

# Effect of Cenosphere Concentration on the Mechanical, Thermal, Rheological and Morphological Properties of Nylon 6

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## ABSTRACT

Cenospheres are widely used as filler in thermoset plastics and concrete mainly for density reduction of the material. But there is no work noted of using cenosphere as filler in thermoplastics. In this paper cenosphere concentration was varied from 0 to 10 phr of nylon 6 and the effect of the same on the mechanical, thermal, rheological and morphological properties of the composite were studied. Elongation was found to have increased by 83% and impact strength by 44% at 2.5 phr loading of cenosphere. Flexural strength increased upto 25% at 10 phr content of cenosphere.

**Keywords:** Nylon 6; Cenosphere; Crystallinity; Reinforcing Agent

## 1. Introduction

In the previous studies use of cenosphere is noted to decrease the density of the material, due to its microspherical nature. Cenosphere is a hydrophilic material and found in fly ash [1]. So, for its use as filler in polymers like PP, HDPE, PS, it is surface treated to induce hydrophobicity giving better compatibility with the matrix.

Abdullah *et al.* utilized amine containing silicone as toughening agent and hollow cenosphere as filler in epoxy resin. Their study was to understand the microstructure formed and its influence on mechanical properties and free volume measurements of the composite. Tensile strength increased and tensile modulus decreased with increase in cenosphere content up to 30%, due to low density of the filler [2]. Gu *et al.* studied epoxy filled with cenosphere surface treated with different chemicals. Surface modified cenosphere were observed to have distributed uniformly into the epoxy matrix. Surface modified cenosphere had a wider glass transition temperature region and a higher loss factor, and had relatively higher impact toughness [3]. Deepthi *et al.* studied the mechanical and thermal properties of high density polyethylene filled with cenosphere. They used cenosphere as filler after silane treatment, and also with a compatibilizer [4]. Cardoso *et al.* studied the effect of particle size and surface treatment of cenosphere as filler on the properties of polyester resin [5]. Huo *et al.* studied the preparation of poly-o-phenylenediamine (POPD)/

TiO<sub>2</sub>/fly ash cenosphere composite and its photo-degradation properties [6]. Chalivendra *et al.* studied the processing and mechanical characterization of lightweight polyurethane composites using cenosphere. Polyurethane was loaded with cenosphere upto 40% and was tested for mechanical properties to estimate the fracture toughness of the material. Cenosphere decreased the density of the composite. The high strain rate constitutive behavior of 100% polyurethane showed monotonic stiffening whereas the composite at higher cenosphere volume fractions (40%) exhibited a stiffening-softening-stiffening behavior, due to easy flowability induced by cenosphere microspheres [7].

In this paper, cenosphere was used as reinforcing agent in nylon 6 matrix. Cenosphere and nylon 6 both are hydrophilic materials, so they possessed good compatibility requiring no use of compatibilizer or surface treatment of cenosphere. Cenosphere obtained was used as such and loaded as 2.5 phr, 5 phr, 7.5 phr and 10 phr in the nylon matrix, and tested for mechanical, thermal, rheological and morphological properties. As cenosphere was used in very low concentration to affect the density of the matrix material, density measurement was not done.

## 2. Experimental

### 2.1. Materials

Nylon 6 for was obtained from Next Polymers Ltd., Mumbai, India. Cenosphere was procured from Nasik thermal power plant (India) having chemical composition as shown in the **Table 1**. Cenosphere was used as ob-

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tained without any purification or chemical modification or surface treatment. Finalux G3 (wetting agent) was obtained from Fine Organics Ltd., Mumbai, India.

