Chemical Engineering Communications

MECHANICAL AND THERMAL PROPERTIES OF NANO-AL$_2$O$_3$/NYLON 6 COMPOSITES

Li-Yun Zheng [a] , Kin-Tak Lau [b] , Li-Xin Zhao [a] , Yong-Qiang Zhang [a] &
David Hui [c]

[a] Key Laboratory of Resource Explore Research of Hebei Province,
Hebei University of Engineering, Handan, China

[b] Department of Mechanical Engineering, The Hong Kong Polytechnic
University, Hong Kong, China

[c] Department of Mechanical Engineering, University of New Orleans,
New Orleans, Louisiana, USA

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis
Taylor & Francis Group

Mechanical and Thermal Properties of Nano-Al$_2$O$_3$/Nylon 6 Composites

LI-YUN ZHENG,[1] KIN-TAK LAU,[2] LI-XIN ZHAO,[1] YONG-QIANG ZHANG,[1] AND DAVID HUI[3]

[1]Key Laboratory of Resource Explore Research of Hebei Province, Hebei University of Engineering, Handan, China
[2]Department of Mechanical Engineering, The Hong Kong Polytechnic University, Hong Kong, China
[3]Department of Mechanical Engineering, University of New Orleans, New Orleans, Louisiana, USA

Nano-Al$_2$O$_3$-reinforced monomer casting nylon (NA/MCN) composites were prepared by using in situ polymerization. The average molecular weight of the matrix nylon was measured using gel permeation chromatography. The thermal-mechanical properties of the NA/MCN composites were characterized by thermo-dynamic mechanical analysis, and the results were compared with micro-Al$_2$O$_3$-reinforced nylon (MA/MCN) composites. A tensile property test was conducted to investigate the mechanical properties of neat nylon and composites. Experimental results showed that the average molecular weight of the matrix nylon filled with nano-alumina had little change and was higher than that with micro-alumina. The glass transition temperature (T_g) and storage moduli of NA/MCN composites were higher than that of neat nylon. During the experiment, it was also found that the tensile strength increased up to 52% when 3 wt.% of nano-Al$_2$O$_3$ particles were added. The thermal and tensile properties of NA/MCN composites were better than those of the MA/MCN composites when the same weight percentage of Al$_2$O$_3$ particles was used.

Keywords Dynamic mechanical thermal analysis; Mechanical properties; Nanocomposites; Thermal properties

Introduction

High-performance polymeric composites have been increasingly used for different engineering applications. These composites must provide unique mechanical, thermal, and tribological properties with low specific weight and high resistance to environmental and chemical degradation in order to ensure safety and economic efficiency. Recently, the launch of new airplanes such as the Airbus 380 and the Boeing 787 has proved the maturity of advanced composites in high-level engineering industries.

Monomer casting nylon 6 is a semicrystalline engineering thermoplastic that is known for its combination of strength, modulus, and chemical resistance. It has

Address correspondence to Li-Yun Zheng, Key Laboratory of Resource Explore Research of Hebei Province, Hebei University of Engineering, 199 Guangming South St., Handan 056038, China. E-mail: zhengliyun@126.com

many potential applications in automobiles, household appliances, and other commercial products in which creep resistance, stiffness, and some toughness are demanded in addition to weight and cost savings. The incorporation of inorganic particulate fillers has proved to be an effective way of improving the mechanical properties, particularly the toughness, of nylon. Wilbrink et al. (2001) have addressed the positive effect of $CaCO_3$ fillers for improving the toughness of nylon. However, a significant enhancement of the properties of the nylon was achieved only when the filler volume fraction reached 10–20%. Undoubtedly, at the condition of such high particle volume fraction, the mixing process of nylon composites often becomes difficult due to agglomeration and clustering effect of the particles. On the other hand, as the density of the particles (inorganic filler) is relatively higher than that of the base polymer, the weight of resultant composites therefore increases. Eventually, the competitive advantage of the composites over the traditional polymeric materials is reduced, thus limiting their applications in various industries. To overcome this drawback, a resultant composite with improved properties and lower particle volume/weight fraction is highly desired.

