Evaluation of Thermal and Morphological Properties of Nylon 6/Cenosphere Composites

Bhaskar I. Oza[1], Ajay S. Amin[2]
Department of Plastic Engineering
Government Polytechnic
Ahmedabad, India.
bhaskaroza@yahoo.com
ajayamin2000@yahoo.co.in

***Abstract*—** PA6/CS composites were prepared with different loading (10, 20 and 30 % w/w) of CS (5-100 µm) by co-rotating twin screw extruder. Injection molded specimens were prepared to evaluate thermal properties of developed composites. Thermal properties like Heat Deflection Temperature (HDT), Differential Scanning Calorimetry (DSC) and Thermo Gravimetric Analysis (TGA) were evaluated for these composites. Morphological properties were also studied for these composites.
Addition of Cenosphere improves HDT of Nylon 6 besides reducing cost of the final product. SEM of fractured surface revealed the evenly distribution of Cenosphere in the matrix. As Cenospheres are generated from fly ash in thermal power plant, they are environment friendly, eco-friendly and help to preserve natural virgin filler.

Keywords- *Cenosphere, Nylon-6, Thermal properties, HDT, DSC, TGA, Morphological properties*

*****

I. INTRODUCTION

A Cenosphere (CS) is a light weight, hard and rigid, waterproof, inert and hollow sphere which can be used as a cost effective filler to improve the properties of Nylon-6 and to produce a new class of engineering composite for automobile application. Cenospheres are 70% lighter than other mineral fillers. Cenospheres are unique free flowing powders composed of hard shelled, hollow, minute Spheres. A small proportion of the pulverized fuel ash (PFA) produced from the combustion of coal in power stations is formed as Cenospheres. Cenospheres are made up of silica, iron and alumina. Cenospheres have a size range from 1 to 500 microns with an average compressive strength of 3000+ psi. Colors range from white to dark gray. They are also referred to as microspheres, hollow spheres, hollow ceramic microspheres, micro balloons, or glass beads.

Nylon 6 – CS composite is less studied area and there is wide scope for research scholar to explore it in various automobile applications. The use of Cenosphere in the production of composite can turn the industrial waste into industrial wealth. This also solves the problem of storage of fly ash as well as brings down the product cost.

Continuous accumulation of fly ash during coal burning in power plant is one of the alarming environmental problems. The amount of continuously producing ash is much higher than its consumption and ash dump is continued to expand. But at the same time some unique properties of Cenospheres obtained from fly ash provides prospects for their use in many applications like ceramics, plastics and construction.

II. MATERIALS AND METHODOLOGY

A. Materials:

Polymeric matrix material Nylon 6 (Grade: M28RC, Manufacturer: GSFC) was procured from GSFC, Vadodara. The MFI of Nylon 6 is 28gm/cc. The filler Cenosphere (Grade: CS100) was procured from Petra Buildcare Products, Bhavnagar). Particle size of Cenosphere is 5-100µm. The general properties of Cenosphere are:

- **Size range :** 5 - 500 micron
- **Wall Thickness :** 2 - 5 micron
- **Color :** White, Off-white or Grey
- **Bulk Density :** 0.3 - 0.6 g/cc
- **Melting Point:** 1250 - 1450 ^{0}C
- **Moisture Absorption :** < 2.5%
- **Coefficient of thermal conductivity :** 0.09W/mK
- **Specific Heat :** 0.28 Cal/g ^{0}C
- **Hardness :** 5 - 6 Mohr scale
- **Loss On Ignition :** 2% maximum
- **Solubility in Water :** Negligible

The chemical composition of Cenosphere is shown in table I.

TABLE I. CHEMICAL COMPOSITION OF CENOSPHERE

Chemical Composition	**Wt.%**
SiO_2	55-61
Al_2O_3	26-30
Fe_2O_3	4-10
CaO	2-6
MgO	1-2
Na_2O, K_2O	0.45 - 0.55
CO_2 Gas	70%
N_2 Gas	30%

Silicon Coupling Agent aminoethyl amino propyl trimethoxysilane (Grade: Xiameter OFS-6020 Silane, Manufacturer: Dow Corning Corporation) was procured from Alekh Testing Centre, Vatva, Ahmedabad.