## 2.2. Preparation of Composite

Concentration of cenosphere was varied upto 10 phr into the nylon matrix. Firstly, dry blending of cenosphere and nylon 6 was done in tumbler mixer for 15 - 20 min, using finalux G3 as the wetting agent. Then the mix was melt blended in a twin screw co-rotating extruder (Lab Tech Engineering Co. Ltd., Germany) having L/D ratio of 32:1 and temperature profile from the hopper to the die as 170°C, 190°C, 200°C, 210°C, 220°C, 230°C, 240°C and 250°C. Extruded strands were water cooled at 30°C and pelettized. Pellets obtained were used for injection molding after pre-drying at 80°C for 8 - 10 hrs. Injection molding (Boolani machineries India ltd, Mumbai, India) was done maintaining temperature profile as 210°C, 230°C and 250°C from the hopper to the ejection nozzle. Standard ASTM based samples for tensile, flexural and impact testing were obtained from injection molding. Samples for impact testing were notch cut before testing.

## 2.3. Characterization and Testing

### 2.3.1. Mechanical Properties

Tensile properties; tensile strength and elongation at break and flexural properties; flexural strength and flexural modulus, were measured at ambient condition using a universal testing machine (LR-50K, Lloyds Instrument, UK), according to ASTM procedures D638 and D790; at a crosshead speed of 50 mm/min and 2.8 mm/min respectively. The notch for impact test was made using a motorized notch-cutting machine (Polytest model 1, Ray Ran, UK). Notched Izod impact strength was determined at ambient condition according to ASTM D256 standard, using impact tester (Avery Denison, UK) having striking velocity of 3.46 m/s employing a 2.7 J striker.

### 2.3.2. Thermal Properties

Differential scanning calorimetry (Q 100 DSC, TA in-

struments Ltd., India) characterization was done to investigate the crystallization and melting behaviour of the composite. Two consecutive heating scans were found to minimize the influence of possible residual stresses in the material due to any specific thermal history. Scanning rate of 10°C/min was maintained for both heating and cooling cycle; whereas nitrogen gas purge rate maintained at 50 ml/min. Melting temperature was determined from the second heating scan while the crystallization temperature ( $T_c$ ) from cooling scan.

### 2.3.3. Rheological Properties

The melt viscosity was measured using rotational rheometer (MCR101, Anton Paar, India) with parallel plate assembly having diameter of 35 mm. Samples were predried before analysis. Viscosity was determined for shear rates from 0.01 s<sup>-1</sup> to 100 s<sup>-1</sup> at the constant temperature of 250°C.

### 2.3.4. Morphological Properties

Scanning electron microscope (SEM) analysis was performed with JEOL 6380 LA (Japan). Samples were fractured under liquid nitrogen to avoid any disturbance to the molecular structure and then coated with gold before imaging.

### 2.3.5. X-Ray Diffraction

The XRD analysis was carried out to determine the percentage crystallinity of the prepared composite. A normal focus copper X-ray tube was operated at 30 kV and 15 mA. Sample scanning was done from 2.00° to 80.00° at the rate of 3.00°/min. The data processing was done using Jade 6.0 software.

## 2.4. Formulation

The formulations prepared are as shown in the **Table 2**. Concentration of cenosphere was varied from 0 to 10 phr of nylon 6, while concentration of wetting agent was maintained constant at 5 phr of nylon 6.

**Table 1. Chemical composition of cenosphere obtained from Nasik thermal power plant.**

Components	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	V <sub>2</sub> O <sub>5</sub>	Fe <sub>2</sub> O <sub>3</sub>
wt%	24.559	50.300	0.409	0.060	6.765	1.109	5.129	0.102	11.566

**Table 2. Formulation of cenosphere/nylon 6 composites.**

Sr. No.	Sample Name	Nylon 6 (gm)	Cenosphere (phr, gm)	Wetting Agent (phr, gm)
1	VNY	500	0.0, 0.0	5, 25
2	NC 2.5	500	2.5, 12.5	5, 25
3	NC 5	500	5.0, 25.0	5, 25
4	NC 7.5	500	7.5, 37.5	5, 25
5	NC 10	500	10.0, 50.0	5, 25

### 3. Results and Discussion

#### 3.1. X-Ray Diffraction

X-ray diffraction pattern of the composites are shown in the **Figure 1**; whereas percentage crystallinity of the composites are noted in **Table 3**. It was found that percentage crystallinity was least for 2.5 phr cenosphere loaded nylon 6; and increased with increase in cenosphere concentration. But, percentage crystallinity remained lower than the base polymer even for 10 phr cenosphere loaded nylon 6.

