Paper ID: MS-13

Preparation and Analysis of Mechanical and Thermal Behavior of Ceramic Nano-Particle Reinforced Polymer Composites

Shahnawaz MD. Bin Sayed[1,a)], Md. Aminul Islam[2,b)]

[1,2]Department of Materials & Metallurgical Engineering, Bangladesh University of Engineering & Technology (BUET), Dhaka, 1000

[a)]Corresponding author: alin.sayed@gmail.com
[b)]aminulislam@mme.buet.ac.bd

Abstract

Composite materials are of extensive interest due to their attractive high strength to weight ratio property. Polymer nanocomposites were prepared by hot pressing the mixture of nylon 6 resin and ceramic particles like SiC, Al_2O_3, CaO, Graphite and Nanoclay. Methyl alcohol is used for adherence of the particles with polymer during mixing. Mechanical and thermal behavior analysis of these composites was carried out using tensile testing, flexural testing and Thermogravimetric analysis (TGA). Incorporation of selected nanoparticles is expected to enhance mechanical & thermal properties to a level that is desired and required for performance driven applications. Addition of ceramic particles enhanced the mechanical properties of the polymer such as Young's modulus and flexural strength. There was no sufficient increase in tensile strength and thermal stability. These can be due to the lack of bonding between organic polymer and inorganic nanoparticles and agglomeration of the reinforcing particles due to improper dispersion.

Keywords: Polymer composite, Nano composite, Composite synthesis, mechanical analysis

1. Introduction

Composites can be defined as materials that consist of two or more chemically and physically different phases (matrix phase and dispersed phase) separated by a distinct interface. The different systems are combined to achieve a system with more useful structural or functional properties not attainable by any of the constituent alone.

Polymer-matrix composites (PMCs) consist of a polymer resin as the matrix with various inclusions as the reinforcement medium. Matrix phase is the primary phase having a continuous character. Matrix is usually more ductile and less hard phase. It holds the dispersed phase and shares a load with it. Dispersed phase is usually stronger than the matrix, therefore, it is sometimes called reinforcing phase.

Nanocomposites are composites in which at least one of the phases shows dimensions in the nanometer range [1]. These are high performance materials that exhibit unusual property combinations and unique design possibilities. It has been reported that at the nanoscale (below about 100 nm), a material's property can change dramatically. With only a reduction in size and no change in the substance itself, materials can exhibit new properties such as electrical conductivity, insulating behavior, elasticity, greater strength, different color, and greater reactivity-characteristics that the very same substances do not exhibit at the micro- or macroscale [2].

In general, there are several key factors crucially influencing the role of nanoparticles as reinforcing fillers in polymer-matrix nanocomposites. In short, the factors/conditions allowing nanoparticles to effectively improve both the strength and elastic properties of host polymers are as follows: (i) Reinforcing inclusions should have high mechanical characteristics such as strength and Young modulus. (ii) Geometry of reinforcing inclusions should be characterized by high aspect ratio and high surface area. (iii) Reinforcing inclusions should be homogeneously dispersed, and their agglomeration should be prevented. (iv) Strong binding between inclusions and polymer matrix should exist [3].

Nanocomposites exhibit light-weight, good dimensional stability, enhanced heat and flame resistance, improvements in strength and modulus with far less loading than conventional composite counterparts, however these properties depend on several factors such as type of nanoparticle, surface treatments, polymer matrix, synthesis methods, and polymer nanocomposites morphology [4].

2. Materials & Experiments

Nanocomposites are prepared by melt mixing in this analysis by using hot press machine. A total no. of six casting was completed by using Aluminium mold. Among them one is pure Nylon 6 casting and others are: (i) Nylon 6 with 1% wt. SiC particles (ii) Nylon 6 with 1% wt. Al_2O_3 particles (iii) Nylon 6 with 1% wt. CaO particles (iv) Nylon 6 with 1% wt. Graphite particles and (v) Nylon 6 with 1% wt. Nano Clay.

2.1 Ball milling

Silicon Carbide (SiC), Alumina (Al_2O_3), Chalk Powder (CaO) and Graphite Powder are Ball Milled for an average of 72 hrs for each constituents. Among them SiC and CaO powder are milled inside a steel made container with steel ball. Al_2O_3 and Graphite are milled inside a ceramic made container with ceramic grinding medium.

2.2 Composites processing

Required amount of Nylon 6 beads are measured and kept in a glass beaker. 1% wt. powder is measured in a precision balance. Glass beaker with Nylon 6 beads is kept inside the furnace for around 20 minutes at 110^0C to remove the moisture. In the meantime Nanoparticles are mixed with Methyl alcohol by using a steel stirrer in another beaker. Casting mold is cleaned with acetone and sprayed with Silicon releasing agent in order to remove the casting after completion. The nanoparticle methyl alcohol mixture is mixed with dried Nylon 6 as soon as removing from the furnace. Thorough stirring is done to mix the particles properly with the polymer resin. The mixture is then distributed into the casting mold equally. The mold with constituents is placed inside the hot press machine. Temperature is set to 120^0C and held there for 15 minutes to remove the water vapor and homogenize the temperature. Then the temperature is raised to 225^0C and held there for around 10 minutes to melt and embed the particles into the polymer matrix. After that the temperature is lowered to room temperature by opening the water cooling channel. Casted specimen is removed from the mold with the help of a chisel and hammer. In case of pure Nylon 6 casting, the measured nylon beads are only mixed with methyl alcohol prior to the insertion into the hot press machine.

2.3 Tensile and flexural testing

Samples for tensile & flexural testing of pure nylon 6 resin and also the composites reinforced with various ceramic particles are prepared by the assistance of hacksaw and final finishing of the sample was done by grinding. The tensile & flexural test is performed in the Universal Testing Machine Instron 3360 as per ASTM D638 & ASTM D790 respectively.

2.4 Thermogravimetric analysis

From the remaining specimen samples are prepared for Thermo Gravimetric Analysis (TGA). Thermogravimetric analysis (TGA) was used to determine the changes in polymer decomposition temperatures. TGA continuously measures the weight of a sample as a function of temperature. The sample is placed in a pan held in a microbalance. The pan and sample are heated in a controlled manner and weight is measured throughout the heating cycle. Changes in weight at specific temperatures correspond to reaction or changes in the sample such as decomposition. Thus, this method allows determination of the analysis of desorption, degradation and decomposition processes.

3. Results & discussion

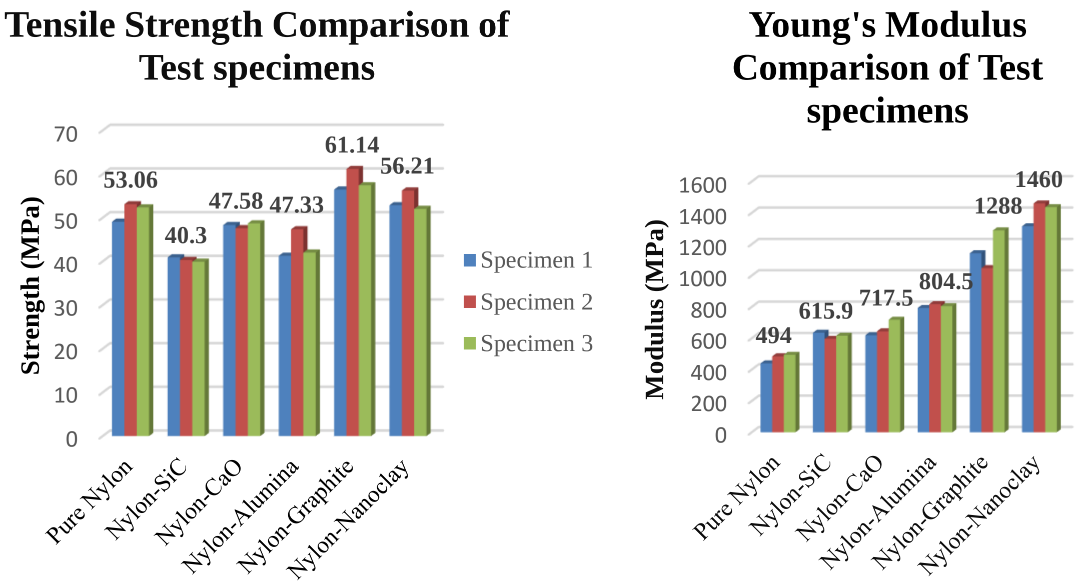
3.1 Visual inspection

All six cast specimens were free from porosity, gas bubbles and any surface defects. The surfaces were smooth and plain. Reddish tint was observed in the CaO-Nylon composites due to the contamination of Calcium Oxide powder with the Ferric Oxide (Fe_2O_3) from the Steel container during ball milling.

