

Surface Modification of Polymeric Nanocomposites of Poly Ether Ether Ketone and Zinc Oxide for Tribological Analysis in Automobile Applications

Nitin Girdhar Shinde¹, Dilip Mangesh Patel²

¹R C Patel Institute of Technology, Shirpur, Maharashtra, India

²D N Patel College of Engineering, Shahada, Maharashtra, India

Abstract— Reinforced materials are an important class for the studies of friction and wear-related applications. PEEK polymer reinforced by nanosized material can form a new type of composite promised to be energy-saving material. Doped nanomaterials are stronger inorganic than PEEK polymer from a formidable combination of organic and inorganic materials. The synergistic effect can form strong material with new properties. In this work, an attempt has been made to synthesize metal and non-metal dopes ZnO-PEEK nanocomposite by ultrasound method to apply friction and wear-related operations. The material has been characterized by SEM, XRD, EDS, TEM, FT-IR, and UV-DRS techniques. The characterization confirmed the addition of metal into ZnO and fabrication with PEEK polymer. C, N, S doped ZnO and Ni, Co doped ZnO-PEEK composites were analyzed for tribological applications. The metal doping was proved significant to enhance the properties. The prepared materials have been compared. The result obtained from the application was important to synthesize a new kind of material for the application of energy-related operations.

Keywords—Nanocomposites, PEEK, ZnO, Surface Modification, Tribology

I. INTRODUCTION

Generation and efficient use of all types of energy sources is the need of today. Friction and wear-related operations are under observation to minimize energy consumption [1]. Polymeric materials with high performance are increasingly studied for their outstanding performance as a friction material [2]. One of the most used top performing polymers is Poly ether ether ketone (PEEK), attributed to its semi-crystallinity, high thermal and mechanical strength, flexibility, workability, high thermal resisting, and many more [3, 4]. The durability and strength of PEEK is exploited for high vacuum operation indicate the diversity of this low cost yet powerful material. PEEK has diverse attractive properties, and thus extensively used in various parts in automobile

industry, electronic industries, etc. [5, 6, 7].

However, current industrial operations demand more strength with high heat resistance and friction for smooth operation and less energy consumption, and bare PEEK shows limitations in fulfilling these extreme conditions [8, 9]. Recently, work has been done on improving the tribological and thermal properties of PEEK to minimize erosion. Since the material is carbon bases, polymer carbon material enforcement is more common. Moreover, the addition of metal oxides to increase synergism is carried out for the modification of PEEK, and it showed excellent improvement in the performance [10, 11].

Metal oxide incorporated polymer composites show exceptional properties due to interfacial bonding between inorganic and organic species [12]. The spaces between cross-linked polymers are occupied by metal oxides, drastically improving the overall strength of the composite. The strength of the metal oxide imparts strength to the composite, and it is found that reduction in the wear rates enhanced due to inorganic addition in the polymer matrix [13, 14]. The dispersion, orientation, and dimension of oxide of metal is an important factor to improve the overall performance of the composite [15, 16]. The addition of nanosized SiC, TiO₂, Al₂O₃, ZnO, and several other metal oxides have shown remarkable enrichment in the friction characteristics, resulting in a considerably reduction in friction coefficient and rate of wear [17, 18, 19].

The physio-chemical properties of metal oxides can be modified by the inclusion of other metals or their oxide by doping method [20]. Transition metals being highly abundant, low cost, and less toxic, can be utilized for the doping in metal oxides like TiO₂, Al₂O₃, ZnO, etc. Transition metals having variable oxidation states can alter the crystal lattice at the atomic level resulting in more durable material with high crystallinity and less particle size [21,22]. This change in the physical and chemical property, when coupled with polymer matrix, can show improvement in the tribological property [23]. ZnO being less toxic, less costly, and highly available can be a successful addition in polymeric material; moreover, doping of ZnO by transition metals improves the physical properties of composite [24].

In the present work, we report microwave-assisted simple

reinforcement of PEEK by addition of nickel (Ni), cobalt (Co) transition metal modified ZnO metal oxides in which non-metal like carbon, nitrogen, and sulphur (CNS) doped ZnO is compared with nickel, cobalt doped ZnO-PEEK composite for their tribological properties.

II. EXPERIMENTAL

A. Materials

Cobalt nitrate hexahydrate: $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Zinc nitrate hexahydrate: $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and Nickel nitrate hexahydrate: $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, were bought from SD fine, India. Nitric acid (HNO_3), Thiourea, CS (NH_3)₂ (99%), and Polyethyleneglycol-200 (PEG) (99.8%), were purchased from Fischer Scientific, India. Poly ether ether ketone (PEEK) powder size 50 microns was purchased from Merck, India.

B. Synthesis

(a) Synthesis of metal, non-metal doped ZnO:

Cobalt, Carbon, nitrogen, Sulphur doped ZnO was synthesized by hydrothermal method. Initially 1.0 mmol of zinc precursor was added in to 0.1 mmol of nitric acid. Then dropwise 1 ml of polyethyleneglycol-200 was added to clear solution until the dissolution for one hour. Thereafter, calculated amount of nickel nitrate was mixed and then stirred for one hour. Further, 3gms of thiourea was mixed and, then stirred for two hours. The resulting suspension was oven dried at 100°C for twelve hrs. Then black residue was claimed at 550°C after three hours for the rate 10°C per minute to obtain greenish-yellow powder of nickel, carbon, nitrogen, sulphur doped ZnO. To synthesized carbon, nitrogen, sulphur doped ZnO metal precursor was avoided (refer Fig.1). Similarly, all the doped ZnO materials have been synthesized by adding respective metal precursor [25, 26].

(b) Synthesis of metal, non-metal doped ZnO-PEEK nanocomposites:

The synthesized metal, non-metal doped ZnO was fabricated with PEEK polymer by the hydrothermal method with ultrasound assistance in which 0.50 g of nanomaterial was added to 20% ethanol with 0.10 g of PEEK polymer and ultra-sonicated for 3 hours. The suspension the shifted to a stainless steel autoclave with Teflon lining, pH was maintained at 8 and heated at 150°C for 10 h. The suspension then cooled and dried in oven at 100°C for ten hours after filtration, to obtain black PEEK nanocomposite (refer Fig.1) [27].

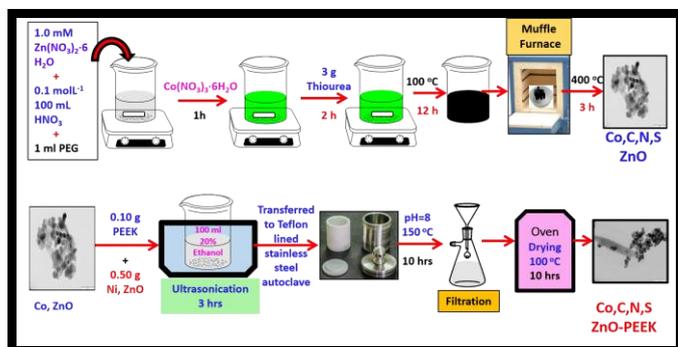


Fig. 1 Synthesis strategy of Co, C, N, S doped ZnO-PEEK nanocomposite

C. Characterization

The XRD (X-ray diffraction) analysis of material was carried out to know crystallinity and phase composition of

material. Transmission electron microscopy (TEM) was carried out to check the fabrication of nanomaterial with PEEK. (SAED), Scanning electron microscopy coupled with EDS analysis was done to obtain surface properties and elemental composition. Fourier transform infra-red spectroscopy (FT-IR) was done to know the functionalities and UV-DRS was carried out to understand the absorption of material.

