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STUDIES ON TRIBOLOGICAL PROPERTIES OF ZnO FILLED POLYMER NANOCOMPOSITES

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ABSTRACT

The tribological behavior of polyester filled with ZnO nano particles was studied. For this study, ZnO nano particles were synthesized and size was found to be 34nm. The synthesized ZnO nano particles organically functionalized with γ-aminopropyltriethoxysilane (APS). The functionalized ZnO nano particles are mixed with polyester resin through ultra sonication for getting uniform dispersion. The wear samples were prepared by mixing 1wt%, 2wt%, 4wt% and 6wt% ZnO nano particles with polyester resin. The wear properties are studied by using pin-on-disc apparatus. The 1% ZnO nano polyester composite has excellent wear properties when compared to pure polyester. The characteristics of ZnO nano polyester composite is also studied by using Scanning Electron Microscopy (SEM). Filling of nano ZnO particles in polyester changed the microstructure of polyester and prevented the destruction of polyester banded structure during the friction process which might be one of the anti-wear mechanisms of nano ZnO. The improved and best tribo-performance of the composite can be attributed due to particular mechanical properties of nano particles.

Keywords: ZnO particles, polymer nano composites, SEM, sonication, wear properties.

1. INTRODUCTION

Nano particles are entities with diameters in the range of 1-100 nm. This new field of nanoparticles is lying between the traditional fields of nanoparticles is lying between the traditional fields of chemistry and solid-state physics. Therefore, a significant gap exists between these regimes with unique characteristics that neither obeys the law of physics nor quantum chemistry. The smaller is the particle, the higher is the surface-to-volume ratio. Thus more atoms tend to reside on the surface than inside the particle itself. Particle chemical/mechanical properties that are once determined by the molecular structures are now influenced by the defects on the surface [1].

The incorporation of fillers into a polymer matrix has shown tremendous promise in increasing longevity and achieving the desired mix of tribological properties in dry sliding. It is also attractive from processing consideration because the same processing methods as applicable to unfilled polymers can be used for filled polymers as well. A large number of tribological studies have been reported [2] to exhibit properties different from their micro scale counterparts. Since they have higher percentages of atoms on their surfaces, they are expected to be more active. In view of this, they would be expected to provide different tribological properties, hopefully beneficial. The wear resistance of polymer composites filled with micro particles depends on the modification of transfer film by the particulate filler material [3, 4]. Because of their high reactivity, nano particles should influence the transfer film more proactively than the micro particles.

Nano composite is a class of materials with unique physical properties and wide application potential in diverse areas [5]. Dispersion of nano scaled inorganic fillers into an organic polymer to form polymer nano composites has gained increasing interest in recent years. Controlling the nanostructure, composition and morphology of nano composites plays an essential role in their applications. Novel properties of nano composites can be obtained by successful imparting of the characteristics of parent constituents to a single material [6]. These materials differ from both pure polymers and inorganic fillers in some physical and nano scale inorganic fillers is opening pathways for engineering flexible composites that exhibit attractive mechanical, thermal, optical and electrical properties compared with conventional composites [7, 8]. ZnO is an important and attractive semi conductive material. It has drawn enormous attention due to its fantastic characteristics in optics, photonics and electronics [9].

Polymers are widely used in aeronautics, automobiles, constructions, oil and gas industries, and so on. However, they are susceptible to damage by scratching and abrasive wear. Such processes impair the appearance and also reduce the mechanical strength by the introduction of flaws [10]. Polymers scratch and abrasive properties are of practical importance and the use of reinforced polymer composites is becoming more common. When nanoparticles are embedded in polymer, the resulted composite material is known as polymer nano composite. Nowadays, polymer composites are widely used in many situations where machine components are subjected to tribological loading conditions [11-15]. For such components, it is imperative to understand the wearing mechanism under specific sliding conditions. Furthermore, the ever-increasing demand for reliability and long life of machine parts (made of polymeric composite materials) are one of the main concerns that during design stage [15, 16]. In view of this, many researchers are interested to study the wear properties at different loadings and found that, different inorganic fillers show distinct effect on the wear behaviors of polymer composites, so the mechanism of filler in reducing wear has been largely focused [17-21].