3.2 Tensile comparison

The experiment was conducted to produce Nanoparticles by ball milling to process Nano structured composites but the minimum size can be produced by ball milling is ~ 0.5-10μm [5]. Therefore Micro-composites were produced instead of Nanocomposites except for the Nylon-Nanoclay composites where manufactured nano sized particles were used.

From the following figure it can be seen that majority of the specimens showed lower mechanical strength compared to pure Nylon 6 casting except for Graphite and Nanoclay casting. However Nylon reinforced with 1%wt SiC, Alumina, Graphite, Nanoclay nanoparticles; all of these nanocomposites showed much greater tensile properties then pure Nylon [6-9]. Generally, the reason for adding inorganic particles into polymers is to improve its mechanical properties such as the tensile strength, modulus or stiffness via reinforcement mechanisms. However, poor compatibility between the polymer matrices and the inorganic particles in nanocomposites prepared by simple physical mixing will create inherent defects which, consequently, result in a deleterious effect on the mechanical properties of the nanocomposites [10-11].



(a) (b)

Fig 1. (a) Composite tensile strength comparison, (b) Young modulus comparison

Composites processed in the experiment also supposed to show better tensile properties due to dispersion strengthening mechanism, the strengthening mechanism involves interactions between the particles and dislocations within the matrix. Nylon- Graphite composite showed higher tensile strength for this particles-dislocations interaction. Composites with SiC, CaO and Alumina showed poor strength due to the lack of intimate bonding between particles and the matrix phases and also for the agglomeration of the particles in the matrix because of poor mixing. As micro or nano-sized particles have large surface area, they tend to possess high free surface energy. In order to minimize this energy, particles attract to each other resulting agglomeration [12].

Because of the incompatibility of the inorganic particles and organic polymer; poor bonding occurs in the particle/polymer interface. These regions act as stress raiser during tensile loading resulting micro cracks around the particles. Composites fail without attaining its theoretical strength. By analyzing the crack surface in figure 2 it can be seen that the cracks originated from sites of agglomerate particles.

For better adhesion of clay particle to polymer resin, an exchange of inorganic cations with organic cations renders the clay organophilic and hydrophobic, and lowers the surface energy of the clay layers. It then becomes possible for the organic polymer to diffuse between the clay layers and to delaminate the clay platelets to individual layers. As a result better bonding of the polymer matrix and clay layer occurs. Long chain alkyl ammonium salts have been widely used for exchanging the inorganic cations because they increase the basal spacing of the clay to a large extent, apart from lowering the surface energy, which can further be helpful in achieving exfoliation of the clay layers in the polymer matrix. [13].

Reinforcing the polymer matrix with micro particles greatly improved the stiffness of the composite. From the above figure it can be seen that Nylon-Graphite and Nylon-Nanoclay composites show a modulus increase of 145% and 196% respectively.

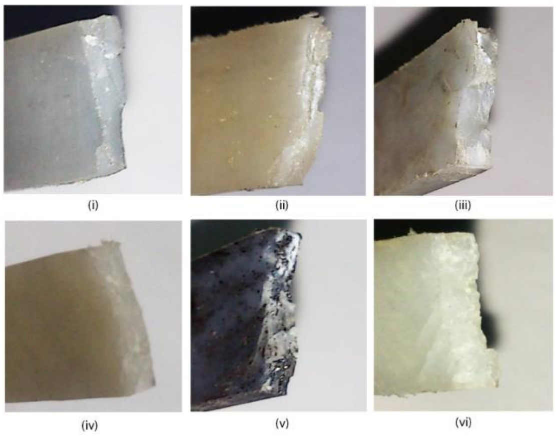
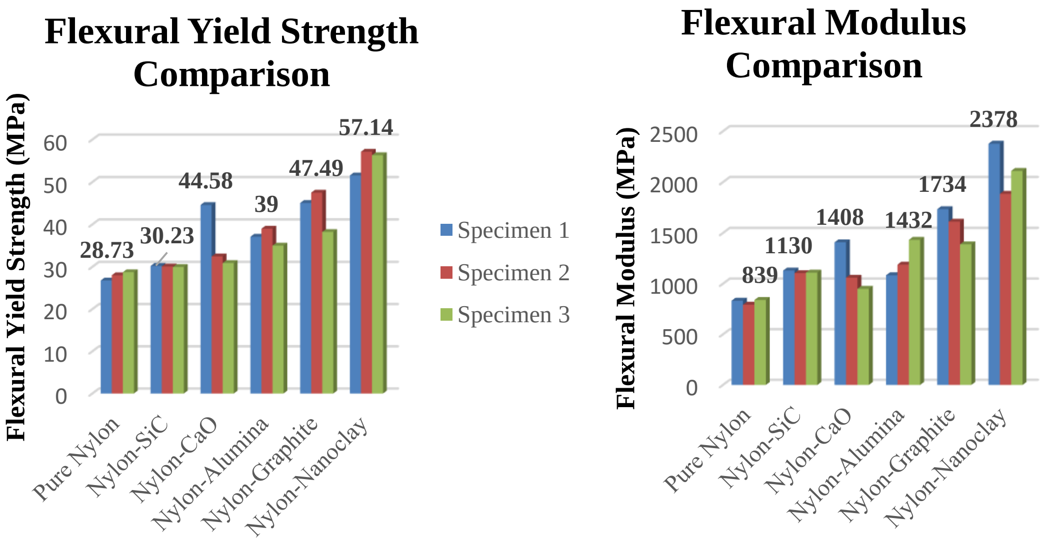


Fig 2. Fracture surface of test specimens; (i) Pure Nylon, (ii) Nylon-Cao, (iii) Nylon-SiC, (iv) Nylon-Al_2O_3, (v) Nylon-Graphite, (vi) Nylon-nanoclay.

3.3 Flexural comparison

Flexure strength of the pure Nylon 6 specimen was found to be too low than the known value. It can be caused due to the moisture absorption nature of Nylon 6, as it lowers the strength below the glass transition temperature [14]. Comparison among the flexure strength of the composites show a sharp contrast than the values observed in the tensile strength comparison. All the composites showed increased flexural strength value which is apparent from the figure 3.

Under flexural loading condition, fillers act as load bearing materials rather than act as stress raisers. Applied compressive stresses tends to close cracks and flaws that are perpendicular to the applied stress, contrary to the crack opening mechanism occurring in a tensile loading situation[15]. This phenomenon results in the increase of flexural strength in the test specimens.



(a) (b)

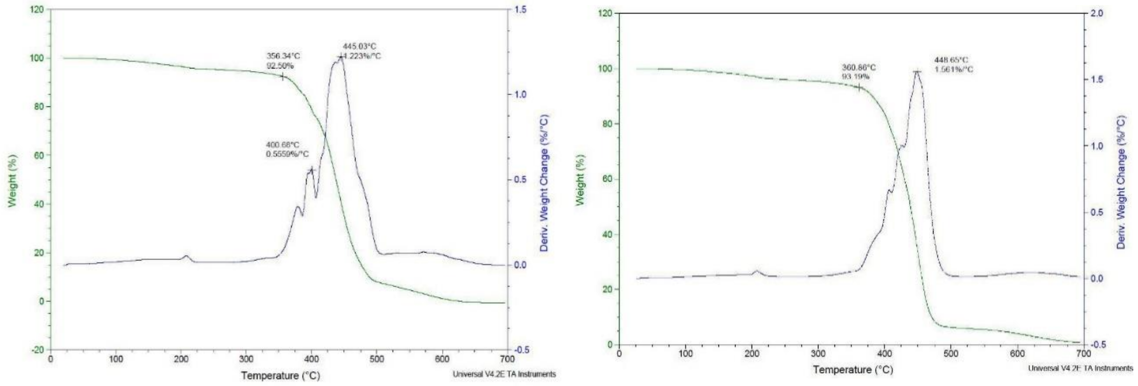
Fig 3. (a) Composite flexural strength comparison, (b) Flexural modulus comparison

3.4 Thermal stability

At the temperature of 200^0C; around 5% weight loss of the sample was observed. The effect is due to the loss of moisture content and is well known to polyamide [16]. The maximum derivative weight change occurred at the temperature of 445^0C for Pure Nylon. Step wise derivative weight curve is observed in the TGA analysis this can be caused due to the gradual decomposition of the part of repeating formula unit. Thermal degradation of nylon leads to the formation of volatile products and causes changes in the residual polymer sample. The chemical changes include crosslinking, the formation of an aromatic-conjugated material, and ultimately an involatile black char [17]. The decomposition behavior of Nylon 6 is found to be in the same way as previously conducted research [18].

Table 1. Decomposition temperature comparison of composites

Test Specimens	Decomposition Temp. (^{0}C)	ΔT
Pure Nylon	356.34	
Nylon-SiC	358.15	2
Nylon-Al_2O_3	356.34	0
Nylon-Graphite	359.96	3.5
Nylon-Nanoclay	360.86	4.5



(i) (ii)

Fig 4. TGA of (i) Pure Nylon, (ii) Nylon-Nanoclay composites.

