Experimental study and optimization of thermal and tribological properties of epoxy hybrid polymer composite reinforced with micro sized ZrB₂ and PTFE particles

Aswathi A Narayanan¹²³ and R S Sudheesh¹

¹Department of Mechanical Engineering, Government Engineering College Thrissur, Kerala, India.
²APJ Abdul Kalam Technological University, Kerala, India.
³E-mail: aswathiii333@gmail.com

Abstract. Epoxy based materials have been extensively used in the friction parts and oil free applications. High local temperature due to the increased wear and coefficient of friction adversely affect the service life of parts. In this study, the thermal and tribological performance of epoxy composite reinforced with Zirconium Diboride (ZrB₂) and Polytetrafluoroethylene (PTFE) particles is investigated. Under a load of 40 N and 1.25m/s sliding speed, the optimum content 5.939 vol% of PTFE and 5.002 vol% of ZrB₂ yields an ultralow coefficient of friction (COF) in conjunction with a low wear rate of composite. Optimized value of Coefficient of friction (COF) and wear rate using Central composite-response surface methodology (RSM) are 0.182 and 0.00033 mm³/Nm respectively. The increase in thermal conductivity is due to the addition of ultra-high-temperature ceramic ZrB₂ particles and solid lubricant PTFE. The optimum composition of the composite can reduce the adhesive wear and high local temperature due to friction which help to enhance the service life of tribological parts.

1. Introduction

The epoxy based materials possess good elasticity, abrasive resistance and light weight characteristics so that it widely used in the fields of high-speed rail, automobile industry and aerospace as gears and shaft parts [1]. However, the adhesive wear and high local temperature due to friction will reduce the service life of the major parts. The introduction of ceramic fillers, such as SiC, Al₂O₃, Si₃N₄ etc. with high wear resistant performance and thermal conductivities is an effective method to improve the tribological and thermal performance of polymeric composites under high loading conditions [2]. Compared with other ceramic fillers, ZrB₂ is regarded as the potential filler with improved tribological performance due to its lamellar crystal structure [3].

Lubrication helps to reduce the heating and improve the tribological performance. Liquid lubricants undergo thermal break down at high temperatures. In such situations, solid lubricants must be employed. Solid lubricants often lead to decrease of friction coefficient and wear rate through the reduction in adhesion with the counter face or creation of transfer film with a low shear strength at the interface. PTFE chains can be drawn out on the surface to form an extended chain crystal structure which is conducive to low shear and thus low friction [4-5].

During sliding, frictional heat and resulting contact temperature determine the tribological performance of polymer composites. Low thermal conductivity usually leads to the accumulation of frictional heat which will degrade the organic ingredient. This affects the capability of composites
adversely. A high thermal conductivity could improve the heat transfer. Hence low friction coefficient and relatively high thermal conductivity are required to achieve good performance [6].

In this work, epoxy hybrid polymer composite reinforced with micro-sized ZrB₂ and PTFE particles were prepared to enhance thermal and tribological properties. ZrB₂ is one of the most important ultra-high-temperature ceramics with high elastic modulus, high strength, excellent wear resistance and high thermal conductivity. Lubrication is another important factor which reduces the effects due to high temperature. Hence PTFE was incorporated as a solid lubricant and friction modifier.

To the best of our knowledge, there is no paper reporting on the ZrB₂ filled PTFE reinforced polymer composites to improve the tribological and thermal performances, implying the significance of this work. The effects of filler content, applied load and sliding speed on the tribological properties of hybrid PTFE/ZrB₂ epoxy composite were investigated. Present work aims to achieve a material with low friction coefficient and high thermal conductivity for tribological applications such as bearing, gears, shaft parts etc.

2. Experimental details

2.1 Materials used
Bisphenol-A based Epoxy resin (Lapox L12), a medium viscous semi-solid material having density 1.1 gm/cm³ is used as the matrix material and an amino group hardener (K-6) is used for hardening the material. The reinforcement materials used here are Zirconium diboride (ZrB₂, 1-3 μm, ceramic particle) and Polytetrafluoroethylene (PTFE, 10-12μm, solid lubricant).

