Effect of functionalizations and concentration of carbon nanotubes on mechanical, wear and fatigue behavior of polyoxymethylene (POM)/carbon nanotube (CNT) nanocomposites

BHANU K GORIPARTHI¹, P.N.E NAVEEN², H.RAVI SHANKAR³ and SOMNATH GHOSH⁴

¹Department of Mechanical Engineering, IIIT RK Valley, RGUKT-AP, India
²Department of Mechanical Engineering, Godavari Institute of Engineering and Technology, Rajamundry, India
³Department of Mechanical Engineering, Central Research Laboratory (CRL), GITAM University, Visakhapatnam, India
⁴Indian Institute of Petroleum and Energy (IIPE), Visakhapatnam 530005, India

*Author for correspondence: Somnath Ghosh, Email: ghoshmnth@gmail.com

MS received

Abstract. The main focus of this work is to improve the mechanical, wear and fatigue behavior of polyoxymethylene (POM) by reinforcing with Carbon Nanotubes (CNTs). In order to improve compatibility between CNTs and POM, the surface of the CNTs was modified by various functionalizations like carboxylation, silanation, carbonylation and amination. The functionalized CNTs were characterized by FTIR spectroscopy to confirm the different functional groups attached to the surface. POM/CNT nanocomposites were developed with functionalized CNTs in different concentrations varying from 0.25wt.% to 2wt.%. Nanocomposites with 1wt.% of silanated CNTs resulted in maximum improvement of tensile, flexural and impact properties. Furthermore, experimental results on fatigue and dry sliding wear tests revealed that the fatigue strength, specific wear rate and friction coefficient are sensitive to functionalization and concentration of CNTs.

Keywords. Carbon nanotubes; Functionalization; silanation; carboxylation; amination; carbonylation; wear; fatigue etc.

1. Introduction

Polymer gears are extensively used in food processing, automobile, aerospace and biomedical industries due to its noiseless performance, oil-less conditions and low cost [1]. Polyoxymethylene (POM) is one among the widely accepted polymer gear material due to its unique properties such as abrasion resistance, low friction coefficient, fatigue resistance, dimensional stability, etc. However, stiffness, fatigue strength and wear resistance of polymer gear material have a detrimental effect on life and load bearing capacity of the gears [2]. In order to widen the range of applicability of the POM gears, these properties need to be enhanced. Improved stiffness and fatigue strength decreases the internal heat generation due to hysteresis effect and the enhanced wear resistance decreases surface temperature generated at the mating gear tooth, which in turn results in increased load bearing capacity and life of the gear. Through the years, many researchers have attempted to improve the life and load bearing capacity of polymer gears by reinforcing the gear materials with fibrous materials (glass fiber, carbon fiber, etc.) and by blending with lubricating additives such as PTFE, MoS₂, etc. A recent trend in polymer research is to explore the synergistic effect of nanoreinforcements in improving the various properties of polymers. Among various nanoreinforcements, carbon nanotubes (CNTs) seem to be a promising alternative for reinforcing polymers due to its excellent mechanical properties, low density, high surface area and high aspect ratio [3-5]. However, the properties of the CNT based nanocomposites strongly depend on the dispersion state of CNTs in the polymer matrix and on the interfacial interaction between CNTs and the polymer matrix [6]. Though, a large quantum of data is available on the polymer/CNT composites with matrices like epoxy, polyamide, polyimide etc, a very little information is available on POM/CNT composites [7-11] due to poor compatibility of POM with other materials.

Dispersion is a challenging issue that needs to be addressed for achieving better mechanical properties of CNT/polymer nanocomposites. Uniform dispersion of CNTs in polymer matrix will result in increase of surface area available for bonding with matrix and also prevents the agglomerations which act as stress concentrators. However, CNTs are difficult to disperse in polymer matrices as they tend to agglomerate and entangle due to their high aspect ratio and van der walls interactions [6]. Apart from dispersion, a strong interfacial bonding between CNTs and the polymer matrix is highly desirable.
as the mechanical properties of the nanocomposites stems from the load transfer capability between the matrix and the reinforcement. The efficiency of load transfer depends on interfacial bonding between the CNTs and the polymer matrix. But, the non reactive nature of the CNTs will cause weak interfacial adhesion with the matrix which in turn impedes the efficient load transfer between matrix and reinforcement [12]. Hence, in order to overcome these two key challenges, the surface of the CNTs has been modified by various chemical functionalization methods. However, very few works were reported on functionalized CNT reinforced POM composites. Moreover, the effect of various functionalizations of CNTs on wear and fatigue behavior of CNT reinforced composites is seldom found.