A lot of zinc compounds, such as ZnO, ZnF_2, and ZnS, were used as fillers of polymers. Bahadur and Kapoor [22] investigated the tribological characteristics of Nylon-11 composites filled with ZnF_2 and ZnS and it is found that both of them had bad anti-wear property as compound to pure Nylon-11. XPS analysis indicated that the two fillers did not decompose during the friction process, so the adhesion strength of transfer films of the composites was too low to maintain the transfer films on the counterpart surfaces. Scanning electron microscope (SEM) observation showed that the transfer films formed on the counterpart surfaces were very thick and easily scraped off. Bahadur and Zhang [23] also studied the effect of two other Zinc compound fillers, ZnO and Zn $(C_{18}H_{35}O_2)_2$, on the tribological behaviors of thermosetting polyester and found that the latter could remarkably reduce the wear rate of this polymer while the former could not. Recently, nanometer inorganic compounds, such as nanometer SiC and SiO_2, were also used as fillers of polymer in order to obtain good tribological properties [24-26]. Because nanometer compounds possess tiny particle size, the polymer composites filled with nanometer fillers may have different tribological characteristics in contrast with those filled with the same kind of micron fillers. In the present paper, the nanometer ZnO was selected as filler of thermosetting polyester and the wear properties of this polymer composite were systematically studied. The mechanism of filler action in reducing the wear of thermosetting polyester is also discussed.

2. EXPERIMENTATION

2.1 Chemicals required for fabrication of wear specimens

(a) Zinc oxide nano powder synthesized by the method reported earlier [27]. It is organically modified with a γ-aminopropyltriethoxysilane (APS) by sonication process.

(b) Resin: Unsaturated polyester has been a popular thermo set used as a polymer matrix in composites [28, 29]. In the present work, unsaturated polyester resin was used. This type of resin is a rigid, low reactivity, thixotropic general-purpose orthopthalic unsaturated polyester resin. It is pre-promoted for ambient temperature cure with addition of methyl ethylketone peroxide (MEKP) as catalyst. It is convenient for hand lay-up applications and easy air release. Unsaturated polyester possesses many advantages compared to other thermosetting resins including room temperature cure capability, good mechanical properties and transparency, low pressure moulding capabilities which make it particularly valuable for large component manufacture at relatively low cost [30]. Curing of unsatured polyester is due to a polymerization reaction that causes cross-linking among individual linear polymer chains. In contrast to other thermosetting resins, no by-product is formed during the curing reaction. Hence resins can be cast, moulded at low pressure and temperature. [28].

2.2 Fuctionalization of ZnO nano particles

Improvements in mechanical properties are dependent upon the nature of interactions between the matrix and filler. A γ-aminopropyltriethoxysilane (APS) is used to disperse/exfoliate the ZnO nano particles in polyester matrix. The compounding process was carried out with varying ZnO contents (1 wt%, 2 wt%, 4 wt% and 6 wt%) and the technique was found highly efficient and environment friendly.

In this study, an ultra sonicator was used to disperse and exfoliate the treated ZnO nano particles in the polyester matrix.

2.3 Synthesis of polyester-ZnO nano composites

Synthesis of polyester ZnO nano composites are prepared by mixing polyester resin with treated ZnO nano particles through ultra sonication for getting uniform dispersion. For fabricating these composites, a smooth wooden mould of 10mm diameter and 100mm in length was prepared and coated with light layer of liquid polyvinyl acetate (PVA) as a release agent. Then mixed polyester/treated ZnO nano particles resin was poured into the mould. Then the material was cured under room temperature condition for 24 hrs and then taken out of the mould and post cured in the air for another 24 hrs. Then the wear specimens are cut as per the dimensions. The above fabrication process is carried for different weight fractions of treated ZnO nano particles. The treated ZnO nano particles are reinforced in different weight percentages such as 1wt%, 2wt%, 4wt% and 6wt% to study the influence of ZnO nano particles.

2.4 Wear experimental procedure

Wear Experiments have been conducted in the Pin-on-disc type friction and wear monitor (DUCOM; TL-20) with data acquisition system, (Figures 1(a) and 1(b)) which was used to evaluate the wear behavior of the composite, against hardened ground steel disc (En-32) having hardness 65 HRC and surface roughness (Ra) 0.5µm. It is versatile equipment designed to study wear under sliding condition only. Sliding generally occurs between a stationary pin and a rotating disc. The disc rotates with the help of a D.C. motor having speed range 0-2000 rev/min with wear track diameter 50 mm-180 mm, which could yield sliding speed 0 to 10 m/sec. Load is to be applied on pin (specimen) by dead weight through pulley string arrangement. The system has a maximum loading capacity of 200N. Dry sliding tests were conducted at ambient conditions of temperature and humidity with different normal loads (5N, 10N, 15N, 20N) and sliding velocity 640 RPM. Prior to each test, the composite specimens was rubbed over a SiC abrasive paper 166-grade to ensure proper intimate contact between the sliding face of the specimen and stainless steel counter face. Also before each test, the wear track on the disc was refreshed by pressing on abrasive paper (silicon carbide water proof, grade 800) for few minutes to ensure same initial condition.

Figure-1(a). Pin on disc set-up.

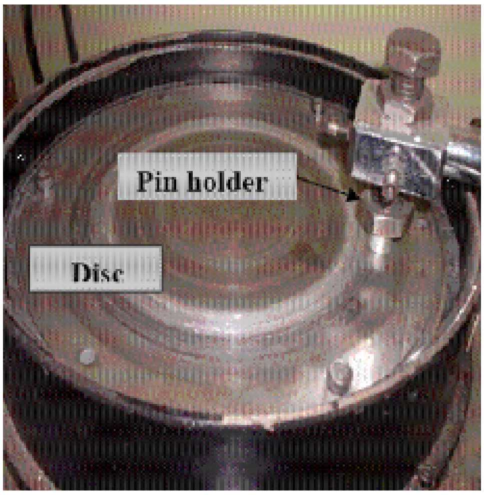

Figure-1(b). Pin on disc

2.5 Characterization of wear specimens

SEM (Model: FEG-Nova 600 Nano SEM) was used to study worn surfaces of composites specimens. For SEM analysis, specimen surfaces were gold coated to make them conductive with the aid of a SC7640 sputter coated of polar division before starting the scanning process.

3. RESULTS AND DISCUSSIONS

3.1 Wear properties of nanometer ZnO filled polyester composites

Most tribological studies with polymer composite sliding against steel counter face reported that tribo-chemical reactions are responsible for enhanced bonding of a transfer film to the counter face. The transfer film of a uniform thin film provides protection to the composite surfaces from aggressive damage of hard metal asperities which in turn reduces the wear rate.

Sliding against metal counter face exhibits two main mechanisms, abrasion and adhesion and the process of building up a thin polymer film goes from one stage to another until steady state is reached. Initially, the process begins with abrasion by which loose wear particles are produced and retained within the interface till their attachment or escape. The attached particles fill in the valleys of surface topography and as wear continues, the effectiveness of abrasion is reduced and a thin polymer film is formed on the meal surface by adhesion, called “transfer polymer film”. During or after this stage, another thin polymer film is simultaneously developed on the composite pin or back transferred from counter face into the composite pin, in either case is called “back transferred film”. The aforesaid transfer polymer film and the back transfer polymer film strongly determine the overall wear behavior.

3.1.1 Effect of filler content on the wear properties of polyester composites

It is well known [15] that small particles or powder fillers are generally embedded in the polyester matrix at the frictional surfaces of composites, and also easily transfer to the counterpart surface with the matrix and embed in the transfer film during sliding. In addition, the particles of nanometer size are impossible to rub markedly against the surface of polyester based composite and counterpart surface as compared with the particles of too large size. Therefore, after the transient wear state, the polyester composites filled with various amounts of nano ZnO exhibits excellent wear properties. The wear properties are studied for 1wt%, 2wt%, 4wt% and 6wt% nano ZnO filled polyester composite and reported in Figure-2. From Figure-3 it is observed that, the wear rate of neat polyester decreased from 0.0267 micrometers/sec to 0.01 micrometers/sec at a load of 5N by reinforcing 1wt% of ZnO nano particles. After this the wear rate increased to 0.0122 micrometers/sec and 0.023 micrometers/sec, respectively by reinforcing 2wt% and 4 wt%. From this, it is observed that the polyester composite filled with 1% ZnO nano particles exhibits lowest wear rate in comparison with the wear rate of pure polyester. It is also observed that, the wear rate difference is very less for 1 wt% and 2 wt% nano ZnO filled polyester composite. Thereafter increasing the percentage of ZnO nano particles, again wear rate of polyester composite is increased. The same trend is observed for 10N, 15N, 20N loads as shown in Figure (4-6). This indicates that the filler content played a key role in the wear property of polyester - based composites.

