-phase peaks of Nylon-6; however, a slight reduction in peak intensity and peak broadening were observed after silica incorporation. These changes suggest partial disruption of polymer chain packing due to interactions between silica particles and the Nylon-6 matrix. The degree of crystallinity decreased from 45% for pure Nylon-6 to approximately 38% for NS1 and 32% for NS4, indicating that increasing silica content restricts crystal growth and polymer chain mobility [2,32].

No additional diffraction peaks were detected in the composites, suggesting that silica was uniformly dispersed within the Nylon-6 matrix without forming any new crystalline phases. The amorphous nature of silica and the reduction in crystallinity indicate that silica mainly interacts with the amorphous regions of Nylon-6 through interfacial interactions such as hydrogen bonding between silanol groups and amide groups [6,32].

The incorporation of silica nanoparticles influenced the crystallization behavior of Nylon-6 in two opposing ways. On one hand, silica acted as a nucleating agent, promoting crystallization and slightly enhancing peak sharpness in some composite samples. On the other hand, strong interfacial interactions between silica and Nylon-6 restricted polymer chain mobility, thereby hindering crystal growth [3,6]. These competing effects resulted in only moderate changes in the overall crystallinity of the nanocomposites. The reduced crystallinity may decrease ductility, while the reinforcing effect of silica can improve stiffness, dimensional stability, and thermal resistance [3]. Overall, the WAXD results confirm successful incorporation of silica into the Nylon-6 matrix and demonstrate the dual role of silica as both a nucleating and chain-restricting agent in the nanocomposite system.

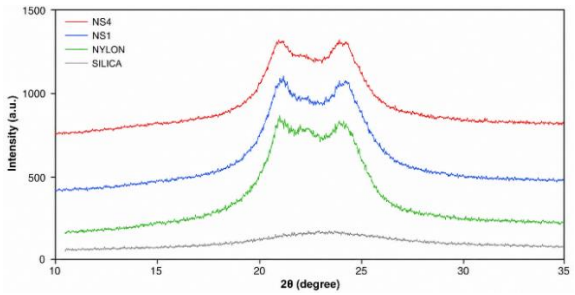

Figure 3: WAXD patterns of pure Nylon-6, silica, and Nylon-6/APTMS-modified silica composites

4. Conclusion

In present work, Nylon-6/silica nanocomposites containing unmodified and APTMS-modified silica were successfully prepared through the melt blending technique. The WAXD analysis confirmed surface modification with APTMS enhanced interfacial compatibility between silica and the Nylon-6 matrix, leading to better structural organization within the nanocomposites. TEM analysis revealed APTMS-modified silica exhibited improved dispersion and reduced particle agglomeration compared to unmodified silica. The formation of an organosilane interfacial layer on the silica surface contributed to better compatibility and more uniform filler distribution within the polymer matrix. Rheological studies demonstrated that the nanocomposites containing APTMS-modified silica showed lower viscosity and improved flow behavior, particularly at higher APTMS loading (4 wt%).

In conclusion, the combined results of WAXD, TEM, and rheological studies show the surface modification of silica using APTMS significantly enhances the structural, morphological, and rheological properties of Nylon-6/silica nanocomposites. The improved dispersion and interfacial interaction achieved through silane modification highlight the potential of APTMS-modified silica-filled Nylon-6 nanocomposites for progressive engineering and high-performance polymer applications.

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