Nanoparticle-filled polymers are attracting considerable attention since they can produce property enhancement that is sometimes even higher than that of conventional filled polymers at volume fractions in the range of 1–5%. A variety of inorganic materials, especially nanoceramic powders such as titanium oxide (TiO_2), zirconium oxide (ZrO_2), aluminum oxide (Al_2O_3), silicon carbide (SiC), and silicon dioxide (SiO_2) (Zhao et al., 2006; Mahfuz et al., 2004; Chen et al., 2004; Chisholm et al., 2005) have been successfully used as additives or reinforcements to improve the stiffness and strength of polymers. Particularly, Wetzel et al. (2003) determined that the addition of a small amount of alumina nanoparticles ($\sim$1–2 vol.%) into epoxy resin can improve its stiffness, impact energy, and failure strain simultaneously. Hasan et al. (2006) have reported that the thermal and tensile properties of nylon could be improved by adding a few percentages of SiO_2 nanoparticles. Li et al. (2005) infused SiO_2 nanoparticles to polyaniline to produce an electrically conductive nanocomposite. The conductivity of polyaniline/nano-SiO_2 composite containing 15% polyaniline reached $0.32\,S\,cm^{-1}$ at 25°C. At this level, it can potentially be used in commercial applications as filler for electromagnetic shielding materials and conductive coatings.

This article reports the synthesis, fabrication, and characterization of nylon 6 filled with Al_2O_3 nanoparticles. The average molecular weight of the matrix nylon was measured using gel permeation chromatography (GPC) to explore the effect of the fillers on the polymerization of nylon. The tensile property test and dynamic mechanical analysis (DMA) of neat nylon and composites were conducted to evaluate mechanical and thermal performance of resultant composites, respectively. To investigate more comprehensively the integrity of the composites, their fracture surfaces were investigated through scanning electron microscopy.

Experimental Methodology

Materials

Nano-alumina and micro-alumina (Al_2O_3) particles were obtained from Nanjing High Technology Nano Co., Ltd. Nano-Al_2O_3 particles had the following characteristics: (i) the average diameter of grain was approximately 80 nm and (ii) specific

surface area was less than $10 \, m^2 \, g^{-1}$; the average diameter of micro-Al_2O_3 particles was $0.5 \sim 2.5 \, \mu m$. All nano-Al_2O_3 particles were treated with surface modifiers, a silane coupling agent, γ-aminopropyltriethoxysilane, prior to use. Caprolactam (CL), sodium hydroxide (analytical grade), and toluene diisocynate (TDI) were used as the monomer, catalyst, and activator, respectively.

Processing

Nano-Al_2O_3-reinforced monomer casting nylon (NA/MCN) composites were prepared by using an impregnation solution plus an in situ anionic polymerization process. The Al_2O_3 contents of the composites were 1, 2, 3, and 4 wt.%. The nanometer powder was treated with a surface modifier to reduce the reunion of nanometer grain and synthesize composite with high relative molecular mass and nanometer grain, allowing improved dispersal in the matrix. First, nano-alumina and caprolactam were melted and ground with zirconium balls of diameter 1.0–1.1 μm at 90°C for 0.5 h, using an oil bath to control grinding temperature. Then the silane coupling agent was added during the grinding process of the nano-alumina and caprolactam. After 2 h, they were filtered. Second, the mixture of nano-alumina and caprolactam was heated and vacuumed in a flask, and NaOH and TDI were added in turn to prepare caprolactam-active materials, while the mold was preheated at 140°–160°C for 90 min. Third, the caprolactam-active materials affiliated with nano-Al_2O_3 were cast into the preheating mold. After in situ polymerization at 170° ± 5°C, followed by the cooling and unloading of the mold, the NA/MCN composites were obtained. At the same time, the composites filled with micro-Al_2O_3 particles (MA/MCN) were prepared for comparison with the result obtained from the NA/MCN composites.