Zhai and Ye [9] enhanced the dispersion and affinity of multiwalled nanotubes with POM by functionalizing nanotubes with PEG-substituted amine. Functionalized CNT/POM composites exhibited notable improvement in mechanical and thermal properties. Hong et al. [13] dispersed pristine and carboxyl (-COOH) functionalized multi walled CNTs into epoxy resin using three roll mill. Carboxylic functionalization has resulted in significant improvement of the modulus as compared to pristine CNTs. Zhao et al. [14] incorporated carboxylated and pristine CNTs into PA6 via in-situ polymerization. At 0.5wt.% of CNTs concentration, tensile strength was increased by 7.6% and 8.2% respectively for pristine CNT/PA6 composites and carboxylated CNT/PA6 composites as compared neat PA6. Kim et al. [15] studied the effect of oxidation and amine functionalization on the fracture toughness of epoxy composites. Amine functionalized composites have exhibited higher fracture toughness as compared to oxidized and pristine CNT composites. Grafting of silane coupling agent on to CNTs surface has improved the dispersion along with mechanical and thermal properties as compared to pristine CNT nanocomposites [16]. Liu et al. [17] prepared PA6/acid-modified CNTs by using melt compounding. A uniform dispersion and strong interfacial adhesion of acid treated CNTs with PA6 were reported. Strength and modulus were found to be significantly improved by approximately 124% and 115% respectively with incorporation 1wt. % of acid treated CNTs. Meng at al. [18] studied the effect of acid and diamine modification of CNTs on mechanical properties of polyamide6/CNT nanocomposites. They found a significant improvement in young’s modulus, yield strength and storage modulus with the incorporation of diamine modified CNTs in PA6. Ma et al. [19] showed that amine modified CNTs had better dispersion and strong interfacial adhesion with Polyimide matrix as compared to raw CNTs. Cui et al. [20] investigated the effect of grafting carboxylation and amino groups on the CNTs on the wear behavior of CNT/epoxy composites. At all the weight fractions considered, composites with amino functionalized CNTs has exhibited lowest specific wear rate and friction coefficient as compared to composites with pristine and acid treated CNT. Sulong et al. [21] observed a better tribological behavior for composites with functionalized CNTs as compared to composites with as-produced CNTs. Lee at al. [22] fabricated Ultra High Molecular Weight Polyethylene (UHMWPE)/CNT composites with oxidized and silanized CNTs. The effect of functionalization of CNTs on wear behavior is investigated through wear tests. The silanized UHMWPE/CNT composites exhibited lower specific wear rate and coefficient of friction as compared to UHMWPE/ oxidized CNT and UHMWPE/ raw CNT composites. Zhang et al. [23] observed that the fatigue crack growth can be reduced significantly by improving the dispersion of CNTs. Reviewing the literature, it can be understood that the surface modification of CNTs has often led to better dispersion of CNTs in the polymer matrix and improved the interfacial bonding between matrix and CNTs. This in turn has resulted in the enhancement of mechanical properties of CNTs based polymer nanocomposites. However, the effect of various functionalizations on CNT/POM composites is seldom found. Nevertheless, for a given polymer, identification of effective surface modification is a key challenge and hence investigating the effect of various functionalizations of CNTs on the same polymer matrix is very important. Hence, an attempt is made to indentify an effective CNT functionalization so as to improve the mechanical properties, fatigue strength and wear resistance of POM, with an ultimate objective to enhance the life and load bearing capacity of POM gears. In the present work, POM/CNT composites were developed by melt compounding using a twin screw extruder. In order to achieve better dispersion of CNTs in the POM and to improve the interfacial bonding with POM matrix, surface of the CNTs was modified by various methods like carboxylation, silanation, carbonylation and amination. Spectral analysis is carried out to ensure the surface modifications of CNTs. Tensile, flexural, impact, wear and fatigue behavior of the developed nanocomposites were investigated to assess the influence of various functionalizations.

2. Experimental
2.1 Materials
Polyoxymethylene (POM) copolymer (also popularly known as polyacetal), the most commonly used engineering thermoplastic was used as base material in this work. Granular POM copolymer with a trade name of Kocetal K 700, supplied by Kolon Engineering Plastics, USA, was utilized in this study. Multiwalled carbon nanotubes (CNT), supplied by Sky spring Nano Inc.,
USA, with outer diameter of 20-30 nm and length of 10-30 µm were used in this work for reinforcing POM. CNTs are synthesized from natural gas via catalytic chemical vapor deposition technique. For functionalization of CNTs, hydrochloric acid, sulfuric acid, nitric acid, ethanol, distilled water, thionyl chloride, acetone and ethylene diamine (EDA) were purchased from Lotus Enterprises Ltd., India. Silane coupling agent 3-aminopropyltrimethoxy silane (ATPS) was procured from TCI Chemicals, Japan.

2.2 Methods

2.2a Functionalization of MWCNT

In order to obtain a uniform dispersion of CNT in the matrix and to achieve the better compatibility of CNT with matrix, surface modifications of CNT were done by using various methods like carboxylation, silanation, carbonylation and amination. The procedure carried out for these surface modifications is detailed in the following sections.

2.2b Purification of MWCNTs

Initially, CNTs were purified in two stages to remove the amorphous carbon and other impurities. As received CNTs were calcinated at 500oC for 45 minutes to remove volatile gases and other impurities. After calcinations, calcined CNTs were dispersed in a mixture of concentrated HCl and distilled water (1:1 by volume) and stirred for 5 hours using a magnetic stirrer. Then the suspension was allowed to settle for 24 hours and after removing these impurities, the suspension was washed thoroughly with distilled water and vacuum filtered using 0.22 µm micron PTFE membrane until pH value of 7 was attained. The filtered solid was dried in a vacuum oven and is referred as R-CNTs hereafter.

2.2c Carboxylation

R-CNTs were oxidized with a mixture of concentrated sulfuric acid and nitric acid (3:1 by volume). For this purpose, R-CNTs were refluxed in a 3:1 mixture of H2SO4:HNO3 at 90oC for 8 hours. After refluxing for eight hours, the resulting suspension was diluted with distilled water and vacuum filtered repeatedly until the pH value of 7 was attained. The sample was then dried in vacuum oven at 60oC for 12 hours. The solid lumps obtained after drying were ground into fine powder using mortar and pestle. Acid treated CNTs are referred as C-CNTs hereafter.

2.2d Silanation

For silane modification of CNTs, acid treated CNTs (C-CNTs) were dispersed in solution of ethanol/water (95:5 by volume) consisting of 2% 3-aminopropyltrimethoxy silane. The mixture was sonicated and aged with stirring for 4 hours. The resulting silanized CNTs were separated by vacuum filtering using acetone and water and was dried in vacuum oven at 60oC for 12 hours. Silanized CNTs are referred as S-CNTs.

2.2e Carboxylation

In this process, C-CNTs were suspended in thionyl chloride (SOCl2) and then refluxed for 24 hours at 65oC. Then the suspension was vacuum filtered using 0.22µm Millipore PTFE membrane and dried in a vacuum oven for 12 hours at 60oC. These CNTs are hereafter referred as T-CNTs.

2.2f Amination

In amination process, T-CNTs were suspended in ethylene diamine and refluxed at 60oC for 24 hours. Later the suspension was vacuum filtered using 0.22µm Millipore PTFE membrane and dried in a vacuum oven for 12 hours at 60oC. Aminated CNTs are hereafter referred as A-CNTs. The figure 1 shows the schematic representation of the functionalization of CNTs.

2.2g Preparation of POM/MWCNT composites

Prior to the preparation of POM/CNT nanocomposites by melt compounding followed by injection molding, POM and CNTs are dried in vacuum oven at 60oC for 12 hours to ensure the removal of moisture if any. Initially to assess the effective functionalization among the various methods considered in this, nanocomposites with constant weight fraction (i.e. 0.5wt.%) of various functionalized CNTs were developed. In order to the study the the effect of CNTs weight fraction, nanocomposites with varying weight fractions of silanized CNTs (0.25%, 0.5%, 1%, 1.5% and 2%) were developed. CNTs were melt blended with POM using DTS 25 twin screw extruder with a barrel diameter of 25mm and L/D of 32. Before melt compounding, desired quantity of POM and CNTs were pre-mixed thoroughly in a high speed mixer. Then this mixture is fed through the throat of the extruder. The temperature along the barrel was set between 180oC to 190oC and screw speed was set at 100 RPM. The extrudate was obtained in the form of cylindrical rod and was subsequently cooled in a water bath before cutting into pellets using pelletizer.

After melt compounding, all the batches were dried overnight in a vacuum oven at 60oC prior to injection molding. All the batches were injection molded into dumbbell shaped and flat test bars using fully automatic vertical screw type injection molding machine. A molding pressure of 125 MPa, temperature of 180oC, fill time of 5 seconds and cooling time of 20 seconds is maintained during the injection molding process. Table 1 provides the nomenclature and weight fractions of the constituents of the different nanocomposites.

