An overview of polymer nanocomposites: Understanding of mechanical and tribological behavior

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Abstract. Polymer nanocomposites are polymeric materials reinforced with various types of nanomaterials. Over last few decades, these materials have drawn a lot of attention particularly as a favorable alternative in extreme condition exposures. Polymer nanocomposites have potential applications in many fields such as automotive, high-barrier food packing films, extremely hard and wear resistant coatings/materials to eco-friendly composites. The main objective of this review article is to give current state-of-the-art of research activities on nanofiller-based-polymer-nanocomposites with particular focus on their application to improve tribological properties. Even an apparently simple object in reality is a technological marvel of nano-engineered materials. For example, a vehicle tyre is generally produced by mixing some specific polymers and nano-fillers. The tribological applications of polymer materials are likely to progress with the practice of polymer nanocomposites being applied to novel uses. The main motivation behind this review is to highlight the key mechanisms governing the effects of reinforcement on the mechanical and tribological behavior of polymer nanocomposites. It is observed that the improvement of one feature or characteristic may not interpret an enrichment of the other properties associated with the system. However, it is significant to comprehend the diverse elements or aspects accountable for performance of the material. To summarize, this overview presents basics of the complexities in the mechanical and tribological behaviour of polymer nanocomposites.

1. Introduction
Polymers are very common in our daily life. We are surrounded by things made of polymers such as paints, adhesives, packaging materials, cosmetics, fertilizers, tyres, fabrics etc. This is due to the fact that it’s very easy to process polymers into complex shapes. Polymers are usually characterized by low energy density, large intramolecular entropy, nanoscopic length scale and $k_BT$ energy scale ($k_B$ is Boltzmann constant and $T$ is temperature). There have been several attempts in recent times to use polymers in tribological applications to control friction and wear of surfaces [1-4]. Polymer composites are interesting for their low weight, high strength-to-weight, high stiffness-to-weight and low material cost [5]. These materials find applications in many fields including automobile body parts, tyres, cams, gears, brake materials, bearing cages, biomedical devices, artificial implants, food industries, energy storage and conversions and aerospace industries [6, 7]. Use of nanoparticle fillers in composites lowers their weight fractions in comparison to the use of microparticles. Additionally high surface-area-to-volume ratios of nanomaterials lead to improved adhesion. Nanomaterials are typically classified on the basis of dimensions ranging from 1 to 100 nm. The 0D-materials are particles with all the three dimensions below 100 nm such as carbon nanomaterials, aluminum oxide, calcium carbonate, copper oxide, silicon dioxide, silicon carbide, silicon nitride, titanium dioxide, zinc oxide and zirconium dioxide. The 1D-materials have two dimensions below 100 nm like carbon nanofillers and nanofibers and the 2D-materials have only one dimension in the nanometer scale comprising of layered sheet like constituents clays, graphene sheets, and molybdenum disulfide. Past studies suggest that
nanoparticle based polymer composites typically termed as “nanocomposites” exhibit improved tribological performance [8–11].

Polymer nanocomposites are comparatively new variety of materials exhibiting great potential in various applications due to the fine balance of strength, hardness and toughness as well as excellent tribological behavior. Studies revealed that a vital path to the perfection of these characteristics is the uniform and homogenous dispersal of the nano-fillers, interfacial bonding and interaction between the particles and the polymer. The fillers are capable of improving the homogeneity of the transfer film and the adhesion to the counter surface. The mechanical/chemical reactions of nanoparticles during rolling/sliding, the capability of the dispersed nanoparticles in the polymer to support asperities in the counter-surface and the tribo-chemical reactions of nanofillers with the counter surface favor the above capabilities. The molecular weight, stereochemistry, degree of crosslinking, polymer blend composition and chemical affinity all are of fundamental importance in determining tribological performances. The polymer blend features are dependent on the dispersion phase in terms of size, degree of dispersion, and interfacial phase interaction between the components of the blend. These factors primarily need to be controlled to attain specific properties of the material [12-14]. Other critical parameters responsible for performance of polymer nanocomposites include contact area, load/stress (collective stress), sliding speed, topography of counter face, temperature and molecular relaxation.

The knowledge of complex structural changes occurring in a tribosystem at molecular scale is vital for designing the materials with desired characteristics. In spite of availability of large variants of nanomaterials, very few have been examined for tribological applications. Continuum theory has limitations in modeling polymer nanocomposites. Continuum modeling does not take into account the atomic-scale details and mechanisms like atomic stick-slip. Nanoscale analysis and modeling techniques that include the molecular structure of the contact is therefore necessary. Molecular simulations are generally used to overcome the limitations of continuum theory. Molecular dynamics simulations aimed at analyzing specific problems are possibly the most effective methods to elucidate complex mechanisms satisfactorily. The fundamental understanding of interacting molecular bonds and their nature is achieved with molecular simulation and modeling techniques [15]. These methods allow modeling of the intricate interfacial occurrences with extraordinary resolution in both length and time scales. These molecular simulations yield understandings into the molecular-scale energetics, structure, dynamics, thermodynamics, transport and rheological behavior under tribological loadings. The focus of this review article is to develop a comprehensive understanding of polymer nanocomposite’s performances under nanoindentation.

2. Literature Review

The practice of using nanoparticles in polymer matrix for tuning tribological characteristics gained importance in mid-1990s. This particular field has potential for detail research as new nanoparticles are consistently and economically designed. The polymer based nanocomposites exhibit properties that depend on the area of interacting interface between the filler (nanoparticles or nanofibers) and the matrix (a polymer) for its improved mechanical and tribological behavior. Almost for all the polymer/nanoparticle systems, there is an optimal amount of the nanoparticles which can be incorporated in the system; otherwise it degrades the toughness as the stiffness and strength increase beyond the optimum limit. Most of the present theoretical systems are obtained from the continuum mechanics models. The continuum mechanics theories are not always valid at nano-scale; rather the discrete-particle based model is commonly used [16].

Experimental studies have revealed extraordinary and remarkable tribological performance of filler polymer composites and nano-filled polymer composites but have also predicted some contradictions. In several studies, addition of filler enhances wear resistance, whereas some studies have shown they deteriorated the performance of the nanocomposite [17]. It is evident from literature that the same filler exhibits contrary trends when the size of filler was varied. The chemical affinity of the fillers is changed with the reinforcement in polymer matrix. The previous studies have considered the influence of addition of the nanofillers on the formation of transfer film [18, 19]. It is also specified that the nanoparticles present on the interface render thin and firm transfer film formation [20]. Other works reveal that accurate dispersion of nanofillers is another vital factor to attain specific properties. The nanoparticles typically tend to agglomerate at higher filler contents thereby leading to shortcomings in efficiency of polymer matrix. The studies recognized that the increased wear resistance is due to rise in the thermal conductivity of nanocomposites. The increase in thermal conductivity enables the heat dissipation produced through friction which reduces the temperature of the working tribosystem [21]. The minimum amount of filler additions have depicted improvements in properties by reduced wear rates [9]. It is manifested by previous studies that the filler content lesser than 1.0 wt.% are sometimes enough for improving wear resistance by 1000 folds. The nano-
Fillers have the capability to impart significant tribological and mechanical features for use in specific systems. There are numerous characteristics of these systems that must be considered to acquire a thorough understanding of the underlying mechanisms [19].

The metal, ceramic, or polymer “nanoparticles” present extensive types of 0D-fillers [22]. These nanoparticles may be either hard or soft, prepared from either distinct or multi-chemical components, exhibiting different shapes or forms [23]. Currently, numerous types of nanoparticles or nanofillers are reinforced into the polymer matrix to increase their tribological performances. Inorganic and hard nanoparticles are frequently used as they exhibit remarkable performance. The importance of these nanoparticles is correlated with their capability to increase elastic modulus and impact wear resistance of the base polymers. In order to reduce coefficient of friction, soft polymeric nanoparticles are also incorporated in the matrix [24, 25]. Existing technologies allow synthesizing nanoparticles with various kinds of forms and dimensions, either restrained or applied in the form of coating on diverse surface categories [26, 22]. 1D-nanofillers include nano-tubes, rods, fibers and wires. They are metal, ceramic, or polymer materials and their molecular structures could be amorphous or crystalline in nature. Studies reveal incorporation of nanoparticles in a polymer matrix has improved performances by increasing load-bearing capability and toughness. The nanofillers facilitate the reduction in wear rate by forming a persistent and few nanometers thick transfer film on the counter face during interaction [27]. 2D-nanofillers include natural caotionic clays, graphene sheets, metal chalcogenides, and various transition metal oxides. These fillers possess a layered like molecular structure having van der Waals bonds between the layers. The thin layer which has only few nanometers thickness exhibit extraordinary electronic, magnetic, thermal, mechanical and tribological characteristics. The usage of the nanomaterials in tribology field has drawn a lot of consideration over the recent years [28].

Simulations of nanoindentation on polymer nanocomposites are very rare. A recent report on nanoindentation simulation study for the quantitative nanomechanical characteristics of polyethylene (PE) and the polyhedral oligomeric silsesquioxane (POSS) composites (POSS-PE) is directed on computation of hardness and elastic modulus of polymers using different shapes of indenter. The different shapes greatly affected the hardness values and elastic modulus of flat indenter is greater than cube-corner and spherical shape indenter. With molecular dynamics (MD) simulation, several mechanical behaviors of polymer nanocomposites with various molecular interactions are studied [29, 30]. The nanoindentation study on graphene based polymer nanocomposites has been conducted using MD simulation. The effects of reinforcement of graphene sheets in PE polymer indentation are investigated. The nanoindentation exhibited that the material resistance is enhanced significantly with the presence of layered graphene sheets. The measured values of this study reveal that resistance to indentation of a single-layer graphene coated PE is around fourteen-fold than that of virgin PE. The alignment and the way graphene sheets disperse in the nanocomposites considerably affect the tribo-mechanical properties [31]. MD simulations have been used to study mechanical and tribological performance of polymer nanocomposite with wrinkled graphene layer placed in-between. PE and polymethylmethacrylate (PMMA) polymers are reinforced with graphene layer to improve interfacial mechanical and tribological properties. The effects of graphene wrinkles, nature of matrix, length of polymer chain and pulling-out velocity of graphene sheet (GR) are revealed. The results indicate that a flat GR in comparison to a wrinkled GR efficiently improved the counter face behavior. The pulled-out velocity of GR (wrinkled) influences the interacting counter face properties of both the polymer nanocomposites used. The effect of degree of polymerization of polymers on the interacting surface properties is insignificant in the graphene reinforced PE system, but very significant in the graphene reinforced PMMA system [32]. The current state-of-the-art understanding is focused on the enhancement of uniformity in dispersion by functionalization, chemical reformation and heat treatment or the supplement of stabilizers/compatibilizers among the polymer matrix and the nano-phases [33-39]. The ultimate challenge is that experimentally measured results of different properties cannot be simply applied and used from one system to another e.g., from a tribological test rig to a real application. The tribological performance is predictable based on theoretical modeling and computer simulation for any particular application only when the operating conditions of the application and test environment are identical. Polymers do not always line up with the rule of improved properties such as mechanical strength and surface hardness for decreased wear rate, thus the need of fine modification for tribological performance without compromising the bulk strength of these materials. Thus, there is possibility of a strong growth in the tribology filed of polymers in all present forms available as virgin/pristine, composites, nanocomposites and hybrids.

3. Conclusion
This overview presents some features of the existing state of progress of polymer-based nanocomposites with better mechanical and tribological performance, main focus on nanoindentation using molecular simulation.
and theoretical approaches. The evolving field of polymer nanocomposites is of immense potential. The vital benefit of nanocomposites over conventional composites is their capability towards reaching and enhancing strength and toughness properties equally. The ideal impact of nanomaterials on improving tribological performances of polymer nanocomposites is still an open area for research in future. The existing research studies in this field are limited. Therefore this might be another major area for polymer tribology research using experimental and theoretical approaches. The present research and development activities in the area of polymers are heading towards polymer nanocomposites and polymer surface engineering reforms and are developing rapidly. There is a need to explore distinctive processing methods for polymer nanocomposite’s use in tribological applications. The tribological study on polymer nanocomposites is still in initial phase and we shall expect pioneering research work in this field.

4. References

[1] M K Singh, P Ilg, R M Espinosa-Marzal, M Kroger, N D Spencer, Effect of Crosslinking on the Microtribological Behavior of Model Polymer Brushes Tribology Letters 63(2) 2016 p.17.

[2] M K Singh, P Ilg, R M Espinosa-Marzal, M Kroger, N D Spencer, Polymer Brushes under Shear: Molecular Dynamics Simulations Compared to Experiments Langmuir 31(16) 2015 pp.4798-4805.

[3] M K Singh, C Kang, P Ilg, R Crockett, M Krooger, N D Spencer, Combined Experimental and Simulation Studies of Cross-linked Polymer Brushes under Shear Macromolecules 51(24), 2018 pp.10174-10183.

[4] M K Singh, Polymer Brush Based Tribology, in: J Katiyar, P Ramkumar, T Rao, J Davim (Eds) Tribology in Materials and Applications Springer, Cham, 2020 (pp. 15-32).

[5] P L Menezes, S V Kailas, and M R Lovell, Fundamentals of engineering surfaces. Tribology for Scientists and Engineers Springer, New York, 2013.

[6] K Friedrich, A K Schlarb, Tribology of Polymeric Nanocomposites: Friction and Wear of Bulk Materials and Coatings Elsevier, 2011

[7] L Guadagno, B D Vivo, A D Bartolomeo, P Lamberti, A Sorrentino, V Tucci, L Vertuccio, and L Vittoria, Effect of Functionalization on the Thermo-mechanical and Electrical Behavior of Multi-wall Carbon Nanotube/epoxy composites. Carbon 49(6) 2011 pp.1919-1930

[8] C Baillie, Green Composites: Polymer Composites and the Environment CRC Press, 2005.

[9] D L Burris, B Boesl, G R Bourne, and W G Sawyer, Polymeric Nanocomposites for Tribological Applications Macromol. Mater. Eng. 292(4) 2007 pp.387-402.

[10] A Sorrentino, M Tortora, V Vittoria, Diffusion Behavior in Polymer–clay Nanocomposites J. Polym. Sci. Pol. Phys.,44(2) 2006 pp.265-274.

[11] A Sorrentino, L Vertuccio, V Vittoria, Influence of Multi-walled Carbon Nanotubes on the β form Crystallization of Syndiotactic Polystyrene at Low Temperature. Express Polym. Lett. 4 2010 pp.339-345.

[12] S Pavlidou, C D Papaspyrides, A Review on Polymer–layered Silicate Nanocomposites. Prog. Polym. Sci. 33(12) 2008 pp.1119-1198.

[13] G Gorras, G Attanasio, L Izzo. A Sorrentino, Controlled Release Mechanisms of Sodium Benzoate from a Biodegradable Polymer and Halloysite Nanotube Composite. Polym. Int. 66(5) 2017 pp.690-698.

[14] S Liparoti, G Landi, A Sorrentino, V Speranza, M Cakmak, H C Neitzert, Flexible Poly (Amide-IImide)-Carbon Black Based Microheater with High-Temperature Capability and an Extremely Low Temperature Coefficient. Adv. Electron. Mater, 2(6) 2016 p.1600126.
[15] B Bhushan, *Nanotribology and nanomechanics: an introduction* Springer Science & Business Media 2008.

[16] A Gouldstone, K J Van Vliet, S Suresh, Simulation of Defect Nucleation in a Crystal. *Nature* **411**(6838) 2001 pp.656-656.

[17] B Bhushan, *Fundamentals of Tribology and Bridging the Gap between the Macro- and Micro/Nanoscales*. Springer, Netherlands, Dordrecht, 2001.

[18] B J Briscoe, S K Sinha, Tribological Applications of Polymers and their Composites: Past, Present and Future Prospects. *Tribology and Interface Engineering Series* (Vol. **55**, pp. 1-14) Elsevier, 2008.

[19] J P Davim, *Tribology of Nanocomposites* Springer Berlin Heidelberg, 2013.

[20] L Chang, Z Zhang, L Ye, K Friedrich, Tribological Properties of Epoxy Nanocomposites: III. Characteristics of Transfer Films. *Wear* **262**(5-6) 2007 pp.699-706.

[21] I Hutchings, P Shipway, Design and Selection of Materials for Tribological Applications. *Tribology Friction and Wear of Engineering Materials* Elsevier, Oxford, 2017.

[22] C F Higgs, M Marinack, J Mpagazehe, R Pudjoprawoto, Particle Tribology: Granular, Slurry, and Powder Tribosystems. *Tribology for Scientists and Engineers* Springer, New York, 2017.

[23] G Schmid, The Nature of Nanotechnology. *Nanotechnology*. pp.3-39, 2010.

[24] G Gorrasi, A Sorrentino, Mechanical Milling as a Technology to Produce Structural and Functional Bio-nanocomposites. *Green Chem.*, **17**(5) 2015 pp.2610-2625.

[25] Q J Wang, Y CHUNG, *Encyclopedia of Tribology*, 2013.

[26] F Delogu, G Gorrasi, A Sorrentino, Fabrication of Polymer Nanocomposites via Ball Milling: Present Status and Future Perspectives. *Prog. Mater.* **86** 2017 pp.75-126.

[27] M B Elinski, Z Liu, J C Spear, J D Batteas, 2D or not 2D? The Impact of Nanoscale Roughness and Substrate Interactions on the Tribological Properties of Graphene and MoS2. *J. Phys. D Appl. Phys.* **50**(10) 2017 p.103003.

[28] B Pan, J Tan, H Jia, J Chen, Y Tai, J Liu, Y Zhang, Q Niu, Tribological Behavior of Phenolic Nanocomposites Reinforced by 2D Atomic Crystal of Boron Nitride. *J. Polym. Mater.* **4** 2016.

[29] E Hu, Y Sun, F Zeng, J Qu, Nanoindentation Simulation of PE/POSS under Different Shapes of Indenters. *Acta Mech. Solida Sin.* **24**(4) 2011 pp.365-372.

[30] E Hu, Y Sun, F Zeng, The Enhancement Mechanism and Deformation Analysis of Polyethylene Incorporated with POSS by Nanoindentation Simulation. *Rev. Adv. Mater. Sci.* **33**(1) 2013 pp.85-91.

[31] A R Alian, M A N Dewapriya, S A Meguid, Molecular Dynamics Study of the Reinforcement Effect of Graphene in Multilayered Polymer Nanocomposites. *Mater. Design* **124** 2017 pp.47-57.

[32] F Liu, N Hu, H Ning, Y Liu, Y Li, L Wu, Molecular Dynamics Simulation on Interfacial Mechanical Properties of Polymer Nanocomposites with Wrinkled Graphene. *Comp. Mater. Sci.* **108** 2015 pp.160-167.

[33] X H Men, Z Z Zhang, H J Song, K Wang, W Jiang, Functionalization of carbon nanotubes to improve the tribological properties of poly (furfurylalcohol) composite coatings. *Compos Sci Technol* **68** 2008 pp 1042–1049

[34] F J Carrión, C Espejo, J Sanes, M D Bermudez, Single-walled carbon nanotubes modified by ionic liquid as antiwear additives of thermoplastics. *Compos Sci Technol* **70** 2010 p 2160–2167
[35] F J Carrion, J Sanes, M D Bermudez, A Arribas, New single-walled carbon nanotubes-ionic liquid lubricant. Application to polycarbonate-stainless steel sliding contact. Tribol Lett 41 2011 p 199–207

[36] O Coban, M O Bora, E Avcu, T Sinmazcelik, The Influence of Annealing on the Crystallization and Tribological Behavior of MWNT/PEEK Nanocomposites. Polym Compos 32 2011 p 1766–1771

[37] M Pollanen, S Pirinen, M Suvanto, T T Pakkanen, Influence of carbon nanotube-polymeric compatibilizer masterbatches on morphological, thermal, mechanical, and tribological properties of polyethylene. Compos Sci Technol 71 2011 p 1353–1360

[38] Y J Shi, L W Mu, X Feng, X H Lu, Tribological behavior of carbon nanotube and polytetrafluoroethylene filled polyimide composites under different lubricated conditions. J Appl Polym Sci 121 2011 p 1574–1578

[39] X H Men, Z Z Zhang, J Yang, X T Zhu, K Wang , W Jiang, Effect of different functional carbon nanotubes on the tribological behaviors of Poly(Furfuryl Alcohol)-derived carbon nanocomposites. Tribol Trans 54 2011 p 265–274