Cenosphere and nylon 6 both are hydrophilic material, providing better compatibility between the two materials. But, the intermolecular forces of attraction between the nylon 6 polymer chains are better than that between nylon 6 and cenosphere. Due to the micro-spherical nature of cenosphere, nylon 6 polymer chains come in contact with cenosphere only at a single tangential point or may be a little more, depending on the molecular arrangement. But, the chance of nylon 6 chains to completely cover the surface of cenosphere is negligible.

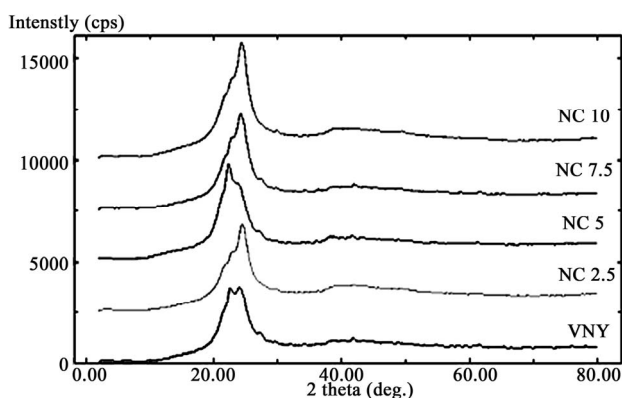
At 2.5 phr concentration of cenosphere, particles are uniformly dispersed in the nylon 6 matrix. So, the number of nylon 6 polymer chains contacting cenosphere tangentially at one point is more. Also, the spherical nature of the cenosphere remained intact at lower concentration, increasing flowability of nylon 6 polymer chains onto each other. As the concentration of cenosphere increased, it started forming agglomerates, decreasing the spherical nature of the cenosphere. This decreases the flowability of nylon 6 molecular chains over it, increasing crystallinity. Due to agglomerate formation, the contact area between cenosphere and nylon 6 also increases, making nylon 6 polymer chains to align more properly increasing crystallinity.

#### 3.2. Mechanical Properties

Mechanical properties; tensile, flexural and impact strengths, are reported in **Table 4**. Tensile strength remained nearly constant with increase in cenosphere concentration, whereas tensile modulus, elongation at break, impact strength,

flexural strength and flexural modulus increased.

Elongation at break was highest for 2.5 phr cenosphere/nylon 6 composites and started decreasing with increase in concentration. But, even for maximum cenosphere content, elongation is still higher than virgin nylon 6. Impact strength was also highest for 2.5 phr cenosphere. Impact strength is proportional to elongation property of the material. At 2.5 phr cenosphere content elongation at break increased by 83% and impact strength by 44%. Impact strength decreased with increase in cenosphere content. But, even for maximum cenosphere content, it was still higher than virgin nylon 6. X-ray diffraction showed lowest crystallinity for 2.5 phr cenosphere/nylon 6 composites. This correlated with the increase in elongation at break and impact strength of the material.



**Figure 1.** X-ray diffraction pattern of nylon 6 and nylon 6/cenosphere composites.

**Table 3.** Percentage crystallinity of the nylon 6 and nylon 6/cenosphere composites.

Sr. No.	Sample Name	Crystallinity (%)
1	VNY	5.15
2	NC 2.5	4.49
3	NC 5	4.58
4	NC 7.5	4.83
5	NC 10	4.99

**Table 4.** Mechanical properties of nylon 6 and nylon 6/cenosphere composites.

Sr. No.	Sample Name	Tensile Strength (MPa)	Tensile Modulus (MPa)	% E @ Break	Impact Strength (J/m)	Flexural Strength (MPa)	Flexural Modulus (MPa)
1	VNY	51.25	1937.8	90.94	56.46	70.66	2455.4
2	NC 2.5	57.93	2061.8	165.71	81.17	72.88	2521.7
3	NC 5	53.29	2277.1	119.57	70.83	87.32	3020.5
4	NC 7.5	49.59	2303.0	119.13	68.33	88.88	3121.3
5	NC 10	50.35	2330.8	79.53	71.50	88.37	3123.3