2.3 Characterization

2.3a Spectral Analysis

Fourier transform infrared (FTIR) spectra of purified and surface modified CNTs were recorded to detect new
absorption bands if any during chemical modification. For sample preparation, about 2 mg of the CNTs were mixed with KBr and milled thoroughly until a fine mixture is obtained. This mixture was compressed into pellets and then analyzed using Nicolet 6700 FT-IR Spectrometer. The spectra were recorded with a resolution of 2 cm⁻¹ in the range of 4000-700 cm⁻¹.

2.3b Mechanical Properties

Prior to testing, all samples were conditioned for 48 hours at 50% (± 5) relative humidity and a temperature of 25°C.

2.3c Tensile Properties

Tensile testing was carried out in accordance with ASTM D 638-08 (Type I), a standard test method for determining tensile properties of plastics. A universal testing machine INSTRON 8801 equipped with 100 KN load cell was used to perform the tensile tests. All the tests were conducted at a stress ratio of 0.3 and the maximum applied stresses ranged between 20%-50% of the static strengths. Three replicate tests were conducted for each stress level to obtain reliable experimental data.

2.3d Flexural properties

Flexural testing was performed using INSTRON 8801 universal testing machine in accordance with ASTM D 790 standard. All tests were carried out in 3-point bending mode with a span length of 48 mm and a cross head speed of 2 mm/min. The tests were repeated for six samples, and their mean values were reported along with standard deviations.

2.3e Impact Testing

Notched Izod impact strength was measured using Tinius Olsen Impact tester according to ASTM D 256. Specimens having dimensions of 63.5 x 12.7 x 3 mm³ with a notch angle of 45° and V-notch depth of 2.54 mm was used for carrying out the tests. Ten samples from each category were tested to determine the mean value.

2.3f Fatigue Properties

Fatigue tests were performed on composites A, B, D, H, and P using Instron 8801 in Tension-Tension regime. The fatigue tests were load controlled with a frequency of 5Hz. The wave form of the cyclic loading is sinusoidal. Tension-Tension fatigue testing was conducted at a stress ratio of 0.3 and the maximum applied stresses ranged between 20%-50% of the static strengths. These loading levels were selected to ensure that the fatigue lives of the studied composites were in the range of low cycle fatigue regimes to high cycle fatigue regimes. Three replicate tests were conducted for each stress level to obtain reliable experimental data.

2.3g Wear Tests

Dry sliding wear tests were performed on the developed nanocomposites using a pin-on-disc apparatus to study the wear behavior of the composites. Wear tests were conducted in accordance with ASTM D 3702. Specimens for wear tests having dimensions 3 x 3 x 25 mm³ were cut from the injection molded flat test bars. The abrasion area of the sample was 3 x 3 mm². Wear specimen pin is rotated on a flat steel disc of approximately 10mm thick and 180mm in diameter. The initial surface roughness of the steel counterpart was maintained at 0.25µm for every test. Each specimen was subjected to three different loads (15N, 25N and 35N) and the test was performed at the sliding velocity of 1m/s for 30 mins. During each test, frictional force was measured and recorded into the computer dynamically. The ratio between the frictional force and load applied gives the coefficient of friction. The specimens and disc were cleaned initially before the beginning of each test to remove the adhered impurities, if any. Mass loss of the specimen was measured before and after the test in order to measure the specific wear rate by using the following equation.

\[ W_s = \frac{\Delta m}{F_n L} (\text{mm}^3/\text{Nm}) \]  

Where \( \Delta m \) is the change in weight of the specimen in grams, \( p \) is the density of the specimen in g/mm³, \( F_n \) is the applied load in Newtons and \( L \) is the sliding distance in meters. Three repetitive tests were performed for each specimen and average values were reported for friction coefficient and specific wear rate.

2.3h Morphological studies

In this work, morphologies of tensile fractured surfaces were examined by using Zeiss EVO 50 Scanning Electron Microscope (SEM). SEM was operated with an acceleration voltage of 10kV. Prior to SEM observations, all samples were ion-sputter coated with gold to make them conductive. An Olympus optical microscope with image analyzer software is used to analyze the morphologies of worn surfaces. TEM images of the composites were carried out using TECNAI F 30 transmission electron microscope.
3. Results and Discussions