B. Silane treatment

The inorganic filler CS was surface treated with a silane coupling agent before being added to Nylon 6. The SCA was added (5% by weight of CS) in water with continuous stirring up to 30 minutes and 5% silane concentrated aqueous solution is prepared. This solution is then distributed through the Cenosphere particles and mixed so each particle was covered with coupling agent. Then it was air dried initially and after 24 hours oven dried to remove any water residue. The technique is widely used in industrial applications because large amounts of filler can be treated in short time.

C. Composites and Specimen Preparation:

Nylon 6 – Cenosphere composites were prepared by Co-rotating Twin screw extruder (Make: SPECIFIC ENGINEERING & AUTOMATES) in processing laboratory, HLC, CIPET, Ahmedabad.. L:D ratio of screw is 40:1 and screw diameter is 21 mm. The temperature range used was 180-220 °C. As nylon 6 is hygroscopic material, it was predried at 85 °C for approximately 3 hours to remove moisture in an oven before compounding. Cenosphere was also predried at same conditions to remove moisture. This is necessary to have void free samples. First, 3 batches of untreated and then 3 batches of treated composites were prepared. Each batch was of 3 Kg size as shown in below table.

TABLE II. BATCH COMPOSITION OF PA6 AND CS (UNTREATED)

Batch (3 Kg)	**Composition**
PA6N	Nylon-6+Cenosphere 0Wt%
PA6CS10	Nylon-6+Cenosphere 10Wt%
PA6CS20	Nylon-6+Cenosphere 20Wt%
PA6CS30	Nylon-6+Cenosphere 30Wt%

TABLE III. BATCH COMPOSITION OF PA6 AND CS (TREATED)

Batch (3 Kg)	**Composition**
PA6CST10	Nylon-6+Cenosphere 10Wt%
PA6CST20	Nylon-6+Cenosphere 20Wt%
PA6CST30	Nylon-6+Cenosphere 30Wt%

The test specimens for HDT were prepared by using Automatic Injection Molding Machine (Make: ELECTRONICA, Model: ENDURA 90) in Processing Laboratory, CIPET, Ahmedabad. Before loading the material in the hopper, the material was predried for about 3 hours at 85 °C to remove moisture which eliminates voids in the samples. The injection molding was carried out at 230 - 275 °C and different test specimens for HDT like bar were prepared.

D. Characterisation Techniques

Various instruments were used to evaluate the thermal and morphological properties of Nylon 6/Cenosphere composites. HDT was measured by using HDT testing machine (P.S.I.SALES (P) LTD,) as per ASTM D 1525 at testing laboratory, CIPET, Ahmedabad. The test was carried out using 66 psi fiber stress with heating rate of 120 °C/hr. DSC test was performed by using DSC Q-200 (TA instruments) at EMD Millipore, Boston, USA. Refrigerated-cooling-system (RCS-90) and Nitrogen purge was used for the analysis. A thin slice (about 4 mg) was cut from a flexural bar and then crimped in a T_{zero} Aluminum pan. Then sample was heated from 0°C to 285°C, cooled down to 0°C, and reheated to 285°C. Throughout the experiment, the heating/cooling rate was maintained at 10°C/min. Universal analysis software was used for the data analysis.

TGA test was performed by using TGA Q-5000IR (TA instruments) at EMD Millipore, Boston, USA. About 20 mg sample was sliced from a flexural bar sample, placed in a tarred high temperature platinum pan, and then heated from room temperature to 1000°C at 10°C/min. The purge was switched from Nitrogen to Air at 800°C to ensure decomposition of carbon-black if present any. Universal Analysis software was used for the data analysis. The Onset Point and Residue functions were used to determine onset of pyrolysis temperature (decomposition temperature) and the amount of inorganic filler content, respectively. SEM analysis was performed with JEOL (JSM-5610LV) at Metallurgy Department, Faculty of Technology and Engineering, M.S. University, Vadodara. Tensile fractured surfaces were utilized for SEM analysis.

