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# PERFORMANCE OF EPOXY PROTECTIVE COATING BASED ON NANOFILLERS: A REVIEW

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## ABSTRACT

In recent time, more and more emphasis has been placed on studding the behavior of erosion of polymeric composites. This may be due to the extensive use of these materials in its mechanical and structural applications. Epoxy is among of the most commonly coatings materials used in the industry that for their good appearance, wear resistance, and excellent adhesion to metal surfaces. The current work is focused to display a review on solid particle erosion of epoxy coating layer reinforced by various fillers was displayed. Erosion wear was evaluated using a solid impact erosion tester using different parameters such as sand particles with different sizes, impact velocity, and impingement angles. Epoxy coatings as a polymer matrix along with the details of the nanoparticle reinforcements, such as alumina, silica, titanium oxide, zinc oxide, clay and carbon-based materials. The effect of these nanoparticles on the properties of composite coatings has also been investigated.

## **KEYWORDS**

Erosion, Epoxy nanocomposite, Coating surfaces, nanoparticles.

## **INTRODUCTION**

Tribological properties are very important to the materials in contact and for the systems with highly sensitive to operating and environmental conditions. Economic and environmental costs can be saved by improving friction and corrosion in technological applications such as in metalworking systems as well as in machine components, [1].

Erosive wear is defined as the gradual loss of a solid surface material because of impact with a fluid or fluid that contains solid particles moving at a significant velocity, [2]. Solid particle erosion occurs when solid particles mix with a gas or liquid medium and impact a surface with any velocity. This type of erosion is a serious problem in many engineering systems, [3]. Sand erosion occurs in many engineering applications such as slurry pumps and turbines when mechanical force is the main effect, followed by corrosion, [4 - 5]. Steel substrates are widely used in many areas of industrial applications due to their superior mechanical performance and the relatively low cost compared to other substrates although there are some critical problems due to the high corrosion rate in harsh conditions, [6 - 7].

Organic coatings are the most common method of preventing corrosion of metal substrates, [6, 8], in which anti-corrosion protection is achieved by electrochemical or barrier mechanisms, [9]. Polymeric coatings are usually used as a layer that is sacrificed to protect components from erosion, corrosion, and abrasion, [10]. Their primary ingredients are resin, solvents, pigments, and additives. The resin is responsible for related properties such as the occurrence of adhesion between the substrate and the coating, cohesion of the dry coating, chemical and mechanical resistance, and other properties, [6, 11 - 12].

Epoxy is widely used as an erosion-resistant coating material due to its excellent mechanical and chemical properties. Carbon steel pipes used in seawater cooling plants can be damaged due to sediments in the seawater, so they are coated by epoxy to reduce erosion, which increases the life of these pipes, [4, 13 - 16].

Traditional coatings do not resist erosion well because of their poor erosion resistance. For increasing their resistance, filler particles are added to the polymer matrix in coating systems. Experiments have shown that the hardness of the coating system and its wear resistance increases by adding filler particles such as silica, silicon carbide and aluminum oxide, [17 - 21].

### 1. Erosion of Material

Erosion is defined as surface wear resulting from the interaction of the body surface with particles in the presence or absence of fluids. There are four types of erosion that have been identified and they are solid particle erosion, hot gas corrosion liquid collision corrosion and cavity corrosion.

#### **1.1 Solid Particle Erosion**

It is considered that the gradual loss of a solid surface material due to the repeated impact of solid particles moving through a flowing fluid is erosion. One of the common problems that occurs in the industry is corrosion in some practical components such as reducers, pipelines, compressors, pumps, and elbows. The failure of any of these components is very dangerous, and otherwise the costs of repair or replacement may be very expensive. SPE is a complex phenomenon as it contains many variables. Among these variables are the properties of the material that undergoes erosion, such as ductility, hardness, surface roughness, properties of solid particles in terms of size and shape, and properties of the fluid that transport the solid particles, such as its viscosity and density, and rate of flow of these fluid and solid particles, [22]. The aim of carrying out sand erosion testing of composite coatings is to protect the surfaces of vehicles and lamps from erosion during dust storms. When testing four types of transparent polymer coatings, they found that the lowest erosion rate occurred at a 90° impact angle and a coating thickness of 0.08 mm. The presence of sand particles inside the samples was indicated by increasing the sample weight after testing. A significant decrease in the wear rate occurs when heat treatment of coatings, [23]. The aim of performing SPE test for a group of materials with different mechanical properties is to discover the relationship between the ER and the mechanical properties, [24].