D. Tribological experimentation

The tribological performance of the synthesized composite samples were examined on a ball on disc tribometer (Make: CETR Model: UMT-5). The tribopair used was a stagnant steel ball and rotating sample of composites. The steel ball was 5.825 mm in diameter with Vickers hardness number 1180. The working load was kept at 5 N for 1-15 minutes with correlative pressure of 62.5 MPa. The speed if slide was 0.15 m/s at 145 rpm. The reciprocating frequency was kept at 2.5 Hz. The force of friction was supervised through a transducer attached to the system. These values of force were further utilized to measure the friction coefficient with the help of equation, Friction of coefficient = (Applied force / Friction force), where applied force and friction force is in newton. The wear volume was determined by weight loss and the density. The wear rate was also calculated by the weight loss. The specified density for PEEK, CNS doped ZnO-PEEK, Ni doped ZnO-PEEK and Co doped ZnO-PEEK was 1.31, 1.41, 1.46 and 1.53 respectively in gm per cubic cm. The wear rate was measured by the formula, Wear Rate = Volume loss / (Load x Erosion distance), here volume loss is in cubic mm, load is in newton and erosion distance in meter [28].

III. RESULTS AND DISCUSSION

A. XRD analysis

A monochromatic Cu $K\alpha$ radiation with high intensity (1.54060 Å) and diffractometer in the 45kV & 40 mA range was used to carry out the study. At 25°C, the data of intensity data were collected in 2θ . The range of 2θ was between 10° to 80°. 0.8709° was the slit size for fixed divergence and 0.017° was the step size for angular slit opening. The XRD spectrums of synthesized nanoparticles with ZnO XRD can be seen in Fig. 2. The trend matches with a greatly crystalline material. This crystallinity is visible from the sharpness of the XRD peaks. Commercial ZnO peaks indexed to (100), (002), (101) observed at 32.72°, 33.65°, 35.39° 2θ represent typical hexagonal wurtzite structure [29]. The (100) and (110) plane indexed to 32.72° and 55.44° 2θ in all the synthesized materials are match with the commercial ZnO representing the presence of hexagonal wurtzite structure in all the synthesized materials [30, 31]. However, (102) peak indexed to 46.83° 2θ in all the structure shows shifting towards lower 2θ indicating the change in crystal arrangement attributed to doping of metal as well as non-metals in the ZnO lattice [32,33]. Change in crystal formation and doping also evident by the absence of (002) and (101) in synthesized martials [34]. The PEEK XRD is given Fig. 3 in which a sharp peak is observed within the range of 5 to 10° 2θ , the similar peak is also present in all the synthesized PEEK nanocomposites in Fig. 2. This belongs to carbon based martials confirm the successful fabrication of nanomaterials with PEEK polymer [35, 36].

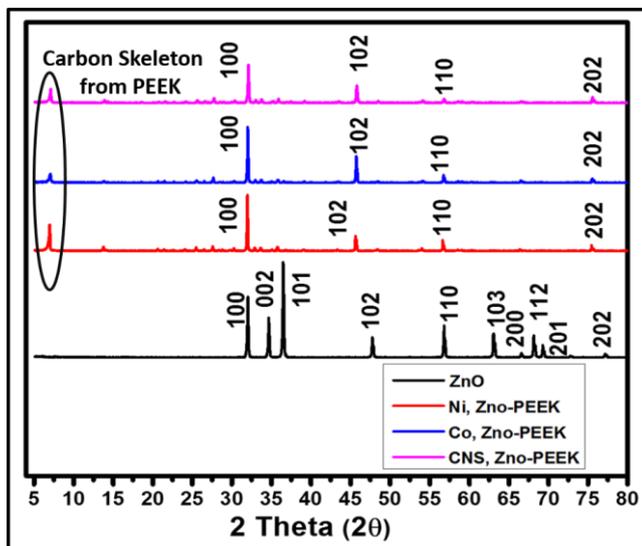


Fig. 2 X-ray diffraction patterns of ZnO, and doped ZnO-PEEK nanocomposites

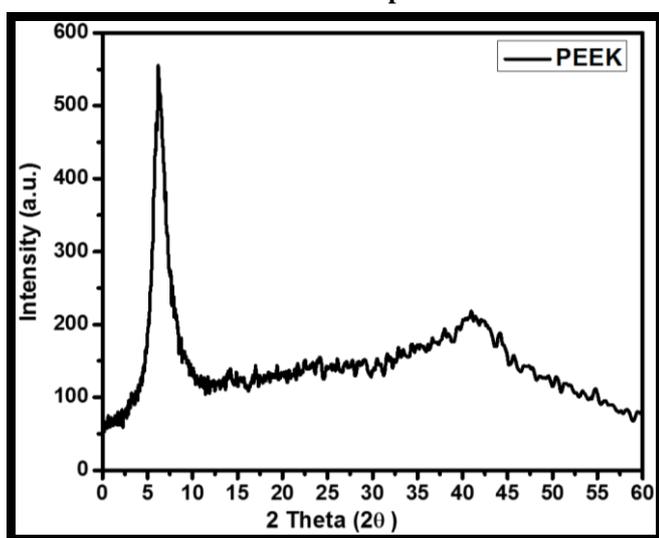


Fig. 3 XRD patterns of PEEK

B. TEM and SAED analysis

TEM analysis of doped ZnO-PEEK nanocomposites was carried out to understand the effectiveness of extent of fabrication of synthesized NP's with PEEK polymer material. Fig. 4 a, c, e shows spherical morphology of C, N, S non-metal, Ni and Co metal doped ZnO NP's. The Fig. 4 b, d, f shows all the NP's are firmly attach to PEEK polymers. The cluster of nanoparticles fabricated with PEEK polymer to form a stable nanocomposite. The polymeric PEEK is visible in the form of small tubes. The heterogeneous nature of composite is an essential factor in the friction and other related properties. The small crystalline structure is evident from small dots in the ring confirming the effective fabrication of NP's with PEEK polymer [37, 38].