III. RESULTS AND DISCUSSION

A. Heat Deflection Temperature

Fig. 1 shows the effect of Cenosphere on HDT of PA6/CS composites at different concentration. As CS content increases HDT increases due to increased stiffness of the composite added by Cenosphere. This is due to increased chain stiffness of the matrix Nylon 6. HDT is increased from 164ºC to 191 ºC at 30% CS concentration. There is no or very marginal change in HDT with silane treated CS compared to untreated one.

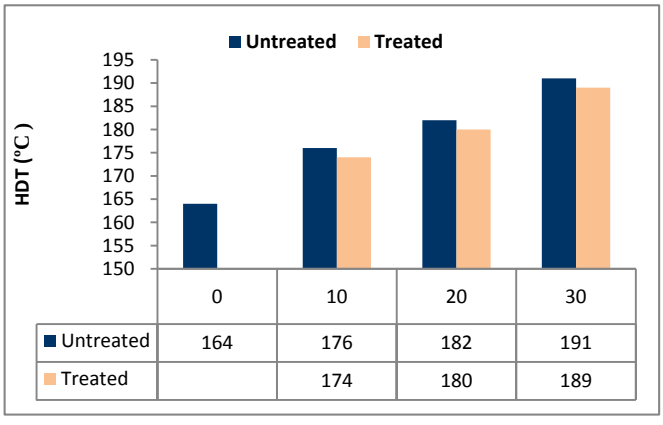

Figure 1: Effect of CS concentration on HDT of PA6/CS composites

B. Differential Scanning Calorimetry

Figure 2 shows the second heat thermo grams of PA6N (virgin) and untreated compositions with 10%, 20%, 30% CS concentrations. Glass transition is found around 51^0C for all the samples remaining unaffected by filler CS. All samples

 ISSN: 2321-8169
4667 - 4671

exhibited melting temperature 220^0C also unaffected by CS filler. Tg 51^0C and melting point 220^0C are the appropriate glass transition temperature and melting temperature of Nylon 6. Figure 4 shows the same behaviour for treated compositions.

Figure 3 shows the overlay cooling (crystallisation) profiles of virgin Nylon 6 and untreated compositions. It shows that crystallisation peak temperature increases by about 2°C on addition of CS filler.