3.1 Spectral Analysis

Both the raw and functionalized CNTs were characterized by FTIR spectroscopy to confirm the surface modifications of CNTs. FTIR spectra of raw and functionalized CNTs in the region 4000 to 400 cm⁻¹ were presented in Figure 2a-e. The peaks observed for acid treated CNTs (figure 2b) at 3400cm⁻¹ (stretching frequency of –OH) and 1380-1740cm⁻¹ region can be attributed to the C=O stretching vibration of carboxylic group, which means that –COOH functional groups were generated on the CNT surface after acid treatment [24]. In the case of T- CNTs (Figure 2c), a sharp peak at 610cm⁻¹ corresponds to the C-Cl bond stretching vibration, indicating the formation of OH-C-Cl moiety during the treatment of acid treated CNTs with thionyl chloride (SOC12). The spectra of aminated CNTs (Figure 2d) reveal that the peaks at 2838 and 2923cm⁻¹ correspond to stretching vibration of –CH bond. Further, small humps observed at 1035cm⁻¹ and 3450cm⁻¹ may be attributed to -NH bonds, which arises because of CNTs reaction with ethylene diamine. From the spectra of silane functionalized CNTs (figure 2e) a peak can be observed at 1021cm⁻¹, which can be attributed to asymmetric stretching vibration of Si-O-Si bonds due to formation siloxane units during silanization of CNTs [25].

3.2 Tensile and Flexural Properties

The effect of CNTs functionalization on tensile strength and modulus of POM/CNT nanocomposites was shown in figure 3. Reinforcing POM with 0.5wt.% of raw CNTs had resulted in a slight decrease of tensile strength by 2.8% and marginal improvement of stiffness by 9% as compared neat POM. In sharp contrast, reinforcing effect of CNTs is clearly apparent in the case of surface modified CNTs. Tensile strength and stiffness were found to be improved by incorporation of C-CNTs, S-CNTs, T-CNTs and A-CNTs. Among various surface modifications, silanization of CNTs (composite D) had resulted in maximum improvement of tensile strength and modulus by approximately 23% and 38% respectively. As evident from the SEM images (figure 4b-e), improved compatibility between CNTs and matrix as compared to raw CNTs might have resulted in improvement of tensile properties. In case of composites with C-CNTs (figure4b), T-CNTs (figure 4d) and A-CNTs (figure 4e), few pullouts were present indicating moderate adhesion between CNTs and POM. Whereas in the case composites with silanized CNTs, pullouts are hardly seen indicating a strong interaction between CNTs and POM.

Decrease in strength of composite B as compared to POM may be attributed to poor dispersion of raw CNTs in POM matrix and low interfacial bond strength between CNTs and matrix. Significant improvement of tensile properties of POM with incorporation of functionalized CNTs might be attributed of uniform dispersion of CNTs in matrix and improved interfacial adhesion between CNTs and Matrix. TEM images of composite B and D are show in figure 4. As it can be seen from figure 4f, raw CNTs (Composite B) has resulted in densely entangled network indicating non uniform dispersion, while silanized CNTs are uniformly dispersed as shown in figure 4g. Lee et al. [26] reported a similar result, where silane modification of CNTs resulted in increase of interfacial strength between CNTs and matrix.

In order to quantitatively determine interfacial adhesion, interfacial shear strength for composites B, C, D, E and F are evaluated by using pukanszky’s model based on classical Kelly – Tyson equation [27, 28].

\[ A = \frac{\sigma m (B - 2.04)}{\eta \alpha} \]  

where, \[ B = \ln[\sigma r (1+1.25\varphi f)/1-\varphi f]/\varphi f \]  and \( r \) is interfacial shear strength, \( \sigma_m \) is tensile strength of matrix, \( \sigma_c \) is relative strength as \( \sigma_c/\sigma_m \) where \( \sigma_c \) is tensile strength of nanocomposite, \( \eta \) is an orientation factor, \( \alpha \) is aspect ratio of CNT as ration of length to diameter of CNT and \( \varphi_f \) is the volume fraction of CNTs. The computed interfacial shear strengths for composites B, C, D, E and F are -1.81, 6.49, 15.69, 9.69, 12.75 MPa respectively. The negative interfacial shear strength for composite B indicates that the reinforcing effect of raw CNT is zero. Among various functionalizations, silanized CNTs exhibited the maximum interfacial shear strength indicating the effective transfer of applied load from matrix to silanized CNTs by means of shear forces at the interface. Thus, the enhanced interfacial adhesion and uniform dispersion of silanized CNTs in matrix might have be the major reasons for improvement of tensile properties of the Composite D.

The effect of functionalization of CNTs on flexural strength and modulus was shown in figure 5. Unlike to tensile strength, flexural strength marginally improved by 3% in the case of raw CNTs as compared to neat POM. Functionalization of CNTs resulted in improvement of flexural properties. Composites with silanized CNTs exhibited maximum improvement of flexural strength and modulus by 29% and 34% respectively. The effect of CNTs content on tensile and flexural properties of the nanocomposites was shown in figure 6 and 7 respectively. From figure 6 and 7, it can be seen that the tensile and flexural strengths increased with increase in CNT content upto 1wt.%. Beyond 1wt% CNTs, a decline in tensile and flexural strength was observed. In contrast to tensile strength, tensile and flexural modulus of the composites increased with increase in CNTs content. However, beyond 1wt.% CNTs improvement in modulus is marginal. Whereas for
the composites with less than 1wt.% CNTs content (i.e. Composites D, G, H) significant enhancement of modulus is observed with increase in CNTs content. Decline in tensile and flexural strength beyond 1wt.% CNTs may be attributed to non homogeneous dispersion and aggregation of CNTs inside the composite. Overall, incorporation of 1wt.% silanized CNTs in POM has resulted in the enhancement of tensile strength, tensile modulus, flexural strength and flexural modulus by approximately 34%, 46% 43% & 48% respectively.

3.3 Impact toughness

The effect of functionalization and weight fraction of CNTs on the impact toughness is presented in figures 8 and 9 respectively. As seen from the figure 7, the addition of raw CNTs in POM decreased impact toughness by approximately 2%, whereas the nanocomposites C, D, E & F with functionalized CNTs exhibited a moderate increase in impact toughness by 6%, 12%, 7% and 11% respectively. In the case of composites with raw CNTs, decrease in impact toughness may be due to weak interfacial interaction between CNTs and matrix. Due to the weak interfacial interaction, crack propagates at a faster rate and thereby results in lower impact toughness as compared to neat polymer. In the case of composites with functionalized CNTs, relatively strong interfacial interaction between matrix and CNTs offers a tortuous path to the propagation of cracks and thereby resulted in enhancement of impact toughness [29]. Many studies have demonstrated that the improved impact strength of functionalized CNT composites is due to enhanced interfacial bond strength between CNT and matrix [30-33]. The strong interfacial adhesion promotes crack bridging phenomenon and local plastic deformation of matrix which in turn offers more torturous path to crack propagation. Higher strain to failure ratio of CNTs allows the CNTs to bridge the range of crack openings and thereby results in absorbing of fracture energy. If interfacial bond strength is weak, effective crack bridging cannot occur and there by resulting faster crack propagation and lower impact strength. Chandrasekharan et al. [32] reported that, in Epoxy graphene composites, crack path gets deflected whenever the crack tip met the graphene sheet and thereby causing the crack to take tortuous path. Wang et al. [33] observed a substantial enhancement of impact strength of by incorporating functionalized CNTs. The authors attributed the enhancement of impact strength to good CNT matrix adhesion that allows effective load transfer at CNTs crack bridging.

Among the various functionalizations considered in this work, composite D (S-CNTs) exhibited maximum improvement in toughness by approximately 12%. As seen from the figure 10, impact toughness increased with increase in silanized CNTs content up to 0.5wt.%. However, beyond 0.5wt.%, impact toughness becomes more or less saturated, indicating that higher content CNTs would not result in any further increase in impact toughness as there is an increasing chance of agglomerations with increasing CNT content. Significant enhancement of tensile properties is achieved in this work by incorporating 1wt.% Silanized CNTs as compared to the some of the already existing reports [34-39] is presented as table 2.

3.4 Wear

Dry sliding wear tests were conducted on the developed composites at three different loads. The effect of CNTs functionalization on the specific wear rate and coefficient of friction is presented in figures 10 and 11 respectively. From these figures, an increase in specific wear rate and decrease in coefficient of friction can be observed with increase in applied load. Worn surfaces of POM at 15 N load and 35 N load were shown in figures 12a, b respectively. Deep groves formed at 35N load (Figure 12b) as compared to shallow grooves formed at 15N load (Figure 12a) indicate the influence of load on the wear of the composites. Enhanced specific wear rate at higher loads may be attributed to increased real contact area between composite surface and counter surface [39]. As seen from the figure 10, an increase in specific wear rate by approximately 9% and 6% can be observed at 15N load and 25N load respectively. Deep grooves formed at 35N load (Figure 12b) as compared to shallow grooves formed at 15N load (Figure 12a) indicate the influence of load on the wear of the composites. Enhanced specific wear rate at higher loads may be attributed to increased real contact area between composite surface and counter surface [39]. As seen from the figure 10, an increase in specific wear rate by approximately 9% and 6% can be observed at 15N load and 25N load respectively. Deep grooves formed at 35N load (Figure 12b) as compared to shallow grooves formed at 15N load (Figure 12a) indicate the influence of load on the wear of the composites. Enhanced specific wear rate at higher loads may be attributed to increased real contact area between composite surface and counter surface [39]. As seen from the figure 10, an increase in specific wear rate by approximately 9% and 6% can be observed at 15N load and 25N load respectively. Deep grooves formed at 35N load (Figure 12b) as compared to shallow grooves formed at 15N load (Figure 12a) indicate the influence of load on the wear of the composites. Enhanced specific wear rate at higher loads may be attributed to increased real contact area between composite surface and counter surface [39].
coefficient of friction is presented in figures 13 and 14 respectively. Wear rates decreased with increase in CNT content up to 1 wt.% at all the applied loads. Beyond 1 wt.% CNT content, wear rate increased with increase in CNTs content. Decrease in wear resistance at higher CNTs content might be ascribable to the abrasive action of CNT aggregates. As seen from the figure 14, friction coefficient decreased with increase in CNTs content. From the worn surface of composite H (Figure 12e), less number of shallow grooves can be observed as compared to composites D (Figure 12d), indicating the effect of CNTs content on the improvement of wear resistance.

