



FUNCTIONALIZED NANOPARTICLES AND THEIR INFLUENCE ON THE PROPERTIES OF NYLON FILAMENTS

Hassan Mahfuz*, Mohammad Hasan**, Justin Stewart*, Vijaya Rangari**, and Shaik Jeelani**

* Department of Ocean Engineering, Florida Atlantic University, Boca Raton, FL 33431,

**Tuskegee University's Center for Advanced Materials (T-CAM), Tuskegee, AL 36088

Abstract

Pristine and functionalized silica (SiO_2) nanoparticles were dispersed into nylon-6 and drawn into filaments through melt extrusion. A silane coupling agent was used through wet chemical treatment to functionalize silica nanoparticles. The silane coupling agent, trimethoxysilane, has an organo-functional group linked to a silicon atom which is attached to a hydrolysable alkoxy group. The alkoxy group in presence of moisture hydrolyzes to an unstable Si-OH bond which then condenses with the surface bound OH group on nanoparticle (SiO_2) surfaces to form a stable Si-O-Si bond. The organo-functional group of silane remains available for covalent reaction with nylon 6. This added chemical bonding between functionalized silica nanoparticles and nylon 6 resulted in 76% and 55% enhancement, respectively in tensile strength and modulus of nylon 6 filaments. On the other hand, improvement with pristine silica particles was rather modest; 36% and 28%, respectively. In both cases, the loading of nanoparticle reinforcement was only 1 wt%. Basic theories of inclusion and micromechanical approaches were employed to estimate the theoretical bounds of Young's modulus of nylon-6 with silica reinforcements. It was observed that even with pristine silica particles, the modulus is within 5% of the upper bound. Modulus of nylon-6 infused with functionalized silica far exceeded the upper bound predicted by micromechanics. Details of functionalization, synthesis of nylon-6 filaments, and theoretical predictions are described in the paper.

1 Introduction

In this paper, the nanocomposite under investigation is Nylon-6 reinforced with spherical silica nanoparticles. Nylon's toughness, low

coefficient of friction and good abrasion resistance make it an ideal replacement for a wide variety of applications replacing metal and rubber. The amide groups of nylon are very polar, and can hydrogen bond with each other. Because of these, and because the nylon backbone is so regular and symmetrical, nylons are often crystalline, and they make very good fiber [1-4]. Nylons are made from a monomer, such as a cyclic amide called lactam. For example, Caprolactam is a lactam with six carbon atoms and nylon made from Caprolactam is called nylon 6, or simply polyamide 6. When nylon is spun into fibers, the long chain-like macromolecules line up parallel to each other. The amide groups on adjacent chains then form strong bonds with each other called hydrogen bonds. These hydrogen bonds hold the adjacent chains together, making nylon yarn strong. When nylon-6 polymerizes, the amide link present in Caprolactam (starting monomer for nylon-6) opens up and the molecules join up in a continuous chain providing an ideal mechanism for bonding with nanoparticles.

On the other hand, silica particles are formed by strong covalent bonds between silicon and oxygen atoms by sharing their electron pairs at the p orbitals. In addition, the surface bound OH groups on silica surfaces may also form stable bonds with nylon during polymerization.

In order to utilize the extraordinary strength and stiffness of carbon nanotubes in bulk materials, several researchers [5-11] have recently infused CNTs into textile polymeric precursors and attempted to align the acicular particles along the length of the drawn filament. Infusion was carried out either through a liquid route using sonication, or a dry route followed by melt mixing in an extruder. Alignment of CNTs in the filament was enforced by extrusion or spinning and followed by stretching. The resulting composites either in consolidated or filament form have no doubt demonstrated improved

mechanical and thermal properties. While it was encouraging to see phenomenal improvements in strength and stiffness [12], it was also observed that the improvement was at the cost of sacrificing a significant amount of failure strain which is not attractive for nylon. In an attempt to improve upon the fracture strain, spherical silica nanoparticles, in place of CNTs, were chosen in the present work. However, the improvements in mechanical properties with spherical silica particles were modest. Functionalization of silica particles was then introduced to enhance the properties.