Initially, the reinforcements ZrB₂ and PTFE of required weights for each composition were preheated to 120°C in muffle furnace to remove the moisture. The reinforcements were added to the matrix, and mixed continuously using ultrasonic mixer for 30 minutes until the reinforcement were properly distributed. Hardener was added to the mixture in ratio of 10:1 and hand stirred gently so as to avoid trapping of bubbles. The mixture was then poured into the moulds. The specimens were allowed to cure in the mould for 24 hours at room temperature. Moulds were prepared as per the specimen standards for testing.

2.2 Hardness Test
Hardness of the composites and the matrix polymer are measured using Rockwell hardness tester at different locations. Steel ball indenter of ¼ inch diameter is used for indentation. The specimen was subjected to the preliminary load of 10kgf. An additional load of 60 kgf is given for 4 to 6 seconds prior to release.

2.3 Wear Test
Wear test of the epoxy hybrid composites and the matrix polymer was conducted using DUCOM Pin-On-Disc Tribometer. The cast composites were machined to a size of 7.5 mm diameter and 30 mm length (ASTM G99 standard) pin as the wear test sample. Pin-on-disc tribometer with EN31 hardened to 60 HRC disc with a diameter of 150mm was used for wear testing. The test parameters namely sliding speed, load and sliding distance are kept constant at 1.25m/s, 40 N and 750 m respectively. The test was run for 3000 number of revolutions at 299 rpm and track diameter of 80mm. The friction coefficient is the ratio of the measured friction force and load. It was measured from the frictional torque gained by a load cell sensor, which was acquired directly by the computer with the aid of vendor supplied software interface.

2.4 Optimization
The levels of vol % of ZrB₂ and PTFE are given in Table 1. The adequacy of the developed empirical relationship for the response variables namely, hardness, wear rate and coefficient of friction was tested using the analysis of variance (ANOVA) technique. Here the quadratic design model is
considered for modelling of responses. Design–Expert 11 is a statistical software package from Stat-Ease Inc. that is specifically dedicated to performing design of experiments (DOE) for developing mathematical model and optimization processes. The experiments are designed according to face-centered design of central composite method of RSM. Optimization is done according to the responses of hardness, wear rate and coefficient of friction obtained from corresponding runs. The parameters used for experimentation and their corresponding response in this study are given in Table 2.

**Table 1. Levels of compositions**

| Parameter     | Levels |
|---------------|--------|
|               | -1  | 0  | 1  |
| A: ZrB₂ (Vol %) | 3  | 5  | 7  |
| B: PTFE (Vol %) | 3  | 6  | 9  |

**Table 2. Design Layout and their corresponding response**

| Run out | ZrB₂ Vol.% | PTFE Vol.% | Hardness HRB | COF | Wear Rate mm³/Nm |
|---------|------------|------------|--------------|-----|-----------------|
| 1       | 5          | 3          | 80.33        | 0.3075 | 0.000669        |
| 2       | 5          | 6          | 79.33        | 0.18  | 0.000334        |
| 3       | 5          | 6          | 79.33        | 0.18  | 0.000334        |
| 4       | 3          | 3          | 70           | 0.3315 | 0.001055        |
| 5       | 7          | 9          | 59.33        | 0.2565 | 0.000736        |
| 6       | 5          | 6          | 79.33        | 0.18  | 0.000334        |
| 7       | 7          | 3          | 63.67        | 0.363  | 0.000703        |
| 8       | 3          | 6          | 65.33        | 0.26  | 0.000837        |
| 9       | 5          | 6          | 79.33        | 0.18  | 0.000334        |
| 10      | 5          | 6          | 79.33        | 0.18  | 0.000334        |
| 11      | 7          | 6          | 60           | 0.21  | 0.000586        |
| 12      | 3          | 9          | 57.67        | 0.29025 | 0.001339        |
| 13      | 5          | 9          | 68           | 0.2295 | 0.000502        |