More amorphous the material becomes, better it is able to transfer the impact force, without undergoing cracking. This increases the impact strength of the material. The spherical nature of the cenosphere was thus best utilized for increasing amorphous characteristic of the nylon 6. Flexural strength increased with increase in cenosphere content. For 10 phr cenosphere/nylon 6 composite, flexural strength was found to have increased by about 25%.

### 3.3. Thermal Properties

Heating and cooling scans of the nylon 6 and nylon 6/cenosphere composites are shown in Figures 2 and 3 respectively. Table 5 reports enthalpy of melting, melting temperature, enthalpy of crystallization and crystallization temperature of nylon 6 and nylon 6/cenosphere composites.

Enthalpy of heating was found to be least for 2.5 phr cenosphere/nylon 6 composites, and started increasing with increase in cenosphere content. But, enthalpy of composite containing highest cenosphere content was still less than that of the virgin nylon 6. Even enthalpy of crystallization gave the same trend. Melting temperature and crystallization temperature didn't change appreciably with change in cenosphere content. Enthalpy of the material is proportional to the crystallinity, thus 2.5 phr cenosphere/nylon 6 showed lowest enthalpy of melting, which

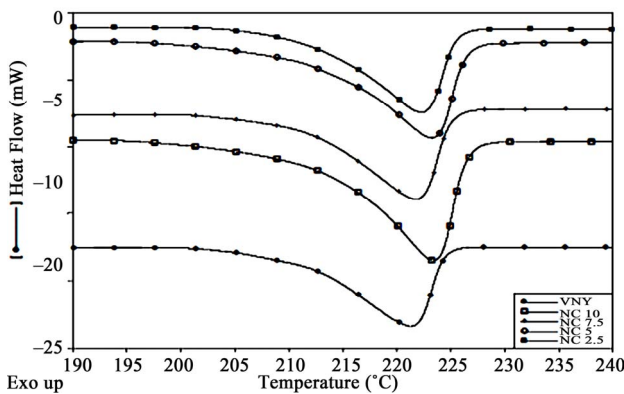


Figure 2. Heating scan of virgin nylon 6/cenosphere composites.

increased with cenosphere concentration. While enthalpy of crystallization increased with increase in cenosphere content.

### 3.4. Rheological Properties

Figure 4 shows the rheological properties of nylon 6 and nylon 6/cenosphere composites. It was found that, at lower shear rate viscosity of nylon 6 and nylon 6/cenosphere composites is same, but at higher shear rate difference becomes prominent. Viscosity of nylon 6 was found to be highest, while that of 2.5 phr cenosphere loaded nylon 6 composites was found to be lowest. Viscosity increased with increase in cenosphere content, but even at maximum loading it was lower than the base polymer.

Lowest viscosity at 2.5 phr loaded cenosphere is due to maximum amorphicity and flowability that it possesses. Viscosity increased with increase in cenosphere concentration. This correlates with the increase in crystallinity as shown by X-ray diffraction, mechanical properties and thermal properties. Also as cenosphere content increased, it started forming agglomerate, decreasing the spherical nature of the material. This decreased the flowability of the composite material, increasing viscosity. All samples showed drastic shear thinning after the shear rate of 10. Zero shear viscosity of all the sample was also found to be nearly same, i.e. at 1000 Pa-s.