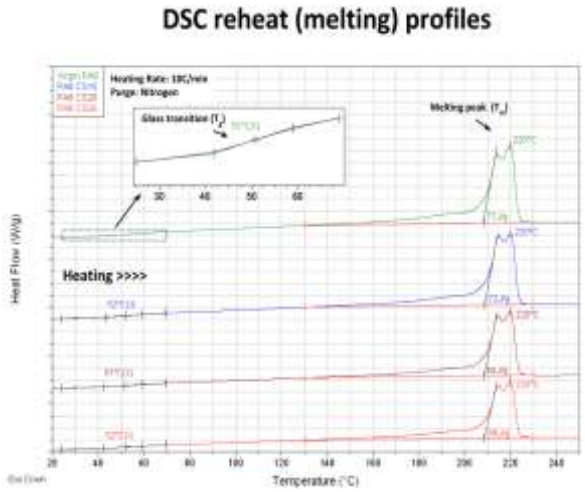

Figure 2: DSC overlay of untreated compositions

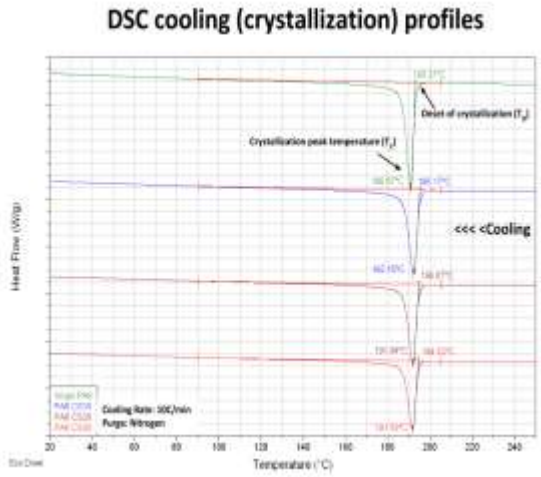

Figure 3: DSC cooling profiles of untreated compositions

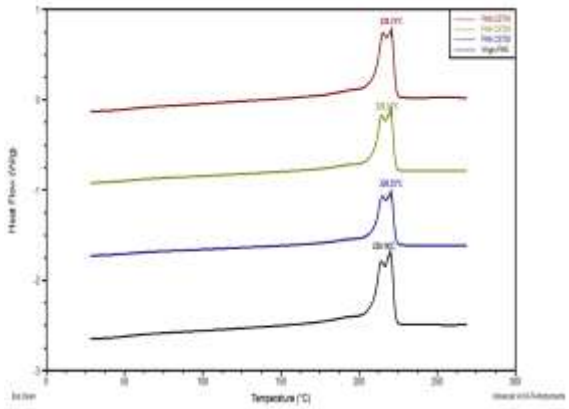

Figure 4: DSC overlay of treated Compositions

C. Thermo Gravimetric analysis

Cenosphere is inorganic in nature, so TGA is an ideal technique to check % filler content leftover after mass loss due to pyrolysis of samples and to analyze decomposition temperature of PA6 natural and PA6 filled with different CS concentration. In TGA, all samples were heated from room-temperature to 800 °C at a constant heating-rate 10°C/min with Nitrogen purge to prevent oxidation and the purge was switched from Nitrogen to Air at 800°C up to 1000°C to ensure decomposition of carbon-black if present any.

Figure 5 and 6 shows the TGA overlay of treated and untreated compositions. In both graphs, the residue left over after pyrolysis confirms the theoretically added percentage of CS filler. It also shows that there is no significant change in the decomposition temperature of PA6 with CS content. Thermal stability of composite is also not affected due to high melting temperature of CS which is about 1450 °C.

Figure 5: TGA overlay of untreated compositions

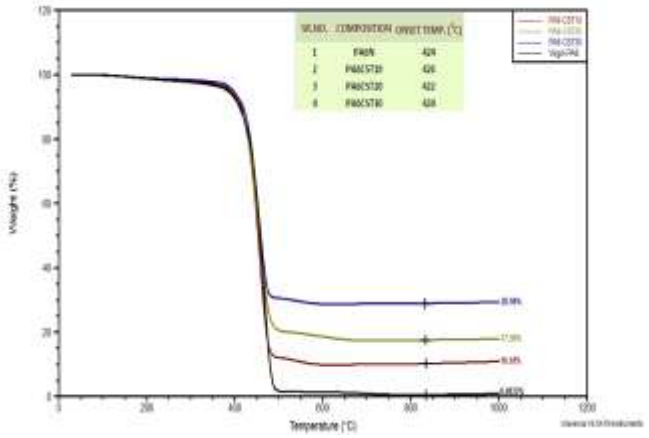

Figure 6: TGA overlay of untreated compositions

D. Morphological properties

From the micrographs shown in Fig. 7 and 8, following observations can be made:

- It is evident that Cenospheres are uniformly distributed in the matrix Nylon 6 material.
- Figures confirm the spherical shape and 5-100 µm size of Cenosphere added to the matrix. Broken Cenosphere reveals the hollow nature of Cenosphere.

- No significant voids are seen indicates absence of moisture during predrying..
- Cenospheres are tightly embedded and mechanically interlocked by the surrounding resin.
- In SEM image PA6CST20 sample, presence of silane coated Cenosphere is visible.