Erosion of polymeric materials takes two erosive behaviors namely, ductile and brittle. If the maximum ER occurs at impingement angles between  $15^{\circ}$  to  $30^{\circ}$ , the material considered

ductile, and if the maximum ER is at an angle close to  $90^{\circ}$ , the material considered brittle, [25]. SPE test of polyethylene (PE) using sand particles was carried out and it was found that the maximum erosion rates occurred at impingement angles between  $20^{\circ}-30^{\circ}$  and the weight loss was close to zero at about  $80^{\circ}$ . There is a change in the wear response of the materials because of a change in eroded particles properties, such as the shape, size, or hardness of sand particles, [26 - 29]. Erosion test at impingement angles of  $30^{\circ}$ ,  $60^{\circ}$  and  $90^{\circ}$  was carried out on samples of steel coated by epoxy having an oil content of (2.5, 5, 7.5 and 10) filling. The results showed that the oil content has a significant effect on the erosion behavior of the material, whether it is ductile or brittle, [30]. SPE test carried out on specimens of glass fiber reinforced epoxy (GF/EP) filled with boric acid at impingement angles of  $30^{\circ}$ ,  $60^{\circ}$  and  $90^{\circ}$ . Angular aluminum (Al<sub>2</sub>O<sub>3</sub>) was used as eroded particles and the impact velocity was 23, 34 and 53 m/s. It was found that ER of GF/EP composites without any filler material is the lowest due to strong bonding strength, [31].

The erosion behavior of epoxy filled with unidirectional and multidirectional carbon fiber (CF) was investigated with Irregular silicon carbide (SiC) particles and impact velocity of 70 m/s at impingement angles range from  $15^{\circ} - 90^{\circ}$ . It was observed that the erosion behavior of carbon fiber reinforced epoxy (CFRE) composites varies due to the position of the fibers. The maximum ER for unidirectional CFRE composites occurs at 90°, adopting the behavior of brittle materials, unlike other samples, [32]. SPE test carried out on square samples sized  $30 \text{mm} \times 30 \text{m} \times$ 

Silica sand particles were used at impingement angles ranging from  $15^{\circ} - 90^{\circ}$  and impact velocity 25 - 66 m/s. Maximum ER of PPS and its composites occurs at impact angle of  $30^{\circ}$ . Increasing the impact velocity and increasing the fiber content led to an increase in ER of PPS composites [34]. SPE behavior of unidirectional CF and GF and bi-directional E-glass fiber reinforced epoxy samples was investigated using silica sand particles at impact velocities of 25  $\pm 2$ , 37  $\pm 2$ , 47  $\pm 2$ , 60  $\pm 2$  m/s. Maximum ER of EP composites occurs at impact velocity of 25 m/s and impingement angle of  $60^{\circ}$ . The ER of bi-directional GF/EP composites is lower than that of the unidirectional composites, [35].

Erosive wear by impact of solid particles of epoxy reinforced by glass fiber (Epoxy/GF) in the presence of synthetic oil, is investigated under different impact angles of  $30^{\circ}$ ,  $60^{\circ}$ , and  $90^{\circ}$ . The minimum erosion occurred for the specimens filled by 10% of the oil, [36]. Paraffin and glycerin oils were used as fillers to epoxy/GF. The electrostatic charge of epoxy/GF in the presence of paraffin or glycerin oil recorded fewer results compared to synthetic oil, [37 - 38]. Epoxy resin reinforced by hybrid short glass fibers and fly ash ecospheres were tested. The steel substrate surface roughing increase adhesion strength of epoxy coating. Epoxy coatings reinforced by 20 % content hybrid with ratio of 1:1 that presented a vital role to improve the erosion resistance. So that the weight loss values remained low during early stage of the test period (2 - 4 h) before they started to increase with time, [39]. The most important and