2 Functionalization of Silica Nanoparticles

The functionalization approach was to use a coupling agent between Nylon and inorganic silica particles. We used organosilanes to modify the surface of silica nanoparticles. Organosilanes has the ability to incorporate both organic- and inorganic-compatible functionality within the same molecule. The inorganic compatibility comes from the alkoxy groups attached to the silicon atom. This bond is hydrolytically unstable and in the presence of moisture hydrolyses to an intermediate Si-OH bond which then condenses with surface bound OH groups on inorganic surfaces to form stable Si-O-Si bonds. Molecular structure of organosilane and its interaction with silica substrates is depicted in Fig. 1. The final result of reacting an organosilanes with a substrate is to utilize the substrate to catalyze chemical transformations at the heterogeneous interface, ordering the interface region, and modifying its partition characteristics. Most importantly, it includes the ability to affect a covalent bond between Nylon and SiO₂ particles.

Functionalization of silica particles were performed in the following manner: The weight (gm) of silica nanoparticles that would be necessary for dispersion into Nylon was first estimated. Since the particles were spherical, and their density was known, one could calculate the specific surface area (gm/m³) of particles. Total surface area of silica particles was then determined from the estimated weight. Since one gram of silane (trimethoxysilane) was able to modify approximately 358 m² of inorganic surface, we could easily estimate the amount of silane needed for the particles. Silane was then added through mechanical stirring into a starting mixture of 95% ethanol and 5% water to yield a 2% final concentration of silane. Mixing was allowed for a few minutes for hydrolysis and silanol formation. In the next step, nanoparticles were added by stirring them into the silane solution for about 2-3

minutes. After the particles settled at the bottom, the solution was decanted. Ethanol and water were dried out by heating the particles in a furnace at around 110°C. If particles were agglomerated, a ball mill was used to bring them back to powder form. Silica nanoparticles are now ready to be dispersed into Nylon.

3 Filament Extrusion

In the present investigation, we dry mixed SiO₂ nanoparticles (both pristine and functionalized) with nylon 6 powder. The amount of nanoparticle loading was 1 wt%. The dry-mixed powder was then melted in a single screw extruder which was followed by distributive mixing, extrusion, stretching, and heat stabilization to continuously draw SiO₂-reinforced filaments. In parallel, control filaments were also extruded following identical procedures.

The dry mixing of nylon powder with SiO₂ was performed in a mechanical blender for three hours. The SiO₂ nanoparticles were procured from *MTI Corporation (2700 Rydin road, unit D, Richmond, CA 94804)*. The nanoparticles were 30-50 nm in diameter. Commercial grade nylon 6 was procured from *UBE Industries, Ltd (UBE building 3-11 Higashi-shinagawwa 2-chome, Shinagawa-Ku, Tokyo 140, Japan)*. A mechanical crusher was used to produce micron-sized powders of nylon which were then used in the mechanical blender for mixing with SiO₂ nanoparticles. The density of nylon 6 was 1.14 g/cm³ with a melting point of 215°C. In order to eliminate moisture, the nylon and SiO₂ mixture was placed into a cylindrical drying chamber. Hot air was supplied to the chamber through an insulated flexible tube using a vortex blower. The dryer was operated for 24 hours with temperature set at 90°C. Prolonged heating accompanied with a vortex flow broke up large agglomerates of silica particles if any left after the mechanical blending. Once the mixture was dried, it was extruded through a *Wayne Yellow Label Table Top Extruder*. Five thermostatically controlled heating zones were used to melt the admixture prior to extrusion. The die zone consisted of a circular plate, a 10 cm long steel tubing with an inner diameter of 4 mm, and the die itself. A distributive mixing of the silica nanoparticles with nylon was enforced through the use of a circular plate with multiple orifices [9, 13]. A specially designed die was used in the process. The die configuration generated two distinct flow regimes that significantly affected the distribution of the particles. After extrusion, filaments were solidified by passing them through chilled water maintained at

approximately 10⁰C. In the next step, filaments were stretched using a tension-adjuster (Godet), and heat stabilized using the *Wayne Yellow Jacket Stabilizing* unit. The heater temperature was set at 110 °C, and the filament travel per minute (FPM) was adjusted in the Godet stations to allow continuous drawing of filaments. Finally, the filaments were wound on a spool using a filament winder at a winding speed of about 70 rpm. Several of these spools were produced.