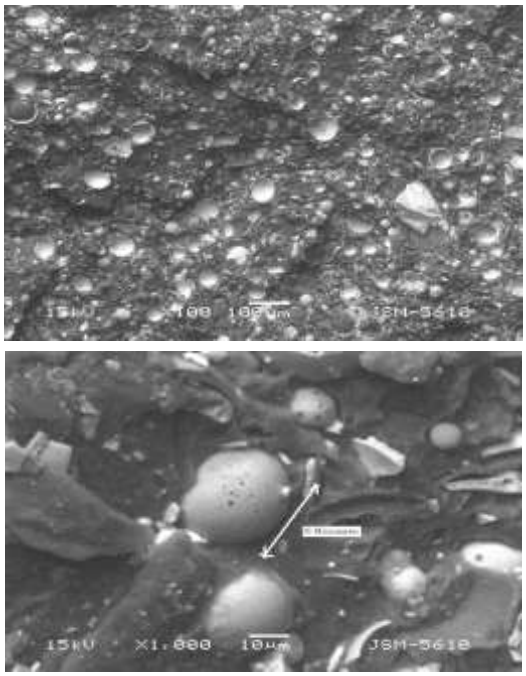

Figure 7: SEM micrographs of tensile fractured surface of PA6/CS20 sample at 100× and 1000× magnification level respectively

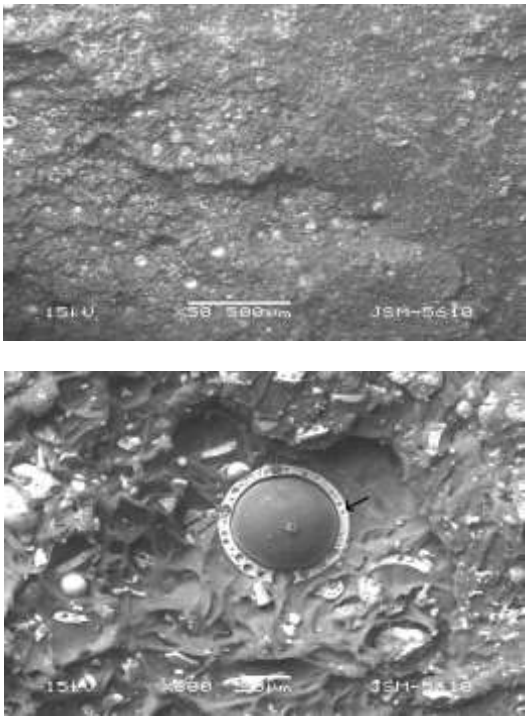

Figure 8: SEM micrographs of tensile fractured surface of PA6/CST20 sample at 50× and 600× magnification level respectively

IV. CONCLUSION

- HDT increases up to 191ºC at 30% CS content which is remarkable.
- The value of glass transition temperature and melting temperature obtained in DSC is unaffected by CS content for all compositions.
- The decomposition temperature in TGA clearly indicates that the thermal stability of the composite is not affected by the increase in CS concentration for all compositions. The residue obtained in TGA reveals uniform distribution of CS in the Nylon 6 matrix and confirms the different CS loading in Nylon 6 matrix.
- SEM micro graphs show uniform distribution of CS filler in the Nylon 6 matrix. With SCA treated CS, good interfacial adhesion of CS and matrix Nylon 6 is found.

ACKNOWLEDGMENT

The authors are thankful to the processing and testing laboratory of CIPET-Ahmedabad, EMD Millipore (Boston, USA) and Metallurgy Department, M.S. University, Vadodara for providing necessary supports to carry out this research.

REFERENCES

[1]. Ajitkumar Senapati, Abhijit Bhatta, Satyajeet Mohanty, P.C. Mishra, B.C. Routra, “An extensive literature review on the usage of fly ash as a reinforcing agent for different matrices”, *International Journal of Innovative science and Modern Engineering (IJISME)* ISSN: 2319-6386, Volume-2, Issue-3, February 2014

[2]. V.B. Fenelov, M.S. Mel'gunov and V.N. Parmon, "The Properties of Cenospheres and the Mechanism of Their Formation during High-Temperature Coal Combustion at Thermal Power Plans", *KONA Powder and Practical Journal*, 2010, 28, 189-207.

[3]. M. Rahail Parvaiz, Smita Mohanty, Sanjay K. Nayak and P.A. Mahanwar, "Polyetheretherketone (PEEK) Composites Reinforced with Fly Ash and Mica", *Journal of Minerals & Materials Characterization & Engineering*, 9 (1), 2010**,** 25-41.

[4]. Elena V. Fomenco, Natalia N. Anshits, Marina V. Pankova, Leonid A. Solovyov and Alexander G. Anshits, "Fly Ash Cenospheres: Composition, Morphology, Structure, and Helium Permeability", *World of Coal Ash Conference*, USA, 2011.

[5]. Sateesh Bonds, Smita Mohanty and Sanjay K. Nayak, "Viscoelastic, Mechanical and Thermal Characterization of Fly Ash-Filled ABS Composites and Comparison of Fly Ash Surface Treatments", *Polymer Composites*, 33 (1), 2012, 22-34.

[6]. Jitendra Gummadi, G. Vijay Kumar and Gunti Rajesh, "Evaluation of Flexural Properties of Fly Ash Filled Polypropylene Composites", *International Journal of Modern Engineering Research*, 2 (4), 2012, 2584-2590.

[7]. Suryasarathi Bose and P.A. Mahanwar, "Effect of Fly Ash on the Mechanical, Thermal, Dielectric, Rheological and Morphological Properties of Filled Nylon 6", *Journal of Minerals & Materials Characterization & Engineering*, 3 (2), 2004, 65-89.

[8]. Suryasarathi Bose and P.A. Mahanwar, "Effect of particle size of filler on properties of Nylon 6", *Journal of Minerals*

& Materials Characterization & Engineering, Vol. 3, No. 1, 2004, pp 23-31.

[9]. Arijit Das, Bhabani K. Satapathy, "Structural, mechanical, thermal and dynamic mechanical properties of cenosphere filled PP composites", *Materials and design 32(2011) 1477-1484*.

[10]. R. J. Cardoso, A. Shukla, A. Bose, "Effect of particle size and surface treatment on constitutive properties of Polyester – Cenosphere composites", Journal of Materials Science 37 (2002) 603-613.

[11]. Baljeev Kumar, Rajeev Garg and Upindrepal Singh, "Utilization of fly ash as filler in HDPE/Fly ash composites: A Review" , *International Journal of Applied Engineering Research*, ISSN 0973-4562 Vol.7 No.11 (2012)

[12]. M.B. Kulkarni and P.A. Mahanwar, "Effect of Methyl Methacrylate-Acrylonitrile-Butadiene-Styrene (MABS) on the Mechanical and Thermal Properties of Poly (Methyl Methacrylate) (PMMA)-Fly Ash Cenospheres (FAC) Filled Composites", *Journal of Minerals & Materials Characterization & Engineering*, 11 (4), 2012, 365-383.

[13]. Tarun R. Nayak and Shiw S. Singh, "Fly ash generation and utilization- An overview", publication in the book titled- *Recent trend in fly ash utilization*, June 1993.

[14]. Seena Joseph, V. A. Bambola, V. V. Sherhtukade and P. A. Mahanwar, "Effect of Fly ash Content, Particle Size of Fly ash, and Type of Silane Coupling Agents on the Properties of Recycled Poly(ethylene terephthalate)/Fly ash Composites", *Journal of Applied Polymer Science*, 2010, 201-208.

[15]. Xiao-li Liu, Ye Han, Ge Gao, Zhi-ying Li and Feng-qi Liu, "Effect of Silane Coupling Agent on the Mechanical, Thermal Properties and Morphology of Tremolite/PA1010 Composites", *Chinese Journal of Polymer Science*, 26 (3), 2008, 255−262.

[16]. S. Bose, H. Raghu and P.A. Mahanwar, "Mica reinforced Nylon 6: effect of coupling agents on Mechanical, thermal, and dielectric properties," *Journal of Applied Polymer Science,volume 100, Issue 5,2006, 4074-4081.*