extensively studied parameter in study the erosion of materials is the angle of impingement [28, 40]. Erosion wear of epoxy reinforced by silicon oxide (Epoxy/SiO<sub>2</sub>) was evaluated using a solid impact erosion tester, the impact distance was 15 and 20 cm at impingement angles of 30°, 60° and 90°. The results show that epoxy/SiO<sub>2</sub> coatings exhibit excellent anti-wear performance than the neat epoxy. The abrasive resistance and hardness value of epoxy coatings enhanced approximately 70 % and 24 %, respectively on loading of SiO<sub>2</sub> nano filler [41 - 42].

#### **1.2 Erosion Parameters**

The reason of why SPE is considered as a complex phenomenon is due to the many different factors that affect it. In this section a brief review of the research work that has been conducted is provided to identify these factors. Some of these factors are impact velocity, impingement angle, characteristics of impact particle in terms of shape, size, and surface properties of the material that is eroded.

Most of the erosion models indicated that the erosion rate is proportional to the particles impact velocity raised to some exponent.

$$ER \propto V^n$$
 E1.1

Where, ER is the erosion rate and V is the impact velocity of the particles. And they suggest that this exponent ranges from 2.05 to 2.44 based on the test conditions, [43]. It was also considered that this exponent does not depend on the eroded material or the mechanism of erosion, but rather depends on the characteristics of the impact particles, [44].

The erosion behavior of ductile and brittle materials varies depending on the impact angle of the particles. The impact angles can range from  $0^{\circ}$  to  $90^{\circ}$ , and the wear occurring at the  $0^{\circ}$  angle can be neglected because the particles do not impact the surface. Severe corrosion may occur at relatively small angles of about 20 when the eroded particles are hard, and the specimen surface is soft. Maximum wear rates occur at impact angles close to 90 when the surface of the material is brittle and severe wear may occur due to surface shattering, [45]. Figure 1 illustrates how the erosion behavior of ductile and brittle materials changes due to the impact angle of the particles, [46]. Particles characteristics such as shape, size and hardness have a significant effect on erosion but has not been researched relatively well. Hard particles occur higher erosion rate than soft particles, [47]. The erosion rate accelerated due to the sharpness of the particle, [48, 49]. Particle size is of great importance, and it has been observed that most erosion problems occur when the particle size ranges between 5 and 500  $\mu$ m [46].





## **1.3 Erosive Wear Mechanism**

SPE occurs when solid particles moving within a fluid impact the target surface and meanwhile the kinetic energy of the particles is partially dissipated through a variety of mechanisms such as heating, ductility, fracture, and phase transitions. These mechanisms are determined by the characteristics of the solid particles, target surface, and operational properties. Usually the application controls these parameters, but they can vary greatly during the operation cycle. Due to solid and hard particles are used, the wear process is like abrasive wear, and if the particles used are liquid, the wear occurs because of repeated stresses on impact.

Low impingement angles lead to abrasive wear, as the particles after the impact complete their movement in the path of the worn surface. In the case of large impingement angles, a typical erosive wear mechanism occurs. The impact velocity has a great effect on the wear process, as very low velocities cause stresses upon impact that lead to plastic deformation and make the wear occurs because of surface fatigue. The eroded material can be plastically deformed upon the impact of the particles, when affected by high impact velocities, and then wear will occur because of repeated plastic deformation and this is what happens in many engineering components, [50]. Figure 2 illustrates types of erosive wear mechanisms. Surface abrasive wear occurs in the event of particles impact with the surface at a low impingement angle, and in the case of a low impact velocity at a large impingement angle, the surface becomes fatigue, [27]. Multiple plastic deformation or brittle fracture occurs when the particles impact with the eroded material at medium velocity and at large impingement angles. It is possible that the surface melts when impacting with the particles at very high velocities and high impingement angles, and in the event of very large particles impact with the eroded surface at high velocity, the surface melts, causing eddies and debris. The crystal lattice of the eroded material decays to form an eroded structure upon impact with atmospheric atoms.