3.5 Fatigue behavior

In order to assess the effect of CNTs functionalizations and content on fatigue behavior, Tension-Tension fatigue tests were carried out on composites A (POM), B (0.5 wt.% R-CNT), D (0.5 wt.% S-CNTs) and H (1 wt.% S-CNTs). Table 2 lists the experimental results of the fatigue tests. Figure 15 shows the relationship between the maximum applied stress and fatigue lives of the studied composites. Fatigue life data were fitted using power law model [41]

\[ \sigma_{\text{max}} = AN^B \]  

(2)

where, A is a fatigue strength coefficient and B is fatigue strength exponent. The constants A and B are given in table 3 and the fitted curves are plotted in figure 16. As seen from the figure 15, addition of 0.5 wt.% raw CNTs has resulted in decrease of fatigue strength. Decrease in fatigue strength with the addition of raw CNTs may be due to the weak interaction between CNTs and matrix. The effect of CNTs functionalization and content on fatigue strength can be observed from the S-N curves of composites D and H. Functionalization of CNTs has resulted in significant improvement in fatigue strength as compared to neat POM and nanocomposite with raw CNTs. Similarly composite with 1 wt.% S-CNTs exhibited more fatigue strength than the composite with 0.5 wt.% S-CNTs. This enhancement might be attributed to strong interfacial bonding between CNTs and matrix.

4. Conclusion

In the present study, tensile, flexural, impact, wear and fatigue behavior of POM/CNTs nanocomposites were studied as a function of CNTs functionalizations and concentration. FTIR spectroscopic studies revealed that, all the functionalization methods used in this study has resulted in modification of CNTs surface. As compared to raw CNTs, functionalized CNTs have resulted in improvement of strength, modulus and impact toughness of the composites. Among various functionalizations, silanized CNTs had higher reinforcing efficiency for POM, which could be ascribed to better dispersion of S-CNTs and stronger interfacial bonding between S-CNTs and POM matrix. Further, it was also found that functionalization and concentration of CNTs have profound influence on wear and fatigue behavior of composites. Nanocomposites with 1 wt.% of S-CNTs has resulted in maximum improvement of wear resistance and fatigue life.

Acknowledgements

The authors would gratefully acknowledge the financial support of the Department of Science and Technology, Government of India for providing financial support to this work.

References

### Table 1: Composites identification and constituent composition

<table>
<thead>
<tr>
<th>Specimen Code</th>
<th>POM (%)</th>
<th>CNTs (%)</th>
<th>Functionalization</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>100</td>
<td>--</td>
<td>Purified</td>
</tr>
<tr>
<td>B</td>
<td>99.5</td>
<td>0.5</td>
<td>Carboxylation</td>
</tr>
<tr>
<td>C</td>
<td>99.5</td>
<td>0.5</td>
<td>Silanation</td>
</tr>
<tr>
<td>D</td>
<td>99.5</td>
<td>0.5</td>
<td>Carboxylation</td>
</tr>
<tr>
<td>E</td>
<td>99.5</td>
<td>0.5</td>
<td>Silanation</td>
</tr>
<tr>
<td>F</td>
<td>99.5</td>
<td>0.5</td>
<td>Amination</td>
</tr>
<tr>
<td>G</td>
<td>99.75</td>
<td>0.25</td>
<td>Silanation</td>
</tr>
<tr>
<td>H</td>
<td>99</td>
<td>1</td>
<td>Silanation</td>
</tr>
<tr>
<td>I</td>
<td>98.5</td>
<td>1.5</td>
<td>Silanation</td>
</tr>
<tr>
<td>J</td>
<td>98</td>
<td>2</td>
<td>Silanation</td>
</tr>
</tbody>
</table>