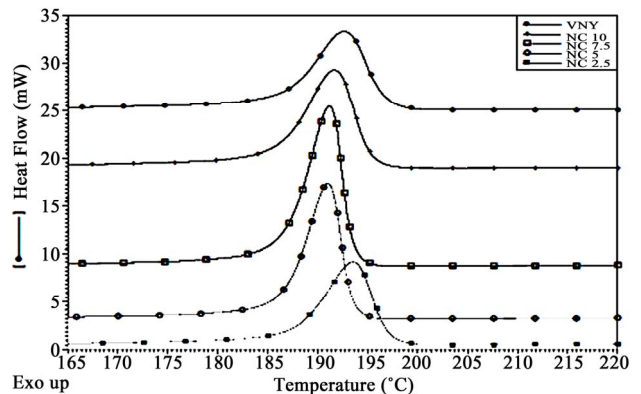


Figure 3. Cooling scan of virgin nylon 6/cenosphere composites.

Table 5. Thermal properties of nylon 6 and nylon 6/cenosphere composites.

Sr. No.	Sample Name	Enthalpy of melting (J/g)	Melting temperature (°C)	Enthalpy of crystallization (J/g)	Crystallization temperature (°C)
1	VNY	69.16	221.23	82.92	192.65
2	NC 2.5	46.68	222.26	48.43	193.50
3	NC 5	59.64	223.24	61.04	191.02
4	NC 7.5	65.61	221.81	65.02	191.16
5	NC 10	66.13	223.24	80.32	191.71

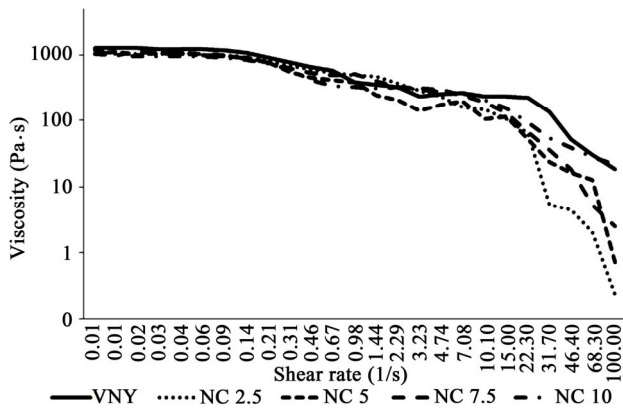


Figure 4. Viscosity vs shear rate graph of nylon 6/cenosphere composites.

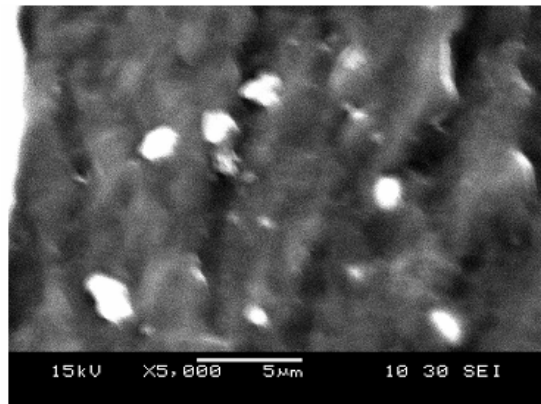
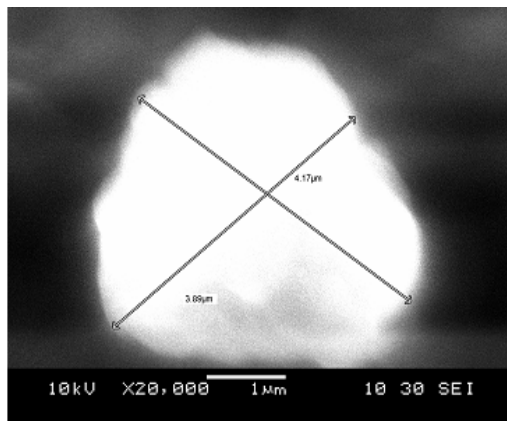
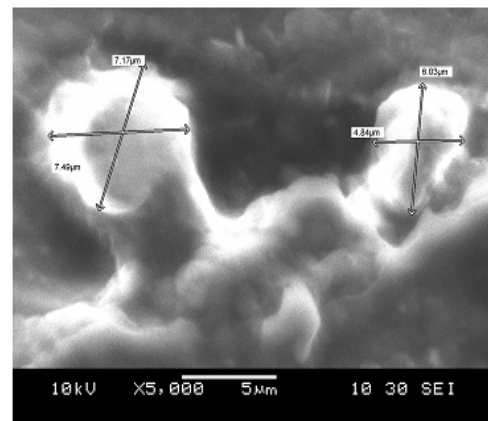