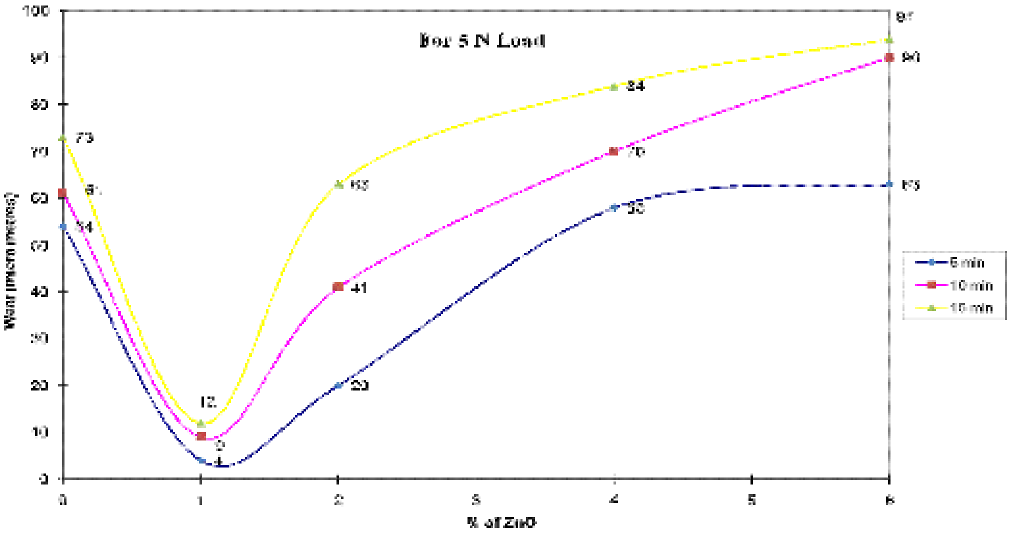

Figure-2. Variation of Wear with % Nano ZnO for different times at a load of 0.5 kg.

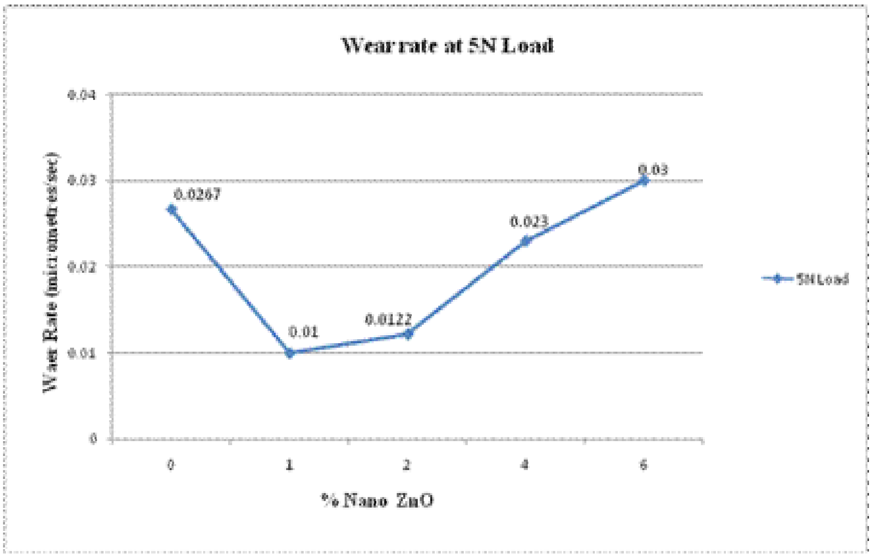

Figure-3. Variation of Wear Rate with % of Nano ZnO at 5 N load.