3. Results and Discussion

3.1 ANOVA results for hardness and wear rate

The response surface obtained from ANOVA is shown in figure 1. It depicts the relationship between hardness, vol% of PTFE and vol% of ZrB₂. The hardness of the base polymer matrix is measured as 53.7 HRC. An increase in the vol. % of ZrB₂ and PTFE particles resulted in increase in hardness. The incorporation of hard ceramic particles improves the hardness of composites positively. By adding reinforcement particles to the matrix, the surface area of reinforcements increases. The presence of hard ceramic particles on the surface offers high resistance to plastic deformation leading to the increase in hardness of the composite. When considering individual reinforcement particles, the hardness increases with the addition of ZrB₂ up to 5% particles and further addition of reinforcement
reduces it. Reduction in hardness may be due to the agglomeration of the ZrB$_2$ particles in the composite [3]. In the case of PTFE reinforcement particles, the addition of reinforcements decreases the hardness. PTFE acts as a solid lubricant in the composite, and PTFE is a soft material compared to the hard ceramic particles like ZrB$_2$. The response surface of wear rate obtained from ANOVA is presented by figure 2. It depicts the relationship between wear rate, vol% of PTFE and vol% of ZrB$_2$. Wear decreases considerably by the addition of both ZrB$_2$ and PTFE. Addition of micro ZrB$_2$ particles increases wear resistance of the material, resulting in less wear. In case of the base matrix epoxy the complete surface area will be in contact with the disc which result in increased wear compared to the composites. The hard ceramic ZrB$_2$ particles acts as protuberances over the surface. These protuberances tends to protect the matrix from the uniform contact with the counter-facing steel disc, thereby reducing the contact area between the test surface and the rotating disc resulting in reduced wear. PTFE acts a lubricant thereby reducing the friction and the resultant wear. Wear gets decreased with the addition of fillers up to a 5%. Any further addition of filler results in increase in wear due to the agglomeration of the fillers [3].

3.2 ANOVA results for coefficient of friction

The surface plot of coefficient of friction for various compositions of hybrid polymer composite is shown in figure 3. It depicts the relationship between coefficient of friction, vol% of PTFE and vol% of ZrB$_2$. Addition of ZrB$_2$ particles increases hardness thereby reducing the COF of the composite. The
protuberances on the surface of composites helps to reduce the contact area between the specimen surface and the counterface disc aiding in the reduction of friction. PTFE provides a lubrication effect between the contact regions which also causes reduction in friction.

3.3 Experimental validation of model
The optimum % volume levels obtained using ANOVA were 5.002% of ZrB2 and 5.939% of PTFE respectively. In order to validate the result experimentally, composite was prepared as per the optimum condition. Hardness test and wear tests were carried out on the prepared composite under a load of 40 N and 1.25m/s sliding speed. The results of the experiment conducted along with the predicted results and error characteristics are given in Table 3. From these results it can be observed that the model has good agreement with predicted results.

3.4 Worn surface
The Worn surface of epoxy hybrid composite was examined using optical microscope. It reveals that the wear mechanism changes from adhesive wear to abrasive wear as the filler content increases. Figures 4. (a) & (b) show the optical images of counter part of pure epoxy. Adhered material can be seen in the figure. It is due to the adhesion of epoxy polymer material on to the counter face. Adhesion is also visible for epoxy composite with 3 vol. % ZrB2 and 3 vol. % PTFE (Figures 4 (c) & (d)), but the quantity of adhered material is less than pure epoxy. As the volume fraction of the composite increases to 6 vol% PTFE and 5 vol. %ZrB2, the small grooves are visible for higher amount of fillers (Figures 4 (e) & (f)). The wear mechanism for composite with higher volume fractions of filler is mainly abrasive wear. The change of nature of wear from adhesive wear to abrasive wear is due to the presence of hard ZrB2 particles.

3.5 Effect of load
To study the influence of load on wear and coefficient of friction at optimum composition, the load varied from 10N to 60N. Sliding speed and the sliding distance were kept constant at 1.25m/s and 750 m respectively throughout the testing. An increase in wear and coefficient of friction is observed as load increased from 10N to 60N due to the increased surface closeness with normal load as shown in Figure 5 and Figure 6. In the beginning with the low load, there was a light contact pressure between the two mating surfaces which lead to lesser material removal. The wear and coefficient of friction due to low load will be less. On increasing the load, the contact pressure gets increased which in turn increase the actual contact area between the mating surfaces. This eventually produces higher deformation and debris formation which lead to increased wear and coefficient of friction. Further the debris formed in the wear track starts cramming between the surfaces and results in more wear. As the load increases, initially the protuberances (particles) in the mating surface of the pin created