Incorporation of nanoparticles into the Nylon matrix results in the increase of the thermal stability of the Nanocomposites [19]. This nanoparticles-matrix interaction produces a barrier which acts as superior insulation and hinders the volatile mass transport that generated during the decomposition of polymer under thermal conditions [10].

Therefore it can be concluded that the reinforcing particle has a positive impact on the thermal stability of the composites. The effect is not that significant as found in the previous experiments of the nanocomposites. This is caused due to insufficient bonding between the particles and the matrix and for the irregular dispersion of the particles throughout the matrix.

4. Conclusion

The following cessations can be disclosed-

Micro-composites were produced instead of nano-composites due to processing restriction of ball milling, except for nylon-nanoclay composites where previously manufactured nano clay particle were used. Mechanical characterization such as; Tensile, Flexure and thermal behavior (TGA) is performed. The results are compared with previously published journals.

All the composites showed lower tensile strength and no significant increase in thermal stability value compared to the previous research on nylon-nano structured composites. Poor compatibility between polymer matrix with inorganic particles along with agglomeration of the reinforcing phase in the composite is responsible for this.

However, the composites showed improved flexural strength and modulus. Under compressive load the filler materials carried the load. The inherent defect caused by the manual mixing and lack of surface treatment of the filler tend to be suppressed by the compressive stress during flexural test.

Sol-Gel process can be applied for the preparation of nanoparticles instead of ball milling. The surface of the particles can be treated to make it more compatible with organic matrix. The particles can then be incorporated into the matrix by using extruder or mixers to obtain proper dispersion of the reinforcing particles in the matrix.

5. Reference

[1] Roy R, Roy RA, Roy DM, Alternative perspectives on “quasi-crystallinity”: non-uniformity and nanocomposites, (1986); 4(8-9):323-328.
[2] P. Mulvaney, MRS bulletin, Volume 26, Issue 12, December 2001.
[3] I.A. Ovid'ko, Enhanced mechanical properties of polymer-Matrix nanocomposites reinforced by graphene inclusions (2013)
[4] S. Anandhan and S. Bandyopadhyay, Polymer Nanocomposites: From Synthesis to Applications
[5] C. Barry Carter, M. Grant Norton, Ceramic Materials: Science and Engineering (2013)
[6] Pattanayak and Jana, S.C. Properties of bulk-polymerized thermoplastic polyurethane nanocomposites, (2005), 46, 3394-3406.
[7] Vijaya K. Rangari, M. Yousuf, and Shaik Jeelani, Influence of SiC/Si3N4 Hybrid Nanoparticles on Polymer Tensile Properties, (2013)
[8] Asma Yasmin, Jyi-Jiin Luo, Isaac M. Daniel, Processing of expanded graphite reinforced polymer nanocomposites, (2006)
[9] J.S. Shelleya, P.T. Matherb and K.L. DeVriesc, Reinforcement and environmental degradation of nylon-6/clay nanocomposites, (2001)
[10] Zhang, X., Simon, L.C. In situ polymerization of hybrid polyethylene-alumina nanocomposites, 573-583 (2005)
[11] Chae, D.W., Kim, B.C. Characterization on polystyrene/zinc oxide nanocomposites prepared from solution mixing, 846-850 (2005)
[12] Zhu J, Kim J, Peng H, Margrave JL, Khabashesku VN, Barrera EV. Improving the dispersion and integration of single-walled carbon nanotubes in epoxy composites through functionalization, 1107-1113 (2003)
[13] Vikas Mittal, Polymer Nanocomposites: Synthesis, Microstructure, and Properties (2010)
[14] Nylons (Polyamide),
[15] Hagstrand, P.O., Bonjour, F. and Manson, A.E.,The Influence of Void Content on the Structural Flexural Performance of Unidirectional Glass Fiber Reinforced Polypropylene Composites, 705-714 (2005)
[16] TGA Interpretation,
[17] Barry J Holland and James N Hay, Thermal degradation of nylon polymers, 943-948 (2000)
[18] Shahryar Pashaei, Siddaramaiah, Maziar Mansouji, Akheel Ahmed Thermal degradation kinetics of nylon6/GF/crysnano nanoclay nanocomposites by TGA
[19] S. C. Lao, J. H. Koo and T. J. Moon, Flammability and thermal properties of polyamide 11-alumina nanocomposites (2009)