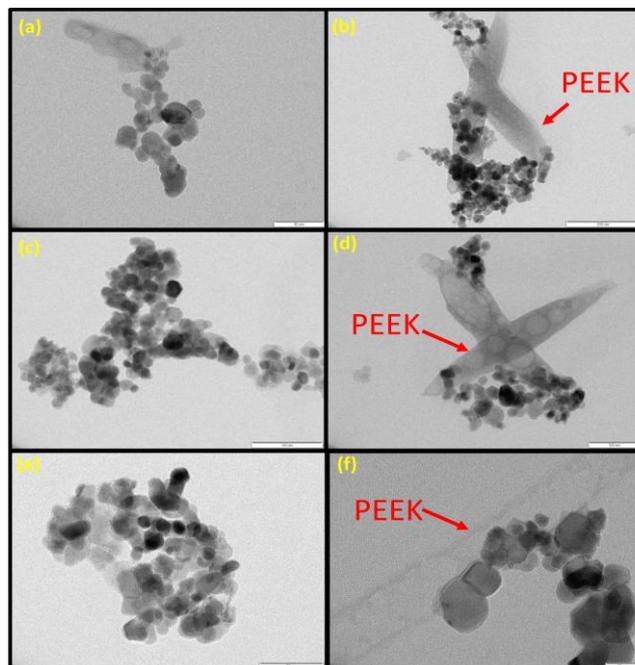


Fig. 4 TEM images of a) CNS doped ZnO nanoparticles b) CNS doped ZnO-PEEK nanocomposite c) Ni doped ZnO nanoparticles d) Ni doped ZnO-PEEK nanocomposite e) Co doped ZnO nanoparticles f) Co doped ZnO-PEEK nanocomposite

C. SEM and EDAX analysis

High resolution Field Emission Scanning Electron Microscope (SEM) was used to analyze synthesized ZnO-PEEK nanocomposite. The SEM image of PEEK in figure 5a shows typical layered carbonaceous morphology which is supported by just carbon and oxygen element in EDAX analysis confirming purity of PEEK material. In figure 5 c, e, g, the CNS, Ni and Co doped ZnO-PEEK shows porous morphology in which doped ZnO NP's are agglomerated in cluster. The surface is amorphous, which is a characteristic feature of carbon based material [39]. The EDAX analysis of nanocomposites are given in Fig. 5 b, d, f, h confirms the absence of impurity in the material and successful incorporation of C, N, S, Ni and Co dopant in ZnO lattice. The presence of PEEK is evident by greater percentage of carbon in all the materials. The weight percentage of nitrogen and sulphur was found 1 to 4% and 3 to 7% respectively. The absence of other metal in the synthesized material confirm the purity of material. However, the extra peaks are appeared due to presence of copper reference during the analysis. [40]. The EDAX analysis again confirm the successful formation of doped ZnO-PEEK nanocomposite.

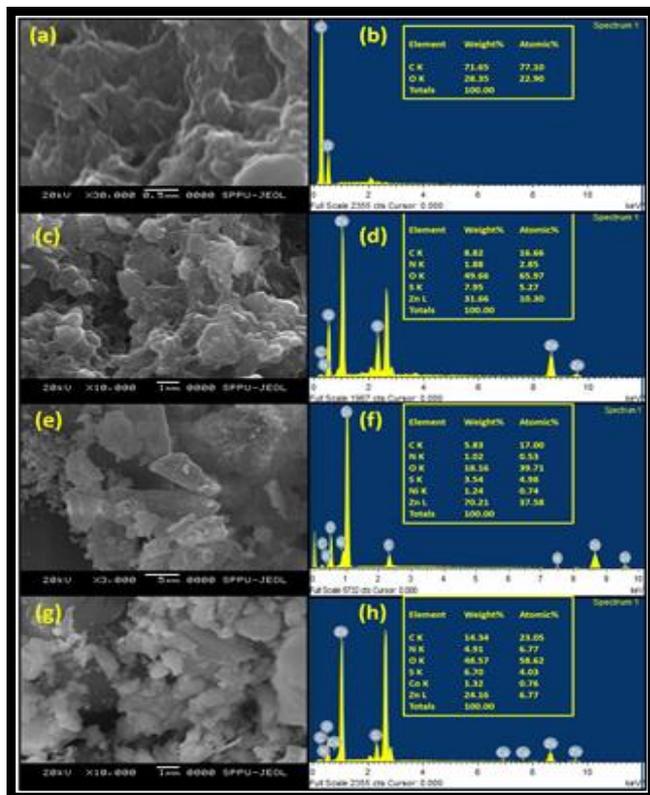


Fig. 5 SEM and EDAX images of a) CNS doped ZnO-PEEK nanocomposite b) Ni doped ZnO-PEEK nanocomposite c) Co doped ZnO-PEEK nanocomposite

D. FTIR Analysis

The functionalities in the synthesized materials are studied by FT-IR spectroscopy. The analysis was kept in between 500-4000 cm^{-1} . FTIR spectrum of the materials is shown in Fig. 6. The bending vibrations of molecules of water is proven by the vast absorption band about 3450 cm^{-1} [41]. The peak in the range of 1620 to 1635 cm^{-1} confirm the presence of C=C which is evident due to polymeric material (PEEK) in the nanocomposite [42]. The presence of C-S and C-N is confirmed by the small peaks within the range of 670 to 720 cm^{-1} [43, 44]. The slight peaks about 750 to 640 cm^{-1} appear due to characteristic metal oxygen bonding which is Zn-O in this case [45]. The FT-IR data confirm the presence of all the metal and non-metal doping with carbon based polymeric material indicate the successful fabrication of doped ZnO-PEEK nanocomposite and 750 to 640 cm^{-1} appear due to characteristic metal oxygen bonding which is Zn-O in this case [46]. The FT-IR data confirm the presence of all the metal and non-metal doping with carbon based polymeric material indicate the successful fabrication of modified ZnO-PEEK nanocomposite.

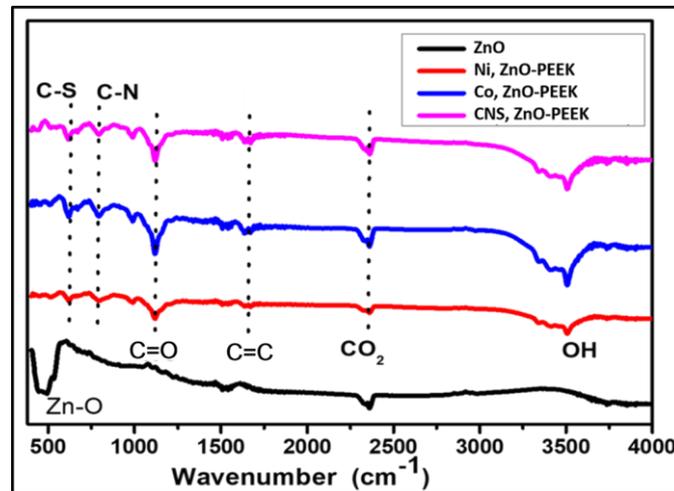


Fig. 6 FTIR spectra of ZnO, and doped ZnO-PEEK nanocomposites

E. UV-Vis DRS Analysis

UV-vis diffuse reflectance spectroscopy (DRS) analysis of all the synthesized materials was carried out. The spectra are shown Fig. 7. The spectra of all the synthesized materials are showing different appearance compared to pure ZnO. The pure ZnO spectra show sharp peak and absorption maxima at 358 nm however, the composites are showing less sharper peaks attributed to the crystallite size and morphology of the material [45]. The sharpness in pure ZnO is due to the small crystallite size and crystalline nature, more the crystals more the absorption and sharper the peak. The peaks of PEEK composites of doped ZnO appear flatter due to the amorphous nature of PEEK polymer confirming the fabrication of inorganic NP's with organic polymeric material [47]. Though the absorption maxima are within the range of 554 to 569 nm the lower absorption in nanocomposite indicate the higher crystallite size which is true due to the addition of polymeric material. The UV-DRS in this case help to confirm the synergism between the NP's and PEEK polymer [48].

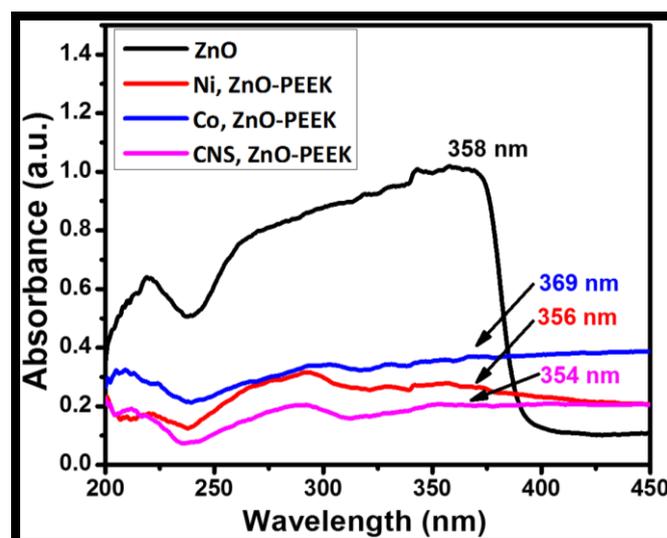


Fig. 7 UV-Vis absorption spectra of ZnO, and doped ZnO-PEEK nanocomposites

F. Friction and wear analysis

In Fig. 8, the average values of friction coefficient of pure PEEK and Ni, Co and CNS doped ZnO-PEEK nanocomposite

are plotted against the time. Without any reinforcement PEEK was on higher side. The average value of friction coefficient for pure PEEK was around 0.45. There was no formation of tribofilm, which might have increased the friction. As polymers are subtler to mechanical stresses, there must be accumulation of friction heat which resulted in increase in the matrix stiffness. The shear strength of polymer also shoots up thus the pure PEEK exhibited displeasing abrasive nature. Such inferior bearing capacity resulted in high value of coefficient of friction [49]. CNS doped ZnO-PEEK nanocomposite shown improvement, probably due to formation of a tribofilm between the ball and sample surface. The average value of coefficient of friction was found around 0.37. With non-metallic CNS doping in ZnO, the structural properties and crystallinity of ZnO enhanced which affected the friction behavior of resulting PEEK nanocomposite as well. The strain produced by virtue of lattice misalliance and variation in coefficient of thermal expansion between the ZnO and non-metals must have increased the friction resistance of nanocomposite [50]. The average value of friction coefficient for Ni doped ZnO-PEEK nanocomposite obtained was 0.31. The mechanical sturdiness between the matrix and reinforcement provided promising aspect ratio. The increased size of ZnO due to Ni doping deteriorated the heat buildup within the tribofilm. Due to such increase in the concentration of ZnO in PEEK, the wear resistance capability of nanocomposite shown improvement and made it less prone to wear [51]. Co doped ZnO-PEEK nanocomposite reveal superior endurance against the wear. The average value of coefficient of friction came by 0.27. The incorporation of hard cobalt in ZnO diminished the straight connection between the PEEK and the abrasive surface. The certain separation of nano metal oxide from polymer matrix plunge into the path of wear and skate over one another. An integrated fine film of oxide has apparently setup. Further, this film acted as coherent lubricant between the two rubbing surfaces. The Co doped nano-ZnO behaved as a third body which imparted solid lubricating ability on surfaces of contact. It resulted in least friction coefficient value [52].

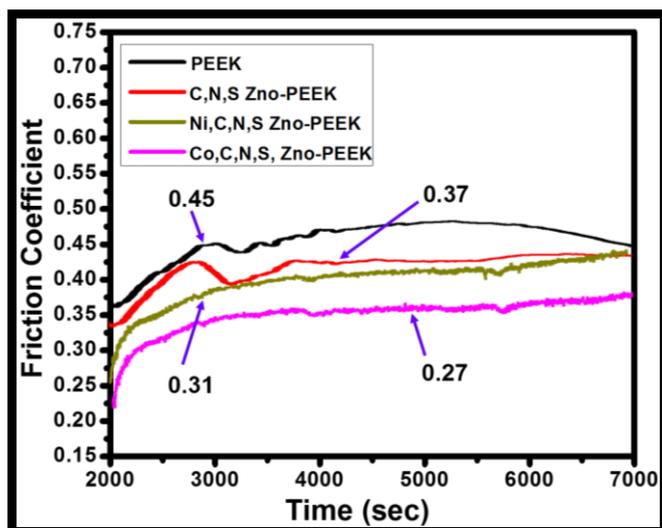


Fig. 8 Coefficient of Friction of PEEK, and modified ZnO-PEEK nanocomposites

In Fig.9, the rate wear of pure PEEK and Ni, Co and CNS doped ZnO-PEEK nanocomposite are presented against the time. The wear rate for pure PEEK obtained was $6.44 \times 10^{-6} \text{ mm}^3/\text{Nm}$. Severe amount of wear can be seen due to absence

of any reinforcement. Molecular adhesion and shatter must have untied the chunks of PEEK causing further erosion. Within the region near contact, the high friction heat depletion may have resulted in immense thermal degradation. Further the substantial strains may have caused the rupture of PEEK [53]. CNS doped ZnO-PEEK nanocomposite shown wear rate as $5.73 \times 10^{-6} \text{ mm}^3/\text{Nm}$. The wear rate was lower than that of PEEK due to double effect of CNS doped ZnO as solid lubricant and reinforcing agent. The embellished distribution of nano-particles clarified the connection between filler nano-particle and the polymer matrix. The slight increase in the hardness may have reduced the wear rate [54]. The wear rate of Ni incorporated ZnO-PEEK nanocomposite was found to be $4.85 \times 10^{-6} \text{ mm}^3/\text{Nm}$. The reinforcement of Ni incorporated ZnO in PEEK exhibited appropriate matrix-filler synergy and even distribution of filler throughout the nanocomposite which provided the stability. The increase in the load bearing capacity of reinforcement prevented the derogation and disintegration of nanocomposite which culminated in reducing of wear rate [55]. Co doped ZnO-PEEK nanocomposite exhibited the lowest wear rate of $2.93 \times 10^{-6} \text{ mm}^3/\text{Nm}$. The harder cobalt improved the anti-sand wear behavior of the nanocomposite. With prolonged wear time, even though the temperature of surface raised, the cobalt nanoparticles impeded the deformation of matrix. During sliding friction the indurate cobalt doped ZnO nanoparticles behaved as a cushion while bearing the load, which restricted the area of contact and subsequently reduced the wear rate. Being compatibilizer, cobalt lessened the interfacial surface tension, and stabilized the nanocomposite making it phase morphologies and least severely worn than the other three materials [56].

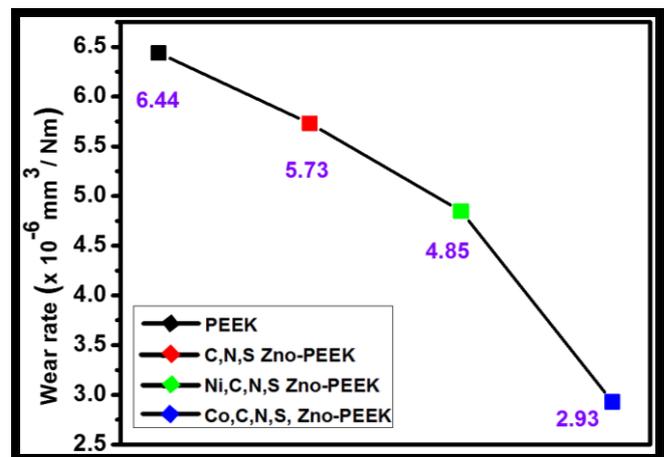


Fig. 9 Wear rate of PEEK, and modified ZnO-PEEK nanocomposites

Fig. 10 represents the histograms indicating the trend of the rate of wear and coefficient of friction of PEEK and modified ZnO-PEEK nanocomposite. The wear rate is gradually decreasing. The pure PEEK shown the highest wear rate of $6.44 \times 10^{-6} \text{ mm}^3/\text{Nm}$ while the cobalt doped zinc oxide-PEEK composition shown the smallest wear rate of $2.93 \times 10^{-6} \text{ mm}^3/\text{Nm}$. The friction coefficient can also be seen reducing gradually. Pure PEEK conceiving the highest value of 0.45 while cobalt doped zinc oxide-PEEK composition showing least value of 0.27. The lower values of wear rate and friction coefficient is an index of favorable wear protection and extended service life [57].

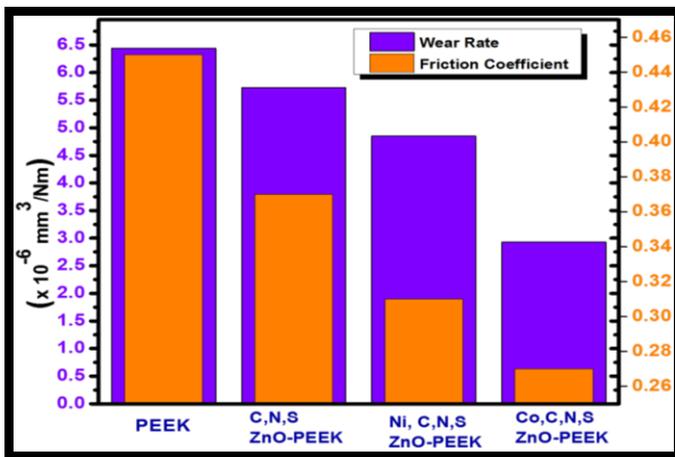


Fig. 10 Wear rate and Friction coefficient of PEEK and doped ZnO-PEEK nanocomposites

G. Worn surface morphology

Fig. 11 shows SEM images of PEEK and modified ZnO-PEEK nanocomposite after wear. In Fig. 11(a), sever abrasion of PEEK can clearly be seen. Bulk of dragging claws are evident due to weak meld shear strength. The edges can be seen plastically flown resulted from sever temperature rise between surfaces of contact [58]. In Fig. 11(b), the CNS doped ZnO-PEEK nanocomposite surface is smoother than pure PEEK. This is the implication of decent affinity between PEEK and CNS doped ZnO. Further it garnished the dispersion of filler in PEEK [59]. Fig. 11(c), showing the worn surface of Ni doped ZnO nanoparticles. The wear residue on the surface are significantly decreased as compared to CNS doped ZnO-PEEK. However, the built-up of the dark areas can be by virtue the extended escape of ZnO nanoparticles during the sliding [60]. In Fig.11 (d), the worn Co doped ZnO-PEEK nanocomposite surface can be seen. It is looking smoothest than the other materials. The accumulated hard cobalt ZnO led to prevent the formation of wear debris. The hard agglomerates of cobalt got crushed into smaller particles caused the plastic deformation in softer region of the surface. The nanocomposite remained chiefly flawless with almost no abrasion traces on the surface. Thus, the nanocomposite of PEEK with Co doped ZnO filler shown greater protection against the abrasion [61].

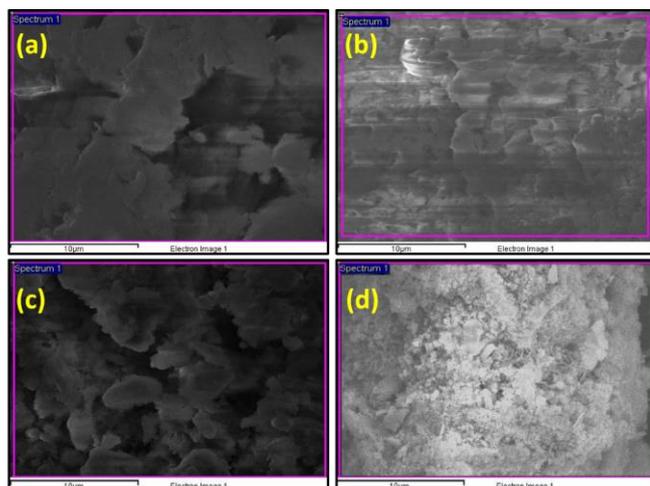


Fig. 11 Worn surfaces of a) PEEK b) CNS doped ZnO-PEEK nanocomposite c) Ni doped ZnO-PEEK nanoparticles d) Co doped ZnO-PEEK nanocomposite

H. Automobile Applications

Currently PEEK is been used in many automobile application related to tribology. In most of such cases the modified materials mentioned in this work can be used as the substitute for pure PEEK. Such applications are seal rings, bearing bushings and bearing cages, engine gears [62], ball bearings, thrust bearings [63], crank shaft bush, and self-lubricating bearing bushes [64]. Further, studies have shown that the metal components like fasteners, clips, brackets etc. can be replaced by PEEK [65], certainly can also be replaced by the material discussed in this study. Various automobile components made from titanium alloys and stainless steel like gaskets, inner covers of engine can be replaced by PEEK plastic [66]. Parts of suspension system like pistons skirts of bearing bush, clutch rings etc. can be made by the PEEK material. Other than these and many such applications, as like PEEK material, various components of transmission system, air conditioning system, engine rams, brakes etc. related to automobile application can substituted by the material posited in this work [67].

VI. CONCLUSION

In present work, the polymeric nanocomposite of PEEK as polymer matrix with surface modified ZnO as nano-filler were developed. The doping of non-metals, namely Carbon-Nitrogen-Sulphur (CNS) and metals namely, Nickel (Ni) and Cobalt (Co) were done on ZnO. These doped ZnO, nano-fillers were prepared by the process of hydrothermal co-precipitation. Further the insertion of modified ZnO into the PEEK was carried by the co-friendly hydrothermal technique with ultrasound assistance. The characterization verified successful fabrication and effective incorporation in ZnO to articulate the nanocomposite. The XRD analysis proven proper incorporation of metals and non-metals in ZnO, compelling synthesis and cohesion of nanocomposite. The TEM analysis revealed the quality of synthesized materials in proper configuration. Effective doping and active synthesis of CNS, Ni and Co in ZnO particles got confirmed by SEM, EDAX analysis. The FTIR proven expected preparation of surface modified ZnO-PEEK polymer for a steady nanocomposite. The altered physical property and composition of nanocomposite were confirmed by UV-DRS analysis. Friction and wear analysis was carried away to assure the tribological response of the prepared materials. The coefficient of friction for pure PEEK, CNS doped ZnO-PEEK, Ni doped ZnO-PEEK and Co doped ZnO-PEEK came out as 0.45, 0.37, 0.31 and 0.27 respectively. The friction coefficient shown gradual reduction. Pure PEEK proven more prone to friction while Co doped ZnO-PEEK nanocomposite exhibits the best friction resistance among the four materials. The wear rate was found to be $6.44 \times 10^{-6} \text{ mm}^3 / \text{Nm}$, $5.73 \times 10^{-6} \text{ mm}^3 / \text{Nm}$, $4.85 \times 10^{-6} \text{ mm}^3 / \text{Nm}$ and $2.93 \times 10^{-6} \text{ mm}^3 / \text{Nm}$ for pure PEEK, CNS doped ZnO-PEEK, Ni doped ZnO-PEEK and Co doped ZnO-PEEK respectively. Wear rate of pure PEEK was on higher side while Co doped ZnO-PEEK shown drastic reduction in wear rate. Worn surface morphology revealed poor degradation of pure PEEK surface. CNS doped ZnO-PEEK, Ni doped ZnO-PEEK and Co doped ZnO-PEEK shown gradual enhancement in abrasion resistance. This was clearly due to existence of doped ZnO nano-fillers. Comprehensively, this work rooted technique for the synthesis of CNS, Ni and Co doped ZnO-PEEK polymeric nanocomposite, validating

their structure and morphology along with indication of their eminent tribological response over pure PEEK. Among the three doping, Co doped ZnO-PEEK nanocomposite proven to be the best in all respect. It shown improved friction coefficient. The wear of Co doped ZnO-PEEK nanocomposite was also the least. The morphology of worn surface as well, revealed the smoothest surface of Co doped ZnO-PEEK among all materials. Hence it can be concluded that Co doped ZnO-PEEK nanocomposite has every potential to be considered a good alternative for PEEK in tribological applications in automobile sector.

REFERENCES

- [1] Holmberg, Kenneth, Päivi Kivikytö-Reponen, Pirita Härkisaari, Kati Valtonen, and Ali Erdemir. "Global energy consumption due to friction and wear in the mining industry." *Tribology International* 115 (2017): 116-139.
- [2] Zhao, Gai, Chuhan Wu, Liangchi Zhang, Jingfu Song, and Qingjun Ding. "Friction and wear behavior of PI and PTFE composites for ultrasonic motors." *Polymers for Advanced Technologies* 29, no. 5 (2018): 1487-1496.
- [3] Sycks, Dalton G., David L. Safranski, Neel B. Reddy, Eric Sun, and Ken Gall. "Tough Semicrystalline Thiol-Ene Photopolymers Incorporating Spiroacetal Alkenes." *Macromolecules* 50, no. 11 (2017): 4281-4291.
- [4] Liu, Xiao-Feng, Bo-Wen Liu, Xi Luo, De-Ming Guo, Hai-Yi Zhong, Li Chen, and Yu-Zhong Wang. "A novel phosphorus-containing semi-aromatic polyester toward flame retardancy and enhanced mechanical properties of epoxy resin." *Chemical Engineering Journal* 380 (2020): 122471.
- [5] Childress, Kimberly K., Marvin D. Alim, Sudheendran Mavila, Vikina Martinez, Yifu Ding, Christopher N. Bowman, and Jeffrey W. Stansbury. "Systematic Modulation and Structure-Property Relationships in Photopolymerizable Thermoplastics." *ACS Applied Polymer Materials* 3, no. 2 (2021): 1171-1181.
- [6] Caldon, Eugene B., John Ryan C. Dizon, Robert Andrew Viers, Vincent Joseph Garcia, Zane J. Smith, and Rigoberto C. Advincula. "Additively manufactured high-performance polymeric materials and their potential use in the oil and gas industry." *Mrs Communications* (2021): 1-15.
- [7] Ziółkowski, Marcin, and Tomasz Dyl. "Possible applications of additive manufacturing technologies in shipbuilding: a review." *Machines* 8, no. 4 (2020): 84.
- [8] Chand, Navin, and Mohammed Fahim. *Tribology of natural fiber polymer composites*. Woodhead publishing, 2020.
- [9] Siacor, Francis Dave C., Qiyi Chen, Jia Yu Zhao, Lu Han, Arnaldo D. Valino, Evelyn B. Taboada, Eugene B. Caldon, and Rigoberto C. Advincula. "On the additive manufacturing (3D printing) of viscoelastic materials and flow behavior: From composites to food manufacturing." *Additive Manufacturing* 45 (2021): 102043.
- [10] Liu, Yu, Björn Rath, Markus Tingart, and Jörg Eschweiler. "Role of implants surface modification in osseointegration: A systematic review." *Journal of Biomedical Materials Research Part A* 108, no. 3 (2020): 470-484.
- [11] Sahoo, Prasanta, Suman Kalyan Das, and J. Paulo Davim. "Tribology of materials for biomedical applications." In *Mechanical Behaviour of Biomaterials*, pp. 1-45. Woodhead Publishing, 2019.
- [12] Ng, Law Yong, Abdul Wahab Mohammad, Choe Peng Leo, and Nidal Hilal. "Polymeric membranes incorporated with metal/metal oxide nanoparticles: A comprehensive review." *Desalination* 308 (2013): 15-33.
- [13] Khurana, Rachna, Jennifer L. Schaefer, Lynden A. Archer, and Geoffrey W. Coates. "Suppression of lithium dendrite growth using cross-linked polyethylene/poly (ethylene oxide) electrolytes: a new approach for practical lithium-metal polymer batteries." *Journal of the American Chemical Society* 136, no. 20 (2014): 7395-7402.
- [14] Boggarapu, Vasavi, Raghavendra Gujjala, and Shakuntla Ojha. "A critical review on erosion wear characteristics of polymer matrix composites." *Materials Research Express* 7, no. 2 (2020): 022002.
- [15] Chen, Hongyu, Valeriy V. Ginzburg, Jian Yang, Yunfeng Yang, Wei Liu, Yan Huang, Libo Du, and Bin Chen. "Thermal conductivity of polymer-based composites: Fundamentals and applications." *Progress in Polymer Science* 59 (2016): 41-85.
- [16] Li, Yu, Xiao-Yu Yang, Yi Feng, Zhong-Yong Yuan, and Bao-Lian Su. "One-dimensional metal oxide nanotubes, nanowires, nanoribbons, and nanorods: synthesis, characterizations, properties and applications." *Critical Reviews in Solid State and Materials Sciences* 37, no. 1 (2012): 1-74.
- [17] Koli, Dinesh Kumar, Geeta Agnihotri, and Rajesh Purohit. "A review on properties, behaviour and processing methods for Al-nano Al2O3 composites." *Procedia Materials Science* 6 (2014): 567-589.
- [18] Díez-Pascual, Ana M., and Angel L. Díez-Vicente. "Nano-TiO2 reinforced PEEK/PEI blends as biomaterials for load-bearing implant applications." *ACS applied materials & interfaces* 7, no. 9 (2015): 5561-5573.
- [19] Vardhaman, BS Ajay, M. Amarnath, J. Ramkumar, and K. Mondal. "Enhanced tribological performances of zinc oxide/MWCNTs hybrid nanomaterials as the effective lubricant additive in engine oil." *Materials Chemistry and Physics* 253 (2020): 123447.
- [20] Zhang, Jinlong, Yongmei Wu, Mingyang Xing, Sajjad Ahmed Khan Leghari, and Shamaila Sajjad. "Development of modified N doped TiO₂ photocatalyst with metals, nonmetals and metal oxides." *Energy & Environmental Science* 3, no. 6 (2010): 715-726.
- [21] Kieslich, Gregor, Giacomo Cerretti, Igor Veremchuk, Raphaël P. Hermann, Martin Panthöfer, Juri Grin, and Wolfgang Tremel. "A chemists view: Metal oxides with adaptive structures for thermoelectric applications." *physica status solidi (a)* 213, no. 3 (2016): 808-823.
- [22] Yuan, Changzhou, Hao Bin Wu, Yi Xie, and Xiong Wen Lou. "Mixed transition-metal oxides: design, synthesis, and energy-related applications." *Angewandte Chemie International Edition* 53, no. 6 (2014): 1488-1504.
- [23] Karatas, Ecem, Okan Gul, Nevin Gamze Karsli, and Taner Yilmaz. "Synergetic effect of graphene nanoplatelet, carbon fiber and coupling agent addition on the tribological, mechanical and thermal

- properties of polyamide 6, 6 composites." *Composites Part B: Engineering* 163 (2019): 730-739.
- [24] El-Naggar, Mehrez E., and Kamel Shoueir. "Recent advances in polymer/metal/metal oxide hybrid nanostructures for catalytic applications: A review." *Journal of Environmental Chemical Engineering* 8, no. 5 (2020): 104175.
- [25] Shinde, Sachin Girdhar, Maheshkumar Prakash Patil, Gun-Do Kim, and Vinod Shankar Shrivastava. "Ni, C, N, S multi-doped ZrO₂ decorated on multi-walled carbon nanotubes for effective solar induced degradation of anionic dye." *Journal of Environmental Chemical Engineering* 8, no. 3 (2020): 103769.
- [26] Shinde, Sachin Girdhar, Maheshkumar Prakash Patil, Gun-Do Kim, and Vinod Shankar Shrivastava. "Multi-doped ZnO photocatalyst for solar induced degradation of indigo carmine dye and as an antimicrobial agent." *Journal of Inorganic and Organometallic Polymers and Materials* 30, no. 4 (2020): 1141-1152.
- [27] Shinde, Nitin Girdhar, and Dilip Mangesh Patel. "Polymeric nanocomposite of PEEK and nickel incorporated ZnO: Synthesis, characterization and tribological behavior." *Materials Today: Proceedings* (2022).
- [28] Jason, Yeoh Jun Jie, Heoy Geok How, Yew Heng Teoh, and Hun Guan Chuah. "A study on the tribological performance of nanolubricants." *Processes* 8, no. 11 (2020): 1372.
- [29] González-Garnica, Marisol, Andrés Galdámez-Martínez, Francisco Malagón, C. D. Ramos, G. Santana, Reza Abolhassani, Pritam Kumar Panda et al. "One dimensional Au-ZnO hybrid nanostructures based CO₂ detection: Growth mechanism and role of the seed layer on sensing performance." *Sensors and Actuators B: Chemical* 337 (2021): 129765.
- [30] Senthilkumar, N., E. Vivek, M. Shankar, M. Meena, M. Vimalan, and I. Vetha Potheher. "Synthesis of ZnO nanorods by one step microwave-assisted hydrothermal route for electronic device applications." *Journal of Materials Science: Materials in Electronics* 29, no. 4 (2018): 2927-2938.
- [31] Umar, Ahmad, M. S. Akhtar, A. Al-Hajry, M. S. Al-Assiri, G. N. Dar, and M. Saif Islam. "Enhanced photocatalytic degradation of harmful dye and phenyl hydrazine chemical sensing using ZnO nanourchins." *Chemical Engineering Journal* 262 (2015): 588-596.
- [32] Toufiq, Arbab Mohammad, Razaqat Hussain, A. Shah, Arshad Mahmood, Asmat Rehman, Amjad Khan, and Shams ur Rahman. "The influence of Mn doping on the structural and optical properties of ZnO nanostructures." *Physica B: Condensed Matter* 604 (2021): 412731.
- [33] Srinivasulu, T., K. Saritha, and KT Ramakrishna Reddy. "Synthesis and characterization of Fe-doped ZnO thin films deposited by chemical spray pyrolysis." *Modern Electronic Materials* 3, no. 2 (2017): 76-85.
- [34] Gong, Chunli, Xuan Zheng, Hai Liu, Guangjin Wang, Fan Cheng, Genwen Zheng, Sheng Wen, Wing-Cheung Law, Chi-Pong Tsui, and Chak-Yin Tang. "A new strategy for designing high-performance sulfonated poly (ether ether ketone) polymer electrolyte membranes using inorganic proton conductor-functionalized carbon nanotubes." *Journal of Power Sources* 325 (2016): 453-464.
- [35] Koli, Prashant Bhimrao, Sachin Girdhar Shinde, Kailas Haribhau Kapadnis, Anita Parashram Patil, Madhukar Panditrao Shinde, Subhash Dharmraj Khairnar, Dipti Bhikan Sonawane, and Raju Shivaji Ingale. "Transition metal incorporated, modified bismuth oxide (Bi₂O₃) nano photo catalyst for deterioration of rosaniline hydrochloride dye as resource for environmental rehabilitation." *Journal of the Indian Chemical Society* 98, no. 11 (2021): 100225.
- [36] Zangeneh, Hadis, Mehrdad Farhadian, and Ali Akbar Zinatizadeh. "A reusable visible driven N and C–N doped TiO₂ magnetic nanocomposites for photodegradation of direct red 16 azo dye in water and wastewater." *Environmental Technology* (2020): 1-16.
- [37] Hao, Linlin, Ying Hu, Yu Zhang, Wenzhen Wei, Xiaochen Hou, Yiqiao Guo, Xiyu Hu, and Dong Jiang. "Enhancing the mechanical performance of poly (ether ether ketone)/zinc oxide nanocomposites to provide promising biomaterials for trauma and orthopedic implants." *RSC advances* 8, no. 48 (2018): 27304-27317.
- [38] Si, Mingming, Jianyu Hao, Enda Zhao, Xueting Zhao, Jing Guo, Hong Wang, and Clive A. Randall. "Preparation of zinc oxide/poly-ether-ether-ketone (PEEK) composites via the cold sintering process." *Acta Materialia* 215 (2021): 117036.
- [39] Thilagashanthi, T., K. Gunasekaran, and K. S. Satyanarayanan. "Microstructural pore analysis using SEM and ImageJ on the absorption of treated coconut shell aggregate." *Journal of Cleaner Production* 324 (2021): 129217.
- [40] Hartig, Sean M. "Basic image analysis and manipulation in ImageJ." *Current protocols in molecular biology* 102, no. 1 (2013): 14-15.
- [41] Suganya, S. "Influence of ultrasonic waves on preparation of active carbon from coffee waste for the reclamation of effluents containing Cr (VI) ions." *Journal of Industrial and Engineering Chemistry* 60 (2018): 418-430.
- [42] Pathak, Abhishek K., Hema Garg, Mandeep Singh, T. Yokozeki, and Sanjay R. Dhakate. "Enhanced interfacial properties of graphene oxide incorporated carbon fiber reinforced epoxy nanocomposite: a systematic thermal properties investigation." *Journal of Polymer Research* 26, no. 2 (2019): 1-13.
- [43] Xu, Xuan, Qiqin Zheng, Guangmin Bai, Lishu Song, Yuewei Yao, Xiaodong Cao, Songqin Liu, and Cheng Yao. "Polydopamine induced in-situ growth of Au nanoparticles on reduced graphene oxide as an efficient biosensing platform for ultrasensitive detection of bisphenol A." *Electrochimica Acta* 242 (2017): 56-65.
- [44] Kaur, Arshpreet, Atul Khanna, Carmen Pesquera, Fernando González, and Vasant Sathe. "Preparation and characterization of lead and zinc tellurite glasses." *Journal of Non-Crystalline Solids* 356, no. 18-19 (2010): 864-872.
- [45] Juma, Albert O., Elhadi AA Arbab, Cosmas M. Muiva, Lucia M. Lepodise, and Genevieve Tessema Mola. "Synthesis and characterization of CuO-NiO-ZnO mixed metal oxide nanocomposite." *Journal of alloys and compounds* 723 (2017): 866-872.
- [46] Mututu, Virginia, A. K. Sunitha, Riya Thomas, Mayank Pandey, and B. Manoj. "An investigation on structural, electrical and optical

- properties of GO/ZnO nanocomposite." *Int. J. Electrochem. Sci* 14, no. 3752-3763 (2019): 3752.
- [47] Alsaad, A. M., Abdul Raouf Al Dairy, A. A. Ahmad, Ayah S. Al-anbar, and Qais M. Al-Bataineh. "Synthesis and characterization of as-grown doped polymerized (PMMA-PVA)/ZnO NPs hybrid thin films." *Polymer Bulletin* (2021): 1-22.
- [48] Sharma, Shelja, S. K. Mehta, A. O. Ibhaddon, and S. K. Kansal. "Fabrication of novel carbon quantum dots modified bismuth oxide (α -Bi₂O₃/C-dots): material properties and catalytic applications." *Journal of colloid and interface science* 533 (2019): 227-237.
- [49] Zhu, Juanjuan, Fang Xie, and R. S. Dwyer-Joyce. "PEEK composites as self-lubricating bush materials for articulating revolute pin joints." *Polymers* 12, no. 3 (2020): 665.
- [50] Kumari, Vijaya, Anuj Mittal, Jitender Jindal, Suprabha Yadav, and Naveen Kumar. "S-, N-and C-doped ZnO as semiconductor photocatalysts: A review." *Frontiers of Materials Science* 13, no. 1 (2019): 1-22.
- [51] Rana, Amit Kumar, Prashant Bankar, Yogendra Kumar, Mahendra A. More, Dattatray J. Late, and Parasharam M. Shirage. "Synthesis of Ni-doped ZnO nanostructures by low-temperature wet chemical method and their enhanced field emission properties." *RSC advances* 6, no. 106 (2016): 104318-104324.
- [52] Chang, Qiang-Qiang, Yi-Wei Cui, Hai-Huan Zhang, Fei Chang, Bao-Hua Zhu, and Shi-Yong Yu. "C-doped ZnO decorated with Au nanoparticles constructed from the metal-organic framework ZIF-8 for photodegradation of organic dyes." *RSC advances* 9, no. 22 (2019): 12689-12695.
- [53] Stolarski, T. A. "Tribology of polyetheretherketone." *Wear* 158, no. 1-2 (1992): 71-78.
- [54] An, V., Y. Irtegov, E. Anisimov, V. Druzyanova, N. Burtsev, and M. Khaskelberg. "Tribological properties of nanolamellar tungsten disulfide doped with zinc oxide nanoparticles." *SpringerPlus* 4, no. 1 (2015): 1-6.
- [55] Song, Hao-Jie, Zhao-Zhu Zhang, Xue-Hu Men, and Zhuang-Zhu Luo. "A study of the tribological behavior of nano-ZnO-filled polyurethane composite coatings." *Wear* 269, no. 1-2 (2010): 79-85.
- [56] Vahtrus, Mikk, Andris Šutka, Boris Polyakov, Sven Oras, Mikk Antsov, Nicola Doebelin, Rünno Lõhmus, Ergo Nõmmiste, and Sergei Vlassov. "Effect of cobalt doping on the mechanical properties of ZnO nanowires." *Materials Characterization* 121 (2016): 40-47.
- [57] Zhu, Juanjuan, Fang Xie, and R. S. Dwyer-Joyce. "PEEK composites as self-lubricating bush materials for articulating revolute pin joints." *Polymers* 12, no. 3 (2020): 665.
- [58] Zhang, Ming Qiu, Min Zhi Rong, Shu Li Yu, Bernd Wetzel, and Klaus Friedrich. "Effect of particle surface treatment on the tribological performance of epoxy based nanocomposites." *Wear* 253, no. 9-10 (2002): 1086-1093.
- [59] An, V., Y. Irtegov, E. Anisimov, V. Druzyanova, N. Burtsev, and M. Khaskelberg. "Tribological properties of nanolamellar tungsten disulfide doped with zinc oxide nanoparticles." *SpringerPlus* 4, no. 1 (2015): 1-6.
- [60] Shi, Peiying, Shanhong Wan, Gewen Yi, Huwei Sun, Yuan Yu, Erqing Xie, Qihua Wang, Shirley Z. Shen, and Nazmul Alam. "TiO₂-ZnO/Ni-5wt. % Al composite coatings on GH4169 superalloys by atmospheric plasma spray techniques and their elevated-temperature tribological behavior." *Ceramics International* 46, no. 9 (2020): 13527-13538.
- [61] Toosinezhad, Amirhosein, Mohammad Alinezhadfar, and Soheil Mahdavi. "Tribological behavior of cobalt/graphene composite coatings." *Ceramics International* 46, no. 10 (2020): 16886-16894.
- [62] Lewis, Simon D., and Robert A. Rowntree. "Hybrid polymeric bearings for space applications." In *7th European Space Mechanisms and Tribology Symposium*, vol. 410, p. 231. 1997.
- [63] Shi, Xiao Chen, Masaya Orito, Yuji Kashima, Koshiro Mizobe, and Katsuyuki Kida. "Observation of cracks of PEEK polymer thrust bearings under rolling contact fatigue in water." In *Key Engineering Materials*, vol. 703, pp. 172-177. Trans Tech Publications Ltd, 2016.
- [64] Zhu, Juanjuan, Fang Xie, and R. S. Dwyer-Joyce. "PEEK composites as self-lubricating bush materials for articulating revolute pin joints." *Polymers* 12, no. 3 (2020): 665.
- [65] Ling, Xuanzhe, Xishuang Jing, Chengyang Zhang, and Siyu Chen. "Polyether Ether Ketone (PEEK) properties and its application status." In *IOP Conference Series: Earth and Environmental Science*, vol. 453, no. 1, p. 012080. IOP Publishing, 2020.
- [66] Mizobe, Koshiro, Takashi Honda, Hitonobu Koike, Edson Costa Santos, Katsuyuki Kida, and Yuji Kashima. "Relationship between load, rotation speed and, strength in all-PEEK and PEEK Race-PTFE retainer hybrid polymer bearings under dry rolling contact fatigue." In *Advanced Materials Research*, vol. 567, pp. 66-70. Trans Tech Publications Ltd, 2012.
- [67] Koike, Hitonobu, Kenji Kanemasu, Kiyoto Itakura, Shota Okazaki, Masahiro Takamiya, E. Costa Santos, and Katsuyuki Kida. "Measurement of fatigue and wear of PEEK bush and A7075 cam plate in humanoid robot joints." *Materials Research Innovations* 18, no. sup1 (2014): S1-38.