3.4 Worn surface

| Exp. No | Hardness (HRB) | Wear rate (mm³/Nm) | COF     |
|---------|----------------|--------------------|---------|
| 1       | 77.9           | 0.000382           | 0.185   |
| 2       | 78.5           | 0.00034            | 0.182   |
| Average | 78.2           | 0.000361           | 0.1835  |
| Predicted | 78.7119   | 0.00035            | 0.1826  |
| %Error  | 0.65034        | -7.78307           | -0.49178|

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small contact area resulting in smaller wear and coefficient of friction. When the load increases, the particles get worn out and the soft matrix part exposes. Hence, the contact area between the mating surfaces increases, resulting in increasing wear.

![Optical microscope images](image)

**Figure 4.** Optical microscope image of counterface (a) & (b) pure epoxy, (c) & (d) 3 vol.% PTFE + 3 vol.% ZrB₂, (e) & (f) 6 vol.% PTFE + 5 vol.% ZrB₂, (g) & (h) 9 vol.% PTFE + 7 vol.% ZrB₂.

### 3.6 Effect of sliding speed
To study the influence of sliding speed on wear and coefficient of friction at optimum composition, the sliding speed is varied from 0.75 to 2 m/s. Load and the sliding distance were kept constant at 40N and 750m respectively throughout the testing. Theoretically, the temperature rise due to the high sliding velocity induces a thermally activated process and causes an increase in wear and coefficient of friction. The specific wear rate is inversely proportional to the sliding velocity in the region of low sliding velocity where the temperature rise is not significant. There was a decrease in wear and coefficient of friction as sliding speed increased from 0.75 to 2 m/s as shown in

![Wear and COF graphs](image)

**Figure 5.** Wear of PMC’s versus Load (N)  
**Figure 6.** Friction Coefficient of PMC’s versus Load (N)
Figures 7 and 8. As usually found in polymer composites, wear decreases at low sliding speeds. This phenomenon is observed in this case also at lower speeds. The wear and coefficient of friction decreases from 0.75 m/s to 1.5 m/s and remains constant for the further increment in sliding speed. Higher sliding speed may cause high temperature between the sliding pair. Since ZrB₂ is an ultra high temperature ceramic material the composite can withstand the high temperature.

3.7 Thermal performance of composite

The current study employs Hot Disk thermal constants analyzer to evaluate the thermal conductivity of the composite. The Hot Disk TPS 500 Thermal Constants Analyzer accurately measures the thermal conductivity, thermal diffusivity and specific heat capacity of wide range of materials. The experimental values of thermal conductivity are given in Table 4. Thermal conductivity increases with increase of ZrB₂ content. PTFE is a self-lubricating material and help to reduce the heat accumulation due to the friction. ZrB₂ is an ultra-high-temperature ceramic with high thermal conductivity, thereby can provide high thermal properties to the composite.

Table 4. Experimental values of thermal conductivity (W/mK)

| ZrB₂  | PTFE (Vol %) |
|-------|--------------|
| (Vol %) | 3 | 6 | 9 |
| 3     | 0.2781 | 0.28 | 0.282 |
| 5     | 0.2961 | 0.2983 | 0.3005 |
| 7     | 0.3113 | 0.3137 | 0.3162 |

4. Conclusion

In this study, tribological and thermal properties of epoxy hybrid polymer composite reinforced with ZrB₂ and PTFE particles are studied. Maximum Hardness of 78.712HRB, Wear rate 0.000334mm³/Nm and coefficient of friction 0.1826 were observed at optimum values of 5.002% of ZrB₂ and 5.939% of PTFE using ANOVA. Analysis of the worn counter face surface shows that wear
is predominantly adhesive in nature. This adhesive wear decreases with the addition of reinforcements. Load and sliding speed also has a significant effect on wear and coefficient of friction. Thermal conductivity of composites is also enhanced by the addition of fillers. Ultra high temperature ceramic ZrB2 particles acts as protuberances over the surface. These protuberances tends to protect the matrix from the uniform contact. The self-lubricating property of PTFE provide reduced wear rate and enhanced thermal conductivity. Reduction of wear rate, coefficient of friction and increased heat transfer will reduce the heat accumulation during the process. Due to these effects, this composite can ensure increased service life for tribological parts.

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