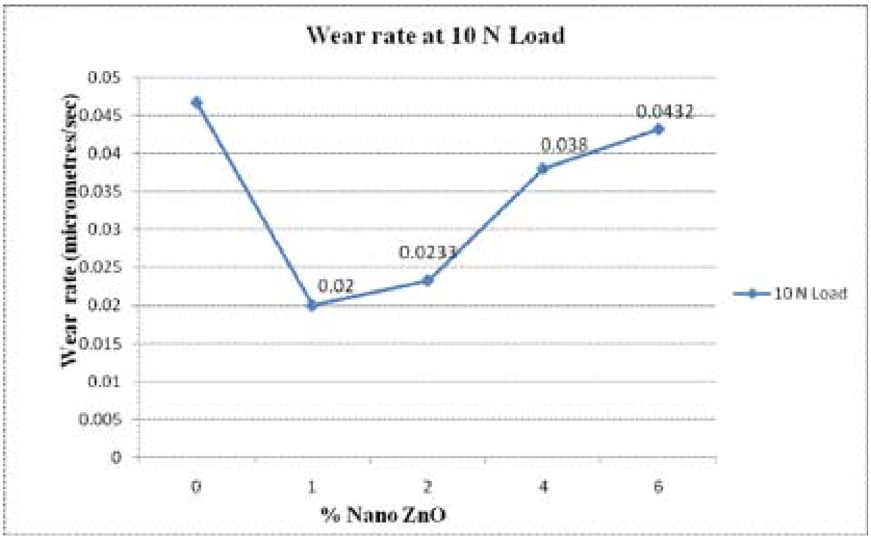

Figure-4. Variation of wear rate with % of Nano ZnO at 10 N load.

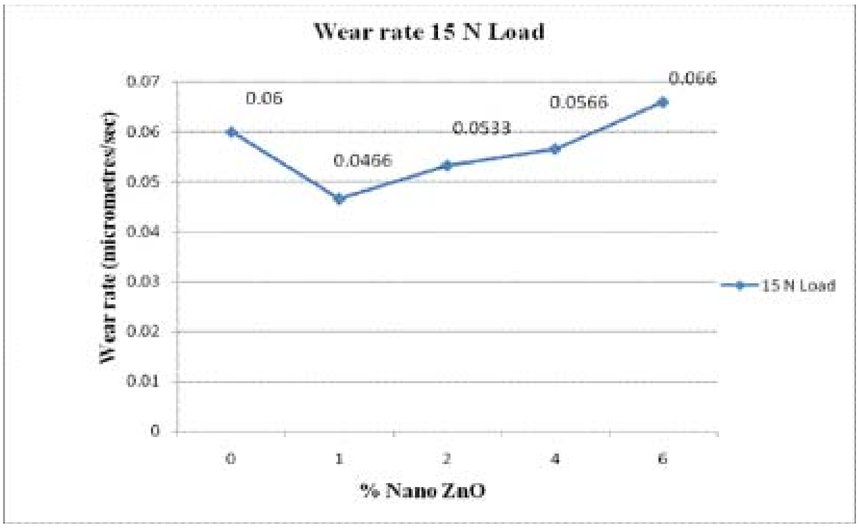

Figure-5. Variation of wear rate with % of Nano ZnO at 15 N load.

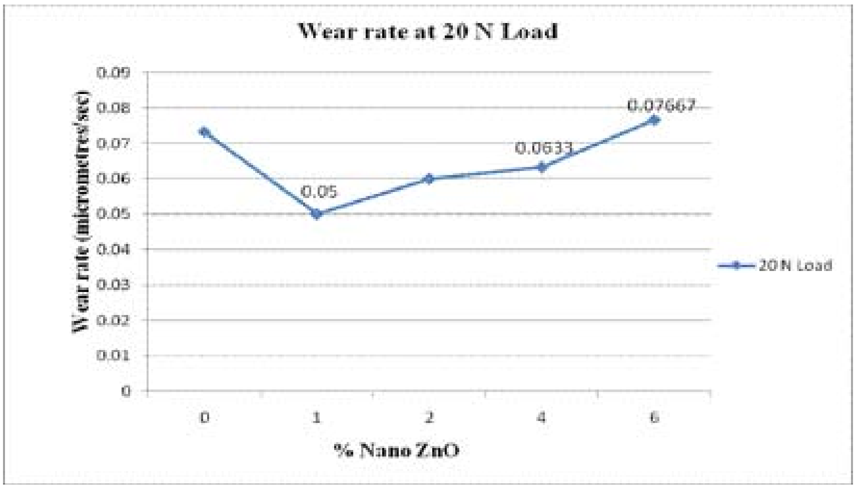

Figure-6. Variation of wear rate with % of Nano ZnO at 20 N load.