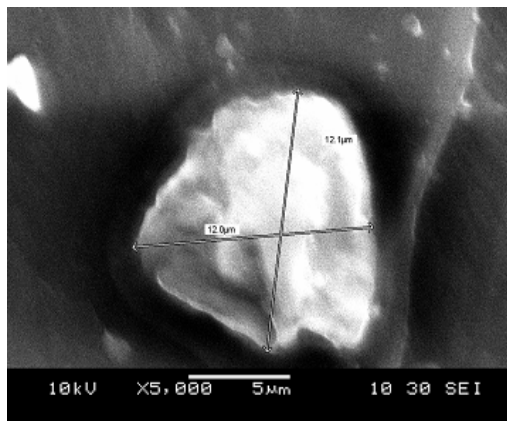
Figure 5. SEM image of 2.5 phr cenosphere loaded nylon 6 at 5000x showing particle size distribution.



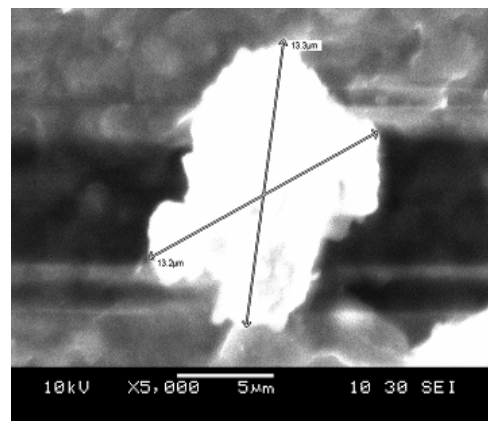
(a)



(b)



(c)



(d)

Figure 6. Showing particle size of (a) SEM image of 2.5 phr cenosphere loaded nylon 6 at 20000x; (b) SEM image of 5 phr cenosphere loaded nylon 6 at 5000x; (c) SEM image of 7.5 phr cenosphere loaded nylon 6 at 5000x; (d) SEM image of 10 phr cenosphere loaded nylon 6 at 5000x.

### 3.5. Morphological Properties

Morphological properties of the cenosphere/nylon 6 composites were found using scanning electron microscopy (SEM). SEM images of 2.5 phr cenosphere/nylon 6 composites showing dispersion, 2.5 phr cenosphere/ny-

lon 6 composites showing cenosphere particle size, 5 phr cenosphere/nylon 6 composites, 7.5 phr cenosphere/nylon 6 composites and 10 phr cenosphere/nylon 6 composites are shown in Figures 5 and 6 respectively.

Particle size of cenosphere is about 3.9 to 4.2 μm, as evident from Figure 6. At 2.5 phr cenosphere content,

cenosphere are uniformly distributed in the nylon matrix, giving better flowability to the nylon 6 matrix. As the cenosphere content increases in the nylon 6 matrix, it forms agglomerate, increasing particle size. Increase in particle size is gradual with increase in cenosphere concentration.

#### 4. Conclusion

Cenosphere has always been used as a material to reduce the density of the material due to its micro-spherical nature. However, cenosphere can be effectively used as reinforcing agent in nylon 6. By use of cenosphere as reinforcing agent in nylon 6 matrix, elongation at break increased by 83%, impact strength by 44%; at 2.5 phr content. Flexural strength increased with increase in cenosphere content. Flexural strength increased by 25% at 10 phr cenosphere content. Cenosphere decreased crystallinity and also increased flowability of nylon 6. No change in tensile strength of the composites was observed with change in cenosphere content.

#### 5. Acknowledgements

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