### Table 2: Comparison study of mechanical properties with the existing works

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Functionalization</th>
<th>Weight fraction</th>
<th>% increase in Tensile properties</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Tensile strength</td>
<td>Tensile modulus</td>
</tr>
<tr>
<td>PI</td>
<td>Acid treatment</td>
<td>7.0%</td>
<td>19</td>
<td>39</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Silane treatment</td>
<td>0.25%</td>
<td>3.6</td>
<td>8.7</td>
</tr>
<tr>
<td>PP</td>
<td>Silane treatment</td>
<td>1%</td>
<td>55</td>
<td>--</td>
</tr>
<tr>
<td>PVC</td>
<td>Silane treatment</td>
<td>1%</td>
<td>26</td>
<td>--</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Silane treatment</td>
<td>1%</td>
<td>50</td>
<td>--</td>
</tr>
<tr>
<td>PA</td>
<td>Di amine treatment</td>
<td>1%</td>
<td>-5.3</td>
<td>6.1</td>
</tr>
<tr>
<td>PE</td>
<td>Amine treatment</td>
<td>1.5%</td>
<td>-17</td>
<td>22</td>
</tr>
<tr>
<td>POM</td>
<td>Silane</td>
<td>1%</td>
<td>34</td>
<td>46</td>
</tr>
<tr>
<td>Composite</td>
<td>Static Strength (MPa)</td>
<td>Stress amplitude level (%)</td>
<td>Maximum stress (MPa)</td>
<td>Mean cycles to failure (Nf)</td>
</tr>
<tr>
<td>-----------</td>
<td>---------------------</td>
<td>---------------------------</td>
<td>---------------------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>A</td>
<td>48.5</td>
<td>50</td>
<td>24.2</td>
<td>3891</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45</td>
<td>21.8</td>
<td>9437</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>19.4</td>
<td>34589</td>
</tr>
<tr>
<td></td>
<td></td>
<td>35</td>
<td>16.9</td>
<td>135677</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>14.5</td>
<td>1000000</td>
</tr>
<tr>
<td>B</td>
<td>47.1</td>
<td>50</td>
<td>23.5</td>
<td>3103</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45</td>
<td>21.2</td>
<td>10349</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>18.8</td>
<td>31993</td>
</tr>
<tr>
<td></td>
<td></td>
<td>35</td>
<td>16.5</td>
<td>128573</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>14.1</td>
<td>1000000</td>
</tr>
<tr>
<td>D</td>
<td>59.9</td>
<td>50</td>
<td>30</td>
<td>5675</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45</td>
<td>26.9</td>
<td>17118</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>23.9</td>
<td>76457</td>
</tr>
<tr>
<td></td>
<td></td>
<td>35</td>
<td>20.9</td>
<td>289421</td>
</tr>
<tr>
<td></td>
<td></td>
<td>32.5</td>
<td>19.5</td>
<td>1000000</td>
</tr>
<tr>
<td>H</td>
<td>65.3</td>
<td>50</td>
<td>32.6</td>
<td>9876</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45</td>
<td>29.3</td>
<td>29419</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>26.1</td>
<td>356391</td>
</tr>
<tr>
<td></td>
<td></td>
<td>35</td>
<td>22.8</td>
<td>1000000</td>
</tr>
</tbody>
</table>
Figure 1 Schematic representation of functionalization of CNTs
Figure 2 FTIR Spectra of (a) Raw CNTs, (b) C-CNTs, (c) T-CNTs, (d) A-CNTs and (e) S-CNTs

Figure 3 Effect of CNTs functionalization on (a) Tensile strength (b) Tensile modulus
Figure 4 SEM Images of tensile fractured surfaces of composites: (a) A [POM only] (b) B [POM+ Raw CNT] (c) C [POM+ C-CNT] (d) D [POM + S-CNT] (e) E [POM + T-CNT] and TEM images of composites: (f) B [POM+ Raw CNT] (f) D [POM + S-CNT]
Figure 5 Effect of CNTs functionalization on (a) Flexural strength (b) Flexural modulus

Figure 6 Variation of (a) Tensile strength and (b) Tensile Modulus with CNTs content
Figure 7 Variation of (a) Flexural strength and (b) Flexural modulus with CNTs content

Figure 8 Effect of CNTs functionalization on Impact toughness
Figure 9 Variation of Impact toughness with CNTs content

Figure 10 Effect of CNTs functionalization on Specific wear rate
Figure 11 Effect of CNTs functionalization of friction coefficient

Figure 12 Worn surfaces of (a) POM at 15 N Load, (b) POM at 35 N Load, (c) Composite B, (d) Composite D and (e) Composite H
Figure 13 Variation of specific wear rate with CNT content

Figure 14 Variation of friction coefficient with CNT content
Figure 15 Fatigue lives of the composites