3.1.2 Effect of load on the wear rate of polyester composites

Variations of wear rate with load for pure polyester composite and nano ZnO filled composites sliding against stainless steel under dry friction conditions are shown in Figure-7. The wear rate of polyester composites is increased with load, but the values were greatly lower than that of unfilled polyester under every load. In this work, the best anti-wear ability was obtained when composite contained 1% nano ZnO.

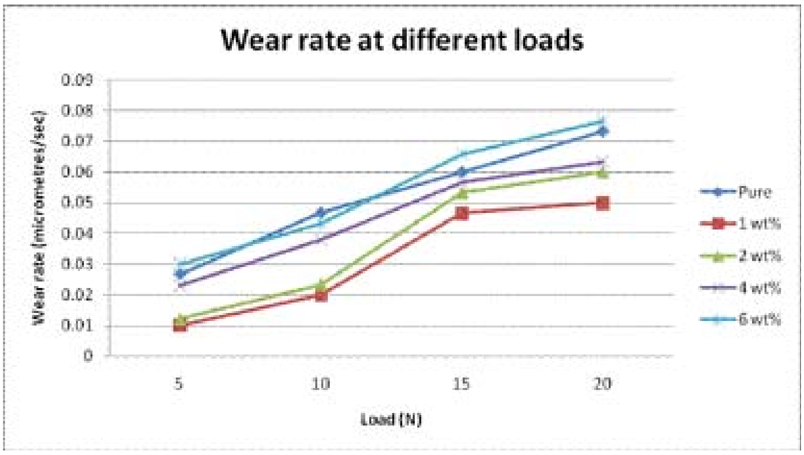

Figure-7. Variation of wear rate with Load for different % of Nano ZnO.

3.2 SEM Analysis of unfilled polyester and nano ZnO filled polyester composite

From the SEM examinations (Figure-8(a-e)) of ZnO filled polyester nano composites, it is clearly observed that the 1 wt% and 2 wt% ZnO nano particles are mixed thoroughly in polymer matrix without any aggregation of ZnO nano particles (Figure-8(b & c)). The surface is also smooth for 1wt% and 2 wt% ZnO nano polyester composites. From the SEM images (Figure-8(d to e)), it is observed that, there is an aggregation of ZnO nano particles in the polymer matrix by reinforcing 4 wt% and 6 wt%. Based on this examination, we infer that ZnO at low percentages distributed uniformly on the subsurface of the polyester composite, which reduces the destruction of polyester during wear process. Also observed, the higher percentages of reinforcing nano particles in the polymer matrix leads to aggregation.

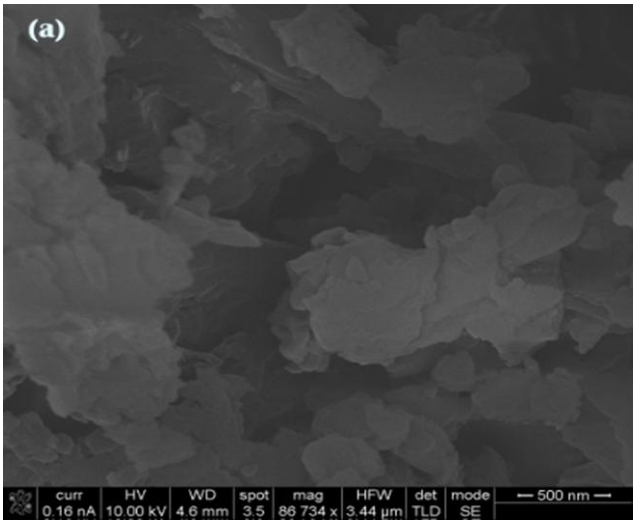

Figure-8(a). SEM image of pure polyester.

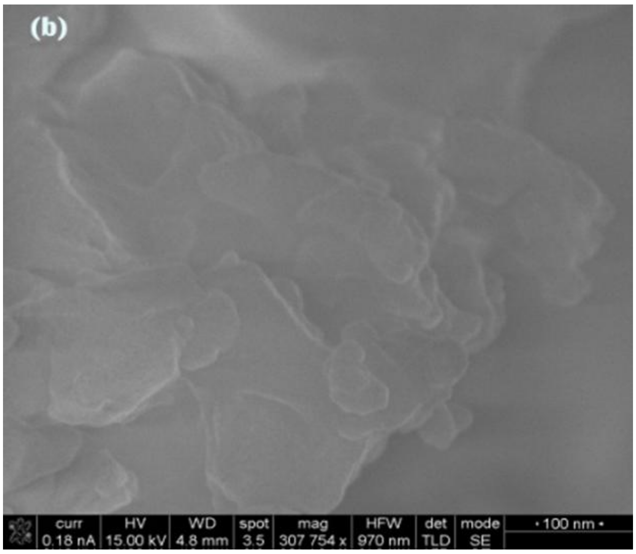

Figure-8(b). SEM image of polyester/1wt%ZnO nano composite.

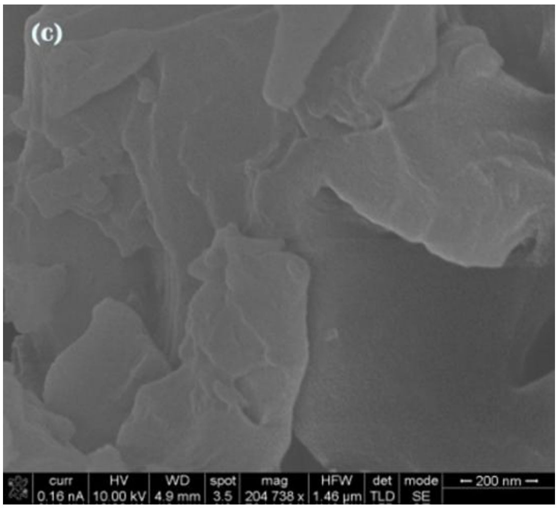

Figure-8(c). SEM image of polyester/2wt%ZnO nano composite.

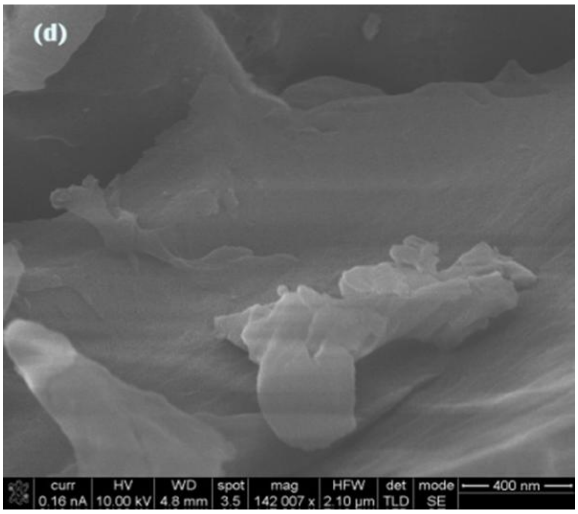

Figure-8(d). SEM image of polyester/4wt%ZnO nano composite.

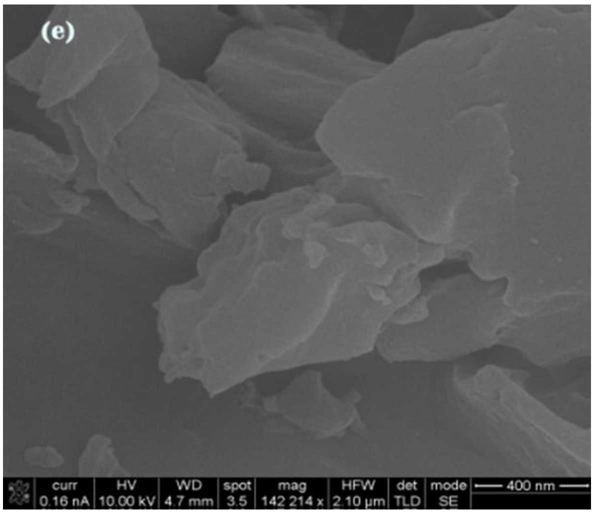

Figure-8(e). SEM image of polyester/6wt%ZnO nano composite.

3.3 SEM investigations of worn surfaces of unfilled polyester and nano ZnO filled polyester composite

To understand the effect of nano ZnO on the wear behaviors of nano ZnO filled polyester composite, the worn surfaces of pure polyester and 1 wt% ZnO filled polyester composite were studied by SEM (Figure). It can be seen from Figure-9(a) that the worn surfaces of pure polyester shows slightly ploughed marks, which were caused by destruction and transfer of the subsurface of pure polyester, appeared on the worn surface. In contrast, very less ploughed marks appeared on the worn surfaces of 1 wt% nano ZnO/polyester composite as observed in Figure-9(b), which means that the filler in the composite dramatically reduce the wear of polyester. With increase of load, the wear become mild to more, which is observed from the comparison between Figure-9(b) and (c). as seen from Figure-9(c), the worn surface of 1wt% nano ZnO/polyester composite sliding under 10N clearly shows large amounts of ploughed marks, which indicates that the amount of wear increases for a polyester composite when sliding under high load.

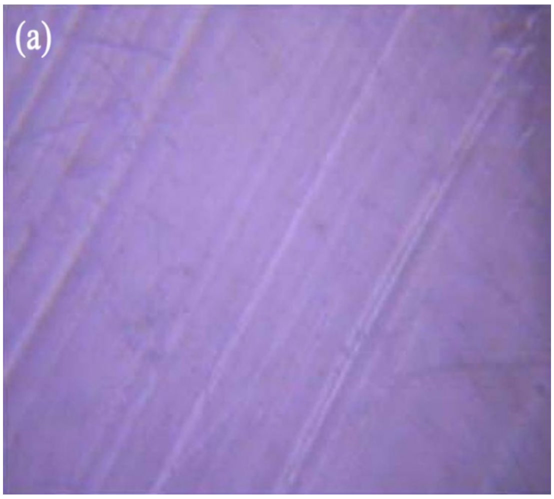

Figure-9 (a). SEM micrographs of worn surfaces of pure polyester (load: 5N).

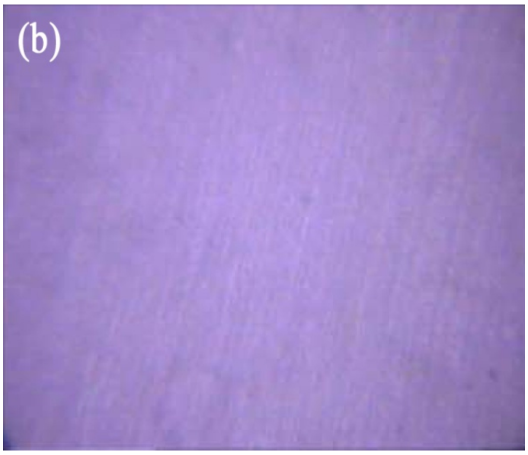

Figure-9 (b). 1 wt% ZnO/polyester (load: 5N).

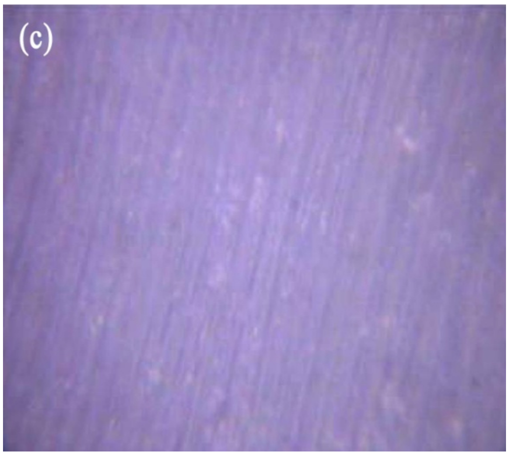

Figure-9 (c). 1 wt% ZnO/polyester (load: 10N).

4. CONCLUSIONS

- The wear rate obtained is very less for polyester composite by reinforcing 1wt% ZnO nano particles in comparison with other polyester composites. So it indicates that polyester/1wt% ZnO nano composite possess best anti-wear properties in comparison with pure polyester composite and 2wt%, 4wt% and 6wt% nano ZnO filled polyester composites;
- Filling of nano ZnO particles in polyester changed the microstructure of polyester and prevented the destruction of polyester banded structure during the friction process which might be one of the anti-wear mechanisms of nano ZnO;
- The improve and best tribo-performance of the polyester/1wt% ZnO nano composite attributed due to
- The agglomerations of nano ZnO particles in polyester composite have been avoided;
- The structural integrity of the polyester composite has been improved; and
- The particular mechanical and anti-wear action of nano-ZnO particles during the friction process due to the particular mechanical property of nano particles.

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