On the other hand, it was considered that the wear process resulting from erosion is the result of two different mechanisms, both of which occur at the same time, but one of them is more prominent than the other. These two mechanisms are: the deformation that occurs because of repeated deformation that leads to the removal of the material and the other is the cutting in which the material is removed in the form of chips [51]. A simplified model was made since the erosion process includes the cutting wear factor, which is the amount of kinetic energy required to release the unit mass from the material surface through cutting, and the deformation wear factor, which is the amount of kinetic energy required to release the unit mass from the forming process.

$$\mathbf{W} = \frac{MV^2 \cos^2 \alpha}{2 \phi} + \frac{M(V \sin \alpha - k)^2}{2\varepsilon}$$
E1.2

Where, W is the value of erosion, M is mass of eroding particles, V is impact velocity,  $\alpha$  is the impingement angle, k is the component of normal surface threshold velocity that no wear occurs below it in the material,  $\emptyset$  is cutting energy factor and  $\varepsilon$  is deformation energy factor, [52]. Although the mechanisms of cutting and deformation are considered the main cause of erosive wear It has also been revealed that surface cracking and crack proliferation may cause material removal, [53 - 54].



Fig. 2 Mechanisms of erosion; a) abrasion, b) surface fatigue, c) brittle fracture or multiple plastic deformation, d) surface melting, e) macroscopic erosion and f) crystal lattice degradation.

It is concluded that the removal of materials due to the mechanisms of cutting and plowing as is known in cases of erosion and abrasion is much less than the removal of materials resulting from surface cracking and cracking propagation, [55]. The behavior of the material under the influence of SPE is classified into two types, ductile and brittle. The first type occurs by removing materials through the plastic flow (cutting or plowing), and in most cases, the maximum ER occurs at a low impact angle ranging from  $20^{\circ}$ -  $40^{\circ}$ . As for brittle behavior, the surface of the material and dissipated by crack initiation, propagation, and intersection.

#### **1.4 Organic Coatings**

The base material for the coating can be phenol, novolac, urethane, nylon, or epoxy. Field data indicated that pipelines that have been coated with layers of epoxy phenol may remain protected for more than 30 years at high temperatures [56 - 58]. The wear resistance of traditional organic coatings is low and as a result, they don't perform well against erosion. Mechanical damage to organic coatings is caused due to particle impact and abrasion, the barrier properties of the epoxy-polyester coating decreased in the abrasive slurry containing sand and 0.6 wt.% of Na2SO4 aqueous solution. The wear resistance of coating decreased significantly with increasing number of abrasion cycles, [59]. Filler materials have been added to these organic coatings to increase their wear resistance.

There are various filler particles added to organic coatings to achieve sever functions. When silica nanoparticles were incorporated with epoxy and polyurethane their wear resistance is improved under the abrasive wear test, [18, 60]. Alumina nano particles with size of 50 nm were added to polytetrafluoroethylene (PTEF) and this increased the abrasive and scratch resistance of the polymeric coating without any decrease in the coating's resistance to corrosion, [61]. Zinc oxide (ZnO) nano particles with size of 50 nm were added to PTFE polymer and as a result the wear rate of this polymer greatly reduced. Wear resistance of PTFE/15 Vol.% ZnO composite coating was higher than coatings without filler particles, [62]. Modulus of elasticity of polypropylene polymer was increased by adding CaCO<sub>3</sub> and Talc fillers but these fillers decrease the yield strength of this polymer, [63]. The ultimate strength of epoxy and vinyl chloride/vinyl acetate coating was exposed to 5% NaCl, it was observed that the addition of MWCNTs improve the corrosion resistance of the polymeric coating, [64]. The addition of carbon nanotubes epoxy coatings improved the wear resistance of the coating and adhesion strength and reduced its porosity, [65 – 68].

The addition of filler particles with large size to the coatings may reduce the coating's anticorrosion performance. Corrosion behavior of epoxy-polyamide amine coatings reinforced by barium sulfate, talcum, and chromate fillers (2  $\mu$ m diameter) using 0.5  $\mu$ l NaCl solution was studded. The porosity of the coating increased because of filler particles and as a result the coating's corrosion resistance decreased [69]. The performance of coatings is greatly affected by the properties of filler particles such as shape, size, vol. %, and surface condition. The effect of incorporating spherical silica particles of various sizes (120 and 510 nm) into epoxy on corrosion resistance was studied using pin on disc method and found that the filler particles with small size improve the wear resistance of this composite, [60]. The effect of spherical alumina with the size of micro and nano scales added to the vinyl ester resin on Young's modulus was studied, and it was observed that a decrease in particle size at the nanoscale leads to an increase in Young's modulus, [70]. The effect of the size of filler particles added to fusion bonded epoxy on the erosion behavior of the composites was studied. Reinforced filler particles of alumina, silica and silicon carbide were used with sizes ranging from 20 to 80 microns. They found that the resistance of the composite to erosion increased with increasing the size of the filler particles, [17]. Increasing the volume fracture of the filler particles increases the resistance of the composite coating to abrasion, but there is a critical value for this volume fracture when exceeding this value decreases the wear resistance. It has also been found that mixing different sizes of filler particles has a better effect on wear resistance than using a single size filler, [71, 72]. A similar trend was found when studded the wear behavior of polyurethane coatings with addition of alumina particles. It was found that when increasing the amount of alumina particles, the wear resistance of the composite coatings increased and then decreased again, [18].

#### 1.5 Degradation of Filler Reinforced Organic Coatings under Erosion

The mechanisms of degradation of filler-reinforced coatings exposed to the environment with both erosion and corrosion are closely related to the structure of the coating material as well as the types of erosion methods used to test them. The degradation process of coating systems is complex and the reason for this is the synergistic effect of erosion and corrosion. When carrying out an erosion test for composite coatings with addition of relatively large filler particles with a diameter of up to 510 nm, it was noted that cracks may form in the interface of the polymer matrix and the filler particles. In the case of coatings with added filler particles of small size with a diameter of 120 nm, it is difficult to notice the cracks of de-bonding as the filler particles impede the spread of these cracks within the epoxy matrix, [18]. Although the filler particles are stiffer than the polymer matrix, upon exposure to solid particle corrosion, these particles may break and be removed together with the polymer matrix. However, the high hardness that the filler particles possess slows down the rate of material removal, [17]. At the beginning of the corrosion test, the polymer matrix is eroded, which causes the filler particles to stand out gradually and due to its high hardness, a slowdown occurs, but over time cracks begin to form at the polymer and filler interface, which leads to the removal of the filler particles, [18].

#### **1.6 Scratch of Polymers**

The scratch test is a simple semi-quantitative method that is sometimes used to measure the adhesion strength between the substrate and the coating material, and one of its most important features is that it simulates the stress conditions of using orthodontic implants more closely to the techniques of testing tensile adhesion strength as well as the possibility of using it in the case of thin coatings without risk of bonding agents coating penetration. In this test a normal load is applied to the sample surface by means of the stylus which is displaced at a constant velocity with respect to the sample, [73]. Whereas scratch damage has become one of the most common tribological damage to polymers. It has become one of the main desires of component manufacturers and polymer producers to improve their scratching performance, [74]. In the recent period, the application of scratch testing on polymer compounds increased to find out the scratch behavior of various test materials, [75, 76]. It is difficult to predict the scratch characteristics of polymers due to their properties are complex and their response to scratching differs from each other, [77]. The mechanical properties of the polymer compounds

are what govern their performance characteristics, [78]. The difference in the fine structure and defect conditions that result from the deposition processes may cause a difference in the mechanical properties of the same material, whether in bulk form or the individual components, [79].

# CONCLUSIONS

The paper discussed the importance of surface modification of nanoparticles as a necessary factor in optimization of the filler, polymer interaction and homogeneous distribution of NPs in matrix material. Note that this process might cause to prevent the phase separation disruption in the composite to achieve desired properties. Furthermore, it has been shown that different NPs has a clear influence on the properties of nano-composite coatings. The erosion rate of epoxy coatings decreases with increasing the content percent of nanoparticles in the specimen to a specified percentage and then increasing again. Finally, the cohesion between epoxy resin and nanofillers gradually begins to decrease, causing a decrease scratch resistance and hardness value.

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