4 Tensile Response

Representative stress-strain responses from filament tests are shown in Fig 2. Improvements in strength and stiffness are listed in Table-1. It is observed that the gain in tensile strength and Young's modulus is around 36% and 28%, respectively with pristine silica infusion. It is also noticed that the fracture strain of the filament in this case is still around 80% and the deformation behavior of the nanophased system is very similar to that of the neat system throughout the loading range. If one considers 0.2% yield strength, the gain is almost in the identical range. Gain in Young's modulus is also clear. A theoretical explanation to such gain in modulus is given in the next section. Enhancement in strength can be attributed to two factors; one is the proper dispersion of SiO₂ into the matrix and the other is the development of interfacial bonding between the nanoparticle and the polymer. Dispersion of nanoparticles in the filament is shown in Fig 3. SiO₂ nanoparticles are seen to be dispersed uniformly over the entire body of the matrix, and are coated with the polymer. Most of the coated particles are in the 20-40 nm range and there is no sign of agglomerations. Large white lumps seen in the figure are nylon which could not be removed by plasma etching.

It is obvious from the 3rd curve (the one with siled silica particles) of Fig. 2 that once the bonding between silica and nylon is enhanced through silane coupling, the strength and modulus increases significantly. The improvement is now 76% and 55%, respectively for strength and modulus over the neat nylon. We also notice a loss in fracture strain in this case. But still it is around 30% which is considerably high compared to other fibers. Again, the stiffening of the filament and reduction in fracture strain suggest that bonding at the silica-nylon interface has increased.

5 FTIR Characterization

In order to determine the development of various functional bonds during polymerization, Fourier Transform Infrared (FTIR) Spectroscopy was performed. FTIR is most useful for identifying chemical bonds that are either organic or inorganic, and its absorption spectrum is almost like a molecular fingerprint. FTIR experiment with nylon 6 and functionalized silica nanoparticle is shown in Fig. 4. Three curves are shown in Fig. 4; a) neat nylon, b) nylon with 1 wt% SiO₂, and c) nylon with 1 wt% functionalized (siled) SiO₂. Three basic bonds of nylon 6, i.e., amide N-H @ 3297 cm⁻¹, hydroxyl O-H @ 2800-3000 cm⁻¹, and carbonyl C=O @ 1637 cm⁻¹ were of primary interests. It is seen in Fig. 4(b) that IR absorbance for each of the three basic bonds has increased significantly characterized by their sharper and higher peaks. Higher peak corresponds to higher absorption of light energy required for excitation.

In other words, the IR absorbance is a direct measure of bond strength indicating that SiO₂ infusion into nylon was responsible for such increase in bond strength. On the other hand after functionalization of SiO₂ particles, it is seen in Fig. 4(c) that three basic bond strengths are somewhat suppressed, but a siloxane Si-O-Si bond @1090 cm⁻¹ is formed which was not seen with 4(a) or 4(b). This is what we expected from functionalization. It is believed that the increase in the bond strength of the three functional groups is due to catalytic effects triggered by the presence of silica nanoparticles. It is also probable that nucleation sites formed surrounding the nanoparticles during polymerization may also influence the bond strength.

6 Theoretical Prediction of Young's Modulus

Basic theory of particle infusion into a matrix has been given as close form solutions in the reference [14]. The formulation is most straight forward and builds upon the original concept given by Mori and Tanaka [15] that a certain average perturbed strain is introduced into the matrix due to the presence of inclusions, and that the perturbed strain correspond to an average perturbed stress. This concept in conjunction with Eshelby's solution [16] of an ellipsoidal inclusion gives rise to a set of equations which can then be solved for unknown elastic moduli, C_{ijkl} of the composite. To determine the longitudinal Young's modulus, E_{11} of the composite, the formulation reduces considerably, and takes a simple form:

$$\frac{E_{11}}{E_0} = \frac{1}{1 + C(A_1 + 2\nu_0 A_2)} \quad (1)$$

Where E_0 and ν_0 are the matrix modulus and Poisson's ratio, respectively, C is the volume fraction of inclusion, and A 's are the parameters that contain Eshelby's tensors given in the reference [14]. Applying the above theoretical prediction to the following set of data shown in Table-2 pertaining to SiO₂-nylon system, we find $E_{11} = 1.11$ GPa using a calculated value of $C = 0.00489$. "C" is calculated from the weight fractions and densities of the matrix and inclusion, respectively. The value of E_{11} is about 21% off from the experimentally observed value of 1.41 GPa of the nanocomposite. The discrepancies in the above theoretical prediction we believe is obvious because of three reasons; the volume fraction of nanoparticles is very low, the formulation does not account for any interaction at the nanoscale, nor does it consider any interface between the particle and the polymer. It is known that the molecular structure of the polymer matrix is significantly perturbed at the inclusion/polymer interface, and this perturbed region is also at the same length scale as that of the reinforcement. Therefore, at the nanometer scale, the polymer and the particle cannot simply be taken as consisting of two phases.

The interaction that occurs at the interphase has been partly accounted by Kerner [17-18] by considering that part of the polymer is bound by filler and as a result, the effective proportion of the inclusion has to increase to C_e ($C_e > C$). According to Kerner [18]

$$C_e = C\left(1 + \frac{\delta}{r}\right) \quad (2)$$

where δ/r is the relative increase in particle diameter as a result of the interaction (the thickness of the surface layer) which may be found from the rheological data or from the comparison of loss modulus of filled (E_c'') and unfilled (E_p'') polymer specimens:

$$\frac{E_c''}{E_p''} = 1 - C\left(1 + \frac{\delta}{r}\right)^3 \quad (3)$$

The original Kerner equation can then be modified to:

$$\frac{E_c}{E_p} = (1 + 1.5C_e)(1 - C_e) \quad (4)$$

According to equation (3), we have performed Dynamic Mechanical Analysis (DMA) tests on neat

and nanophased samples as shown in Fig 5. The ratio of E_c''/E_p'' is around 1.19 as determined from the two peaks shown in Fig 5. Using equations (2) through (4) we calculated the value of E_c to be 1.11 GPa.

It is therefore, observed that both methods predict almost identical modulus and it is considerably lower than what we have found experimentally. We also notice that the predicted values are very close to the lower bounds, $E_c \geq 1.10$ GPa, as defined by micromechanical formulations available in the literature [19]

$$\frac{1}{E_c} \leq \frac{1-C}{E_p} + \frac{C}{E_i} \quad (5)$$

On the other hand, the upper bound on the composite modulus is described in references [19-21] based on principle of minimum potential energy

$$E_c \leq \frac{1-\nu_i-4\nu_i\nu+2\nu^2}{1-\nu_i-2\nu_i^2} E_i C + \frac{1-\nu_p-4\nu_p\nu+2\nu^2}{1-\nu_p-2\nu_p^2} E_p (1-C) \quad (6)$$

and

$$\nu = \frac{(1-\nu_p-2\nu_p^2)\nu_i E_i C + (1-\nu_i-2\nu_i^2)\nu_p E_p (1-C)}{(1-\nu_p-2\nu_p^2)E_i C + (1-\nu_i-2\nu_i^2)E_p (1-C)} \quad (7)$$

where subscripts p and i correspond to polymer and inclusion, respectively. Our calculation according to

equations (6) and (7) shows, $\nu = 0.39$ and $E_c \leq 1.48$ GPa. We see that the experimental value of 1.41 GPa is within 5% of the upper bound.

7 Summary

It is demonstrated that infusion of pristine silica nanoparticles can modestly increase the strength and modulus of nylon. FTIR analysis has shown that mere presence of silica nanoparticles can significantly influence the three primary bonds of nylon 6 which results in 28% and 36% increase in modulus and strength, respectively. Once the silica particles are functionalized, the primary bonds are somewhat suppressed, but a new silane bond is formed which improves the modulus and strength even further to 55% and 76%, respectively. Basic inclusion and micromechanical theories are employed to estimate the modulus and their bounds. It is seen that even with 1 wt% pristine silica infusion we can achieve filament modulus within 5% of the upper bound predicted by micromechanics. Once functionalized, the value of Young's modulus far exceeds the upper bound. It is

also noticed that Young's modulus of the composite predicted by basic theories of inclusion is within the bounds defined by micromechanics but very close to the lower bound.

References

- [1] Kohan MI, editor. "Nylon plastics". John Wiley & Sons, New York 1973, p.3-4.
- [2] Fornes TD, Paul DR. "Crystallization behavior of nylon 6 nanocomposites". *Polymer*, Vol. 44, No. 14, pp 3945-3961, 2003.
- [3] Kim, Young. *Materials Research Society Symposium – Proceedings*. Vol. 740, pp 441-446, 2002.
- [4] Zhang, Wei-De. "Polymer Nanocomposites Using Urchin-Shaped Carbon Nanotube-Silica Hybrids as Reinforcing Fillers". *Macromolecular Rapid Communications*. Vol. 25, No. 21, pp 1860-1864, 2004.
- [5] Jin L, Bower C, Zhou O. "Alignment of carbon nanotubes in a polymer matrix by mechanical stretching". *Applied Physics Letters*, Vol. 73, No. 9, pp 1197-1199, 1998.
- [6] Cooper CA, Ravich D, Lips D, Mayer J, Wagner HD. "Distribution and alignment of carbon nanotubes and nanofibrils". *Composite Science Technology*. Vol. 62, pp. 1105-1112, 2002.
- [7] Thostenson ET, Chou TW. "Aligned multi-walled carbon nanotube-reinforced composites: processing and mechanical characterization". *Journal of Physics*. Vol. 35, No. 16, pp. L77-L80, 2002.
- [8] Gao J, Itkis ME, Yu A, Bekyarova E, Zhao B, Haddon RC. "Continuous Spinning of a Single-Walled Carbon Nanotube-Nylon Composite Fiber". *Journal of American Chemical Society*. Vol. 127, No. 11, pp. 3847.
- [9] Mahfuz H, Adnan A, Rangari VK, Jeelani S. "Manufacturing and characterizing of carbon nanotube/polyethylene composites". *International Journal of Nanoscience*. Vol. 4, No. 1, pp. 55-72, 2005.
- [10] Haggemueller R, Gommans HH, Rinzler AG, Fisher JE, Winey KI. "Aligned single-wall carbon nanotubes in composites by melt processing methods". *Chemical Physics Letters*. Vol. 330, No. 3, pp. 219-225, 2000.
- [11] Mahfuz H, Islam MS, Rangari VK, Jeelani S. "Response of sandwich composites with nanophased cores under flexural loading". *Composites Part B: Engineering*. Vol. 35, No. 6-8, pp. 543-550, 2004.
- [12] Mahfuz H, Adnan A, Rangari V, Hasan MM, Jeelani S, Wright WJ, DeTeresa SJ. "Enhancement of strength and stiffness of Nylon 6 filaments through carbon nanotubes reinforcement". *Applied Physics Letters*. Vol. 88, No. 083119, 2006.
- [13] Mahfuz H, Adnan A, Rangari VK, Jeelani S. "Carbon nanoparticles/whiskers reinforced composites and their tensile response". *Composites Part A: Applied Science and Manufacturing*. Vol. 35, No. 5, pp. 519-527, 2004.
- [14] Tandon GP, Weng GJ. "The effect of aspect ratio of inclusions on the elastic properties of unidirectionally aligned composites". *Polymer Composites*. Vol. 5, No. 4, pp. 327-333, 1984.
- [15] Mori T, Tanaka K. "Average stress in matrix and average elastic energy of materials with misfitting dislocation". *Acta Metall Mater*. Vol. 21, pp. 571, 1973.
- [16] Eshelby JD. *Journal of Mathematical and Physical Sciences*. Vol. 241, No. 376, 1957.
- [17] Lipitov, YS. *Polymer Reinforcement*, ChemTec Publishing, Toronto, Canada 1994.
- [18] Kerner E. *Proc Roy Soc*. Vol. 69B, No. 808, 1956.
- [19] Jones R. "Mechanics of Composite Materials". 2nd edition, Hemisphere Publishing Corporation, New York, USA 1998.
- [20] Paul, B. *Trans. Metallurgical Society of AIME*. pp. 36-41, 1960.
- [21] Halpin, JC, Tsai, SW. *AFML-TR 67-423*, 1969.