Testing

The molecular weight of the matrix nylon was measured by using a Walters 515-410 gel permeation chromatograph (GPC). The GPC analysis conditions were room temperature, solvent and mobile phase m-cresol/chloroform in the volume ratio 1/9, column temperature at 35°C, injected sample volume 100 μL, flowing rate 1.01 mL/min, and standard sample nylon 6.

In order to investigate the thermal stability of the neat nylon and NA/MCN and MA/MCN composites, DMA was performed with a DMA 2980 TA instrument. Samples 60 mm long, 13 mm wide, and 2.2–2.4 mm thick were made and tested in a three-point bending mode (span length 50 mm) at fixed frequency (3.33 Hz), at the heating rate of 3°C min^{-1}. Storage (elastic) modulus E′ and tan(δ) (damping or loss factor) were recorded as a function of temperature. The glass transition temperature (T_g) was determined from corresponding peak top temperatures seen in the tan(δ) curves.

The tensile property test was carried out according to ASTM D638 standard. Three types of specimen, namely neat nylon and MA/MCN and NA/MCN composites, were tested. In order to capture more accurate results, at least ten samples of each specimen were tested. After the test, the fracture surfaces of the NA/MCN and MA/MCN composites were examined using a JEOL JSM 6360 scanning electron microscope (SEM).
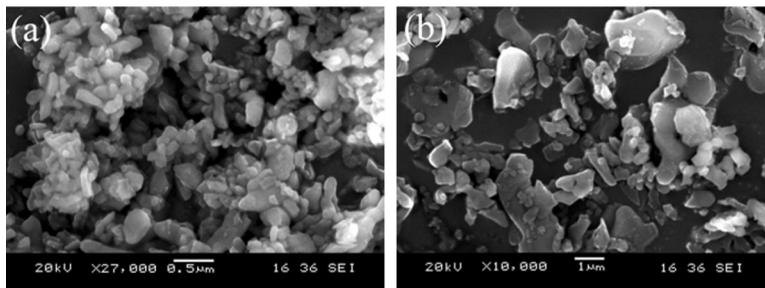
Figure 1. Morphologies of (a) nano-Al_2O_3 and (b) micro-Al_2O_3 particles.

Results

Morphologies of Al_2O_3 Particles

Figure 1 shows the morphologies of nano-Al_2O_3 and micro-Al_2O_3 particles. It can be seen that the size of nano-Al_2O_3 is well proportioned while micro-Al_2O_3 is uneven.

Molecular Weight of the Matrix Nylon

Table I shows the number-average molecular weight (M_n) and mass-average molecular weight (M_w) of the matrix nylon, as determined by GPC. It can be seen that the average molecular weight of the matrix nylon filled with micro-alumina was lower than that of neat nylon and the matrix nylon filled with nano-alumina. In general, the filler in the composite system results in a decrease of the average molecular weight of the polymer matrix (Li et al., 2002) due to its blocking effect on polymerization. In this research, however, the average molecular weight of the matrix nylon filled with nano-alumina had little change and was higher than that of neat nylon when the filler content was 3 wt.%. This is due to the nano-alumina being spread around with caprolactam, which was melted as a decentralization medium, adding the silane coupling agent for surface treatment during the decentralization process. After the decentralization process of the nano-alumina in caprolactam liquid, the mixture of nano-alumina and caprolactam was filtered and used to make caprolactam-active materials and polymerize in situ. During the polymerization, the nano-alumina acted as the nucleation center and improved the interaction between nano-alumina and the polymer segments, resulting in no restraint for polymerization. Therefore, a proper dispersion of the modified nano-alumina in

