Applied Science and Engineering Progress, Vol. 14, No. 4 (Special Issue), pp. 606–613, 2021

Review Article

Desirability of Tribo-performance of Natural Based Thermoset and Thermoplastic Composites: A Concise Review

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DOI: 10.14416/j.asep.2021.07.001
Received: 15 April 2021; Revised: 9 May 2021; Accepted: 31 May 2021; Published online: 5 July 2021
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Abstract
Tribology, which may be defined as an interdisciplinary subject, deals with relative motion between two or more bodies, i.e., surfaces that are interacting relatively. Thus, tribology is a science covering three vital classes, namely, wear, friction and lubrication. The focus of this article is to bring out the elements that are influencing the wear-resisting behavior of thermosetting and thermoplastic composites with natural-based constituents. Based on the literature resources, the treatments on the natural fibers acting as reinforcement, and the addition of fillers in resin acting as matrix could improve the wear-resisting behavior of the composites. Additionally, other conditions such as sliding speed, sliding velocity, sliding distance and operating temperature could also influence the friction coefficient and specific wear rate of the natural-based composites.

Keywords: Tribology, Thermoset, Thermoplastic, Friction, Lubrication

1 Introduction

Polymer-based composites have emerged as a successful alternative to traditional materials such as steel and aluminum. Today, composites have been employed in many sectors, namely marine, aviation, transportation industries, production industries, oil industries, automobile industries, etc. Thermoplastic-based composites have the upper hand over the thermoset-based composites in the semi-structural and non-structural

Please cite this article as: A. Dhandapani, S. Krishnasamy, T. Ungtrakul, S. M. K. Thiagamani, R. Nagarajan, C. Muthukumar, and G. Chinnachamy, "Desirability of tribo-performance of natural based thermoset and thermoplastic composites: A concise review," *Applied Science and Engineering Progress*, vol. 14, no. 4, pp. 606–613, Oct.–Dec. 2021, doi: 10.14416/j.asep.2021.07.001.

applications due to their advantages such as compatibility with dyeing agents, ease of manufacturing, permits recycling and re-use, low cost, lightweight, and mass production. Thermoset composites are obtained in a solid-state from pre-existing liquid forms by a non-reversible process or a chemical change through the mixing of hardener, which induces the crosslinking action within the polymeric chains of the thermoset resin [1]. On the other hand, the thermoplastic composite materials are transformed into solid-state through a thermal curing process that involves applying heat and pressure.

Thermoplastic matrices have high chemical stability, unlike thermoset matrices. They soften on heating, and hence, they can be remolded into the finished shape on cooling without much degradation in their properties. This process of heating followed by cooling can be carried out multiple times, which contributes to the indefinite shelf life of thermoplastics [2]. Moreover, techniques employed for metal and woodworking, such as forming, cutting, joining, etc., could be used to shape thermoplastic composites. Also, the tough nature of thermoplastic matrices contributes to increasing their recycling and damage tolerances. Thermoplastics can be categorized further as commodity plastics and engineering plastics.

2 Natural Based Thermoplastic Composites

The composites of thermoplastic are fabricated with different combinations of resins, fibers, fillers, etc., which could be synthetic as well as natural. This is carried out to obtain specific required material properties. Natural-based thermoplastic composites involve natural compositions as a solution for issues related to the environment. These thermoplastic composite materials containing different matrices, reinforcements and/or fillers are subjected to wear, friction, and lubrication issues in their applications. Figure 1 shows different combinations of natural-based composites.

Some of the natural fibers, which include sisal, jute, hardwood, softwood, and various others, improve the properties of composites due to their reinforcement with polymer matrices. Many reports are available using natural fibers as reinforcement with matrices or resins that are also natural. Still, there is enormous scope for identifying new natural materials, which are continuously progressing. Researchers have been working on the development of entirely bio-composites [3]–[5].

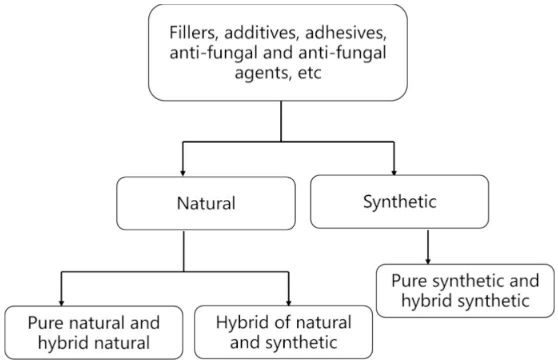


Figure 1: Combinations of natural-based composites.

3 Tribological Analysis

A tribological analysis is the science concerned with surfaces that move relatively and they cover 1) friction, 2) lubrication, and 3) wear. The interface could be between two or more bodies that move relative to each other. Examples are motion occurring in bearings, gears, propeller shaft – propeller bearing, piston-cylinder assembly, and gyroscopes.

3.1 *Need for tribological analysis*

Continuous improvements and engineering innovations have increased the demand for materials with enhanced stability at higher temperatures and extreme loads with excellent tribological properