Improved wear resistance and mechanical properties of multifunctional polymer nanocomposites for advanced engineering applications

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Abstract. Improvement of wear behaviour and mechanical properties of polymers as bulk and surface coating materials for advanced engineering applications have been research interest. Improved wear resistance and mechanical properties were achieved in this study by incorporation of surface modified graphene and titanium dioxide nano-powder in poly (vinylidene fluoride) matrix via solution blending and melt compounding. The morphology of the nanocomposites was studied using scanning electron microscope (SEM). The nanocomposites showed significant reduction in wear volume and enhanced mechanical properties due to the presence of surface modified nanofillers. About 76.5% reduction in wear volume, 52% and 186.5% increase in tensile strength and Young modulus respectively were achieved in this study. The surface modification of the nanofillers was essential in dispersion of the nanofillers in the polymer matrix and the improved properties recorded. Such nanocomposites can find applications as protective surface coating materials for high frictional condition and bulk materials for automobile and aerospace components.

1. Introduction

Surface modification of materials without changing the bulk properties of the materials to protect them against aggressive environments such as corrosive media and frictional conditions has drawn research and industrial interests. Polymeric materials are often used in such aggressive environments because of their excellent performance in resistance to chemical attacks and self-lubrication in the case of friction [1]. Polymeric materials have good properties required for various engineering applications such as protective surface coating, solid lubricant, electronic, electrical, mechanical and structural applications. Their wide applications are due to their distinct properties such as light weight, flexibility, toughness, easy processing etc. For instance, polytetrafluoroethylene among others have the capability to provide low frictional coefficient under sliding condition. Notwithstanding, they are associated with challenge of high wear rate, which hinders their wide applications in high frictional conditions [2]. Therefore, using such materials as protective surface coating in high frictional environment became industrial challenge despite their high corrosion resistance. Addressing this challenge associated with polymers has drawn attentions of researchers. In the past years, ceramic powders have been incorporated in polymer matrix on the efforts to overcome this shortcoming [3-6].

The recent discovering of carbon-based nanofillers such as graphene and carbon nanotubes has
created pathways for improving wear resistance of polymers, while maintaining their self-lubrication and low frictional coefficient properties. For instance, it has been demonstrated that introduction of graphene nanofillers in polymer matrix improves its wear properties [7-10]. About 40% reduction in wear rate by introduction of graphene oxide in polymer matrix has been achieved [11]. In a study carried out by Han et al [12], approximately 49.4% enhanced wear performance was recorded with reduced graphene oxide in polymer. Also, Shen et al [13] measured high reduction in wear rate when graphene oxide was incorporated in polymer matrix. These results showed the capability of graphene nanofillers in addressing the problem of high wear rate associated with polymers.

Friction and wear mechanisms are well known to be surface phenomenon. Understanding the full detail principles of wear is a challenge, since it varies from one material to another. Understanding the principles of wear mechanisms will aid in addressing challenges associated with friction and wear not only for bulk materials, also for protective coated surfaces. Basic wear mechanisms are by initial removal of materials from a bulk material surface by the countersurface, followed by subsequent detachment of the material on the countersurface [2]. Comparing materials’ removal from polymer composites filled with micro and nano fillers, nanofillers have insufficient size required for low wear rate in polymer matrix [14]. 2D materials such as graphene nanofillers offers large in-plane dimension when incorporated in polymer matrix due to their large surface area. Therefore, obtaining appreciable thickness of such nanofillers will address the challenge of insufficient thickness level and improve wear performance of polymers containing such nanofillers for protective surface coating and bulk materials applications.

This study attached titanium dioxide (TD) nano-powder on surfaces of 2D graphene nanofillers and incorporated into poly (vinylidene fluoride) matrix. During wear operation, there was initial removal of TD attached on graphene surfaces, then removal of graphene sheets from the polymer matrix. This promoted reduction in wear volume of the nanocomposites. Also, the rough surfaces of graphene sheets due to attachment of TD promoted interlocking of the polymer molecular chains, which resulted to improved mechanical properties. Good interfacial interaction between the two nanofillers and the polymer matrix was necessary in achieving the enhanced wear and mechanical performance. This was achieved by surface modification of graphene and TD via functionalization and hydroxylation respectively. There was significant increase in wear resistance and mechanical properties of the developed nanocomposites. The materials combination and methodology demonstrated in this study will be able to address the industrial challenges of high wear rate and poor mechanical properties associated with polymeric materials. For instance, such developed nanocomposites can find application as surface coating materials in high frictional environment. It can be used as solid lubricant where liquid lubrication is not suitable such as high temperature condition. Aerospace and automobile industries where materials with good flexibility, light weight and high mechanical strength are required can be beneficiaries of such fabricated nanocomposites.

2. Materials and methodology

The following materials were sourced from Sigma-Aldrich and were used in the course of this study; poly (vinylidene fluoride) (PVDF) powder, slightly oxidized graphene nanoplatelets (G), anatase titanium dioxide nano-powder (TD), 3-hydroxytyramine hydrobromide (HTHB), N, N-dimethyl formamide (DMF), ammonia solution, hydrogen peroxide (H$_2$O$_2$) and nitric acid (HNO$_3$).

Graphene (G) was functionalized with HTHB to promote its dispersion in PVDF matrix. First, 50mg of G was added in 50mL of distilled water and ultrasonicated at 80°C for 1 hour. Then, 40mg of HTHB was introduced into the suspension at the same condition. Ammonia solution was added in drops to activate the reaction process. The suspension was kept under ultrasonication and mechanical stirring for 6 hours at 80°C. Then, the particles were severally washed with distil water and DMF to obtain functionalized graphene (fG). H$_2$O$_2$ and HNO$_3$ were used in hydroxylation of TD to improve its wettability on fG in the polymer matrix.

In fabrication of the nanocomposites, certain amount of fG and TD were introduced in PVDF matrix by solution blending. fG and TD were first mixed in DMF. The blended nanofillers were added
into pre-dissolved PVDF. The suspension was homogenously mixed with the help of ultrasonicator and mechanical stirrer for 1 hour at 80°C. Then, the mixture was dried overnight in an oven at 80°C. The nanocomposites were then ground and melt-mixed using HAAK rheomix 600 OS for 15 min at 200°C and 150 rpm. The nanocomposites were finally hot pressed to desired shapes for analysis using carver press moulder at 200°C and 10 MPa for 5 min.

Attachment of TD on fG surfaces was investigated using Transmission Electron microscope (TEM) as reported in our previous work [15]. Morphology of the nanocomposites were investigated using Scanning Electron Microscope (SEM). Wear performance of the nanocomposites was obtained using tribometer (Anton Paar). This was carried out in accordance with ASTM G99-95 standard at room temperature and speed of 200rpm with steel ball of 0.3cm radius and 0.03µm roughness (Ra). Each sample was subjected to 1 hour wear test under applied normal load of 10N. Wear volume of the nanocomposites was obtained from their respective weight losses. Average of three tests were taken for each sample. Mechanical properties of the nanocomposites were determined using universal testing machine at ambient temperature. The tests were conducted according to ASTM D638 (Type V) standard. Crosshead rate of 5 mm/min was set. Each nanocomposite was tested five times and the average is presented as previously reported by Le, Huang [16].

3. Results and discussion

3.1. Morphological study of the nanofillers and nanocomposites

Figure 1 shows successful attachment of TD on fG surfaces. Large surface area of G can be seen from figure 1(a). After blending with TD, it was noted that TD was attached on the surfaces of fG as shown in figure 1(b). The attachment of TD on fG gave the nanofillers appreciable thickness, which helped in improving wear resistance of the polymer. Again, there was good wettability between fG and TD since there was no noticeable segregation of the nanofillers. This resulted from the surface modification of the nanofillers, which was essential in good compatibility of nanofillers. On the other hand, figure 1(c)
shows smooth microstructure of PVDF because it was still a homogenous material. On addition of 3.34 wt% fG/10 wt% TD in the matrix, the morphology changed as shown in figure 1(d). fG layers can be seen with dot-like surfaces, indicating the presence of TD on fG surfaces. As fG increased to 6.67 wt%, the presence of TD suppressed in the matrix due to high content of fG as shown in figure 1(e). Notably, there was no significant agglomeration of the nanofillers in the matrix. This indicates good bonding between the constituents of the nanocomposites due to surface functionalization of G and hydroxylation of TD.

3.2. Wear performance of the nanocomposites
The wear test conducted showed that there was significant reduction in wear volume of the nanocomposites when compared to pure polymer as shown in figure 2. The reduction in wear volume was due to the presence of nanofillers in the polymer matrix. The attachment of TD on fG played a vital role in reduction of wear volume of the nanocomposites by increasing the thickness of fG. It is believed that during wear process, TD on fG are first removed by the sliding counter surface, before detaching the large in-plane fG from the bulk material. Again, the initial removal of TD formed debris, which was transferred on the sliding counter surface. When this happened, it took longer duration before detaching fG, thereby increasing wear resistance of the nanocomposites. Due to the large dimension of fG in the matrix [2], it was possible for the counter surface to slide across fG without easy detachment. This is because after initial transfer of TD to the sliding counter surface, the wear operation continued by material to material contact instead of bare sliding counter surface to material contact. Therefore, reduction in wear volume was noted compared to pure polymer. For instance, wear volume reduction of about 69% was measured for 1.67 wt% fG/10 wt% TD nanocomposite when compared to pure polymer. Further increase in the nanofillers to 3.34 wt% fG/10 wt% TD, further reduced the wear volume to about 76.5%. At this concentration, there was thinner material transfer to the counter surface, uniform covering of counter surface and good bonding of transferred material on the counter surface. These conditions favour self-lubrication and low wear rate [1]. Beyond 3.34 wt% fG/10 wt% TD content, the wear resistance started decreasing as shown in figure 2(b) but was still better than pure polymer and 1.67 wt% fG/10 wt% TD nanocomposite. This can be attributed to high wt% of the nanofillers, especially fG as shown by the SEM image in figure 1(e). This might have reduced polymeric resin binding the nanofillers, resulting to easy detachment of the nanofillers with increasing wear volume when compared to 3.34 wt% fG/10 wt% TD nanocomposite. The significant reduction in wear volume shows that such nanocomposites are potential materials for high frictional environment.

3.3. Mechanical properties of the nanocomposites
Figure 3 shows tensile strength and Young modulus of the nanocomposites. The tensile strength of the
nanocomposites revealed improvement when compared with pure polymer. The improved strength was due to well distribution of the nanofillers and strong interfacial interaction with the polymer matrix. This often result to improved tensile strength [16]. With the presence of fG in the polymer matrix, there was formation of network structures by interconnection of the nanofillers. This resulted to restriction in mobility of the polymer chains when load was applied and increase in strength of the nanocomposites. It was noted that tensile strength was increasing continuously with increasing nanofillers content as shown in figure 3(a). As revealed in figure 3(b), tensile strength percentage increment of about 15.5%, 25.8% and 52% were respectively recorded for 1.67wt%fG/10wt%TD, 3.34wt%fG/10wt%TD and 6.67wt%fG/10wt%TD nanocomposites compared to the pure polymer. These indicate that there was good load transfer from the matrix to the nanofillers when external load was applied. This was due to good entanglement between the nanofillers and the polymer’s molecular chains. This resulted from surface modification of the nanofillers, which enhanced interaction with the polymer matrix.

![Graphs showing tensile strength and Young modulus](image)

**Figure 3.** (a) Tensile strength (b) Percentage increase in tensile strength (c) Young modulus and (d) Percentage increase in Young modulus of the nanocomposites.

On the other hand, the Young modulus of the nanocomposites showed significant increase compared to the pure polymer as shown in figure 3(c). There was steady increase in Young modulus with increase in nanofillers content. The increase in Young modulus was due to increase in stiffness of the materials, which resulted from good interfacial bonding between the nanocomposites’ constituents [17,18]. Also, the dot-like surfaces of fG in the polymer matrix due to the attachment of TD as revealed by SEM image in figure 1(d) promoted mechanical interlocking of the polymer molecular
chains. This resulted to reduction in interfacial sliding between the nanofillers and polymer’s chains. Hence, there was increase in stiffness and Young modulus of the nanocomposites compared to the pure polymer. High percentage increase in Young modulus of about 90%, 130.5% and 186.5% were obtained for various nanocomposites concentrations as shown in figure 3(d). Therefore, such nanocomposites are potential materials for various advanced engineering applications.

4. Conclusion
This study has been able to improve wear and mechanical properties of polymer using hybrid mixture of nanofillers. The nanofillers were noted to be well distributed in the polymer matrix due to surface modification. The nanocomposites showed significant increase in wear resistance. About 76.5% reduction in wear volume was recorded. Also, mechanical properties of the nanocomposites were improved. About 52% and 186.5% increase in tensile strength and Young modulus were measured respectively. With the improved wear resistance and mechanical properties, such nanocomposites can find application as protective surface coating materials for high frictional environment and mechanical components for automobile and aerospace industries.

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