Table I. Average molecular weight of the matrix nylon

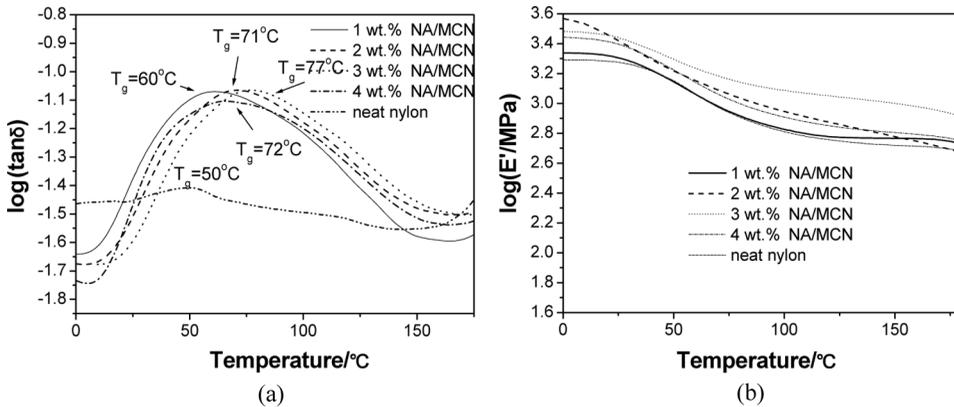| Specimen	Al_2O_3 particle content	M_n ($\times 10^4$)	M_w ($\times 10^4$)	M_w/M_n
1	0	3.13	5.26	1.68
2	1 wt.% nano-Al_2O_3	3.12	5.37	1.72
3	2 wt.% nano-Al_2O_3	3.15	4.8	1.52
4	3 wt.% nano-Al_2O_3	3.19	5.28	1.66
5	4 wt.% nano-Al_2O_3	3.10	4.83	1.56
6	2 wt.% micro-Al_2O_3	2.91	3.93	1.35
7	3 wt.% micro-Al_2O_3	2.88	4. 2	1.46

Figure 2. (a) Log(tan(δ)) and (b) storage modulus vs. temperature curves of neat nylon and NA/MCN composites.

composites can be formed, and the nano-alumina had good effect on the polymerization. Thus, the molecular weight of the matrix nylon filled with nano-alumina was higher than that of neat nylon.

Thermo-Mechanical Properties

The thermal stability of as-fabricated nanocomposites and neat nylon was characterized by DMA. Figure 2(a) shows the log(tan(δ))-temperature curves of neat nylon and NA/MCN composites. In the present study, the derivative peaks are considered as the glass transition temperature (T_g). The T_g values of NA/MCN composite samples with 1, 2, 3, and 4 wt.% Al_2O_3 are 61.5°C, 71.2°C, 77.5°C, and 72°C (Table II), respectively, whereas for neat matrix it is 50°C. This indicates that the T_g of NA/MCN composites was influenced by the addition of Al_2O_3 particles. An optimal percentage should exist, which is reflected in the curves of T_g gradually increasing and then decreasing with continuous increase of the weight percentage of the particles. This phenomenon may be attributed to a strong adhesion between aluminum dioxide and the surrounding matrix, which formalizes interfacial strength against movement of main chain segment in the uncrystal area of nylon. Therefore, the enhancement of T_g indicates better interfacial properties between nanoparticles and matrix. In

Table II. Effect of Al_2O_3 particles on glass transition temperature and maximum of tan(δ)

Specimen	Al_2O_3 particle content	T_g (°C)	$(\tan \delta)_{max}$	Increase of T_g/%
1	0	50	0.03909	0
2	1 wt.% nano-Al_2O_3	61.5	0.08506	23
3	2 wt.% nano-Al_2O_3	71.2	0.08597	42
4	3 wt.% nano-Al_2O_3	77.5	0.08598	55
5	4 wt.% nano-Al_2O_3	72	0.08296	44
6	2 wt.% micro-Al_2O_3	60.1	0.08164	20
7	3 wt.% micro-Al_2O_3	67	0.0792	34

addition, with the same amount (weight percentage) of Al_2O_3 particles in NA/MCN and MA/MCN composites, the T_g of MA/MCN composite was relatively lower than that of NA/MCN composite.

Figure 2(b) shows the $log(E')$-temperature curves of neat nylon and NA/MCN composites. It can be seen that the storage moduli of the nanocomposites were higher than that of the neat nylon and increased with rising filler content. And then the storage moduli of the nanocomposites decreased when the filler content was higher. The rise range of the storage moduli was the biggest (temperature $>25°C$) when the nano-alumina content was $3 \, wt.\%$. The reason may be that the nano-alumina after surface treatment and decentralization in caprolactam not only had good interfacial interaction with nylon matrix but also was well dispersed in the nanocomposites. This contributed to the higher storage modulus.

Figure 3 shows the $log(tan(\delta))$ and $log(E')$-temperature curves of MA/MCN and NA/MCN composites with 2 and $3 \, wt.\%$ Al_2O_3 particles. Figure 3(a) shows that T_g of the NA/MCN and MA/MCN samples with $2 \, wt.\%$ and $3 \, wt.\%$ Al_2O_3 particles are $71.2°$ and $50.1°C$, and $77.5°$ and $67°C$, respectively. On one hand, although the weight contents of Al_2O_3 particles of NA/MCN and MA/MCN composites (specimens 3 and 6, and specimens 4 and 7) were the same, the total surface bonding area, which governs the surface energy of NA/MCN composites, was relatively larger than that of MA/MCN composites. Thus, stronger surface activity and adsorptive capacity can influence the T_g of the NA/MCN composites. On the other hand, the nano-Al_2O_3 has very large specific surface area and lots of hydroxy groups; it had strong interaction with nylon molecule chain. Impeded chain mobility is possible if the nanoparticles are well dispersed in the matrix. Good adhesion of nanoparticles with the surrounding polymer matrix would additionally benefit the dynamic modulus by hindering molecular motion to some extent. The hard particles incorporated into the polymer would act as additional virtual network nodes. Therefore, the T_g of NA/MCN composites increased.

In Figure 3(b), it can be seen that the storage moduli of NA/MCN composites were higher than that of MA/MCN composites, which indicates that good interfacial adhesion between the nano-alumina and the matrix nylon also contributes to the average storage moduli of composites
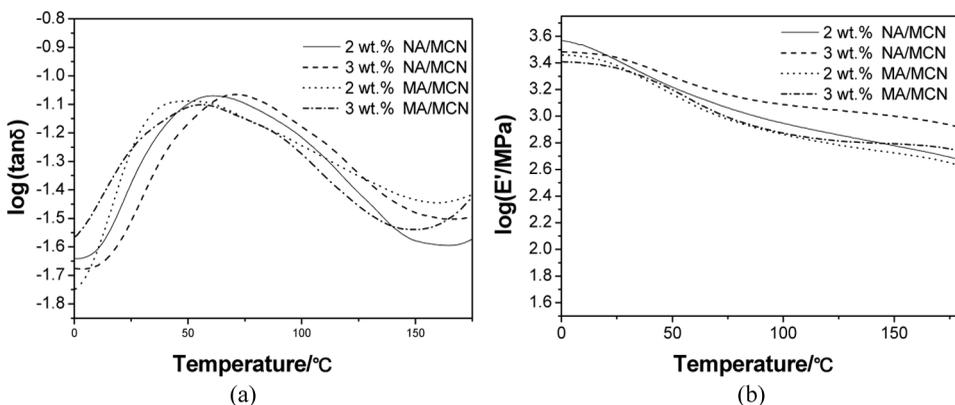

Figure 3. (a) $Log(tan(\delta))$ and (b) $log(E')$-temperature curves of NA/MCN and MA/MCN composites.

Tensile Strength

Figure 4 shows the tensile strength and fracture elongation of NA/MCN and MA/MCN composites and the strain-stress curves of neat nylon and NA/MCN composites. It can be seen that the tensile strength and fracture elongation of NA/MCN composites increased and then decreased with increasing content of nano-Al_2O_3. The reason is that there existed very strong interaction between the nano-Al_2O_3 particles and the matrix nylon. At the same time, the nanoparticle also drove the other macromolecule chain, which has strong interaction with it in one end and combines with another nanoparticle in the other end. Thus the fracture elongation of the NA/MCN composites increased. But when the content of nanoparticles increased to a certain value, this strong interaction increased greatly and the molecule chain was restricted in movement and even could not even slip. Then the fracture elongation decreased.

The tensile strength and fracture elongation of MA/MCN composites decreased with continuously increasing particle content. The higher tensile strengths of nanocomposites are attributed to restricted segmental motions in the neighborhood of organic-inorganic interfaces.
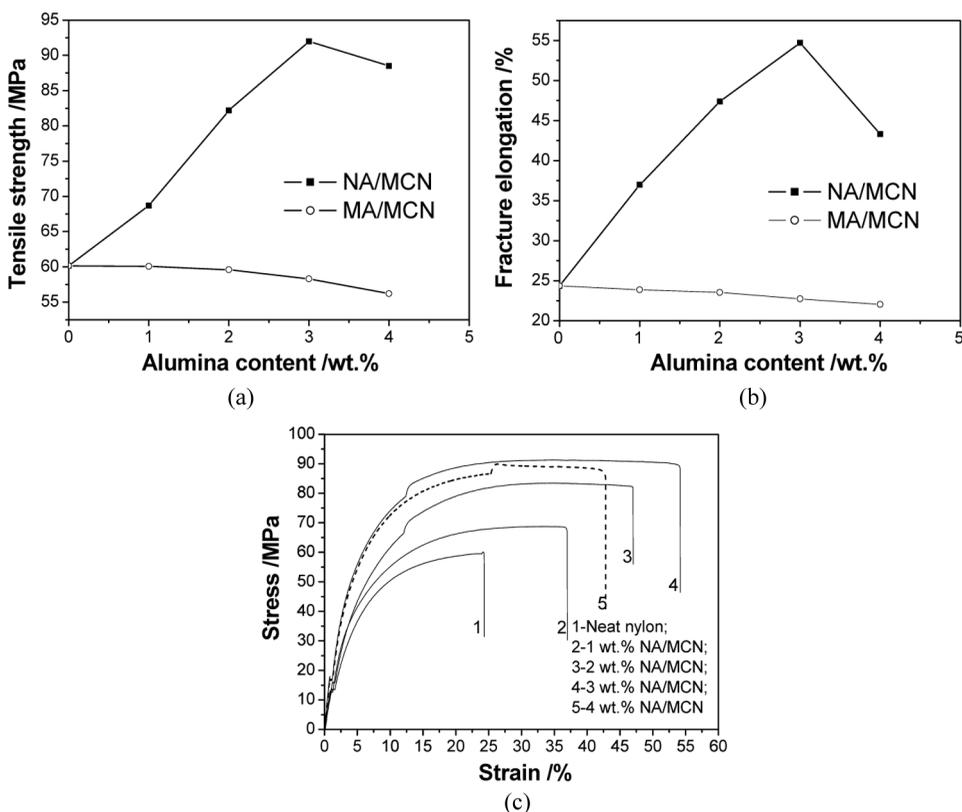

Figure 4. (a) Tensile strength and (b) fracture elongation of NA/MCN and MA/MCN composites, (c) strain-stress curves of neat nylon and NA/MCN composites.
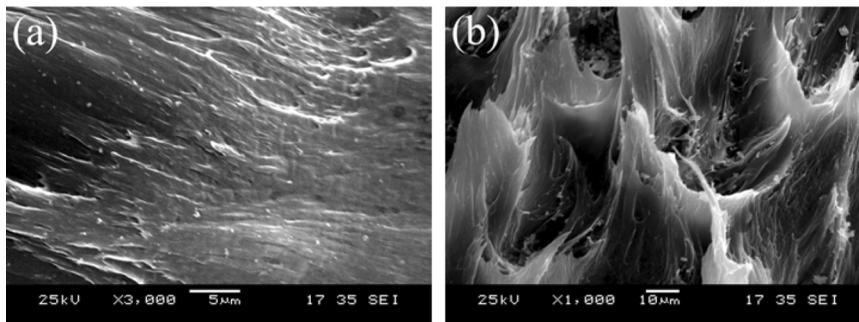
Figure 5. Fracture surface of (a) NA/MCN and (b) MA/MCN composites with 3 wt.% Al_2O_3.

Morphological Studies

To deeply understand their tensile failure behavior, fractographs of NA/MCN and MA/MCN composites were taken using SEM. Figures 5(a) and 5(b) show the fracture surfaces of NA/MCN and MA/MCN composite samples with 3 wt.% alumina particles. Figure 5(a) shows that nano-Al_2O_3 was well dispersed in the matrix. But the particles weren't well distributed in the matrix, and failure was initiated at the micro-Al_2O_3 particle of MA/MCN composites in Figure 5(b).

Conclusions

GPC, thermo-mechanical, and tensile property tests were conducted on neat nylon and NA/MCN and MA/MCN composites. It was found that the average molecular weight of the matrix nylon with nano-alumina was less influenced by the nanoparticles and higher than that filled with micro-alumina. The T_g and storage moduli of NA/MCN composites was apparently higher than that of neat nylon 6 and MA/MCN composites. When the total amount of nano-Al_2O_3 and micro-Al_2O_3 particles are the same as in nylon 6, the thermal and tensile properties of NA/MCN is better than that of MA/MCN. The result from the tensile property test shows that when the nano-Al_2O_3 content was up to 3 wt.%, the highest tensile strength was achieved.

Acknowledgments

References

Chen, G., Luo, G., Yang, X., Sun, Y., and Wang, J. (2004). Anatase-TiO_2 nano-particle preparation with a micro-mixing technique and its photocatalytic performance, *Mater. Sci. Eng.*, **A380**, 320–325.

Chisholm, N., Mahfuz, H., Rangari, V. K., Ashfaq, A., and Jeelani, S. (2005). Fabrication and mechanical characterization of carbon/SiC-epoxy nanocomposites, *Compos. Struct.*, **67**, 115–124.

Hasan, M. M., Zhou, Y., Mahfuz, H., and Jeelani, S. (2006). Effect of SiO_2 nanoparticle on thermal and tensile behavior of nylon-6, *Mater. Sci. Eng.*, **A429**, 181–188.

Li, Y., Yu, J., and Guo, Z.-X. (2002). The influence of silane treatment on nylon 6/nano-SiO_2 *in situ* polymerization, *J. Appl. Polym. Sci.*, **84**(4), 827–834.

Li, X., Wang, G., and Li, X. (2005). Surface modification of nano-SiO_2 particles using polyaniline, *Surf. Coat. Technol.*, **197**, 56–60.

Mahfuz, H., Rangari, V. K., Islam, M. S., and Jeelani, S. (2004). Fabrication, synthesis and mechanical characterization of nanoparticles infused polyurethane foams, *Compos. Part A: Appl. Sci. Manuf.*, **35**, 453–460.

Wetzel, B., Haupert, F., and Zhang, M. Q. (2003). Epoxy nanocomposites with high mechanical and tribological performance, *Compos. Sci. Technol.*, **63**, 2055–2067.

Wilbrink, M. W. L., Argon, A. S., Cohen, R. E., and Weinberg, M. (2001). Toughenability of nylon-6 with $CaCO_3$ filler particles: New findings and general principles, *Polymer*, **42**, 10155–10180.

Zhao, L., Zheng, L., and Zhao, S. (2006). Tribological performance of nano-Al_2O_3 reinforced polyamide 6 composites, *Mater. Lett.*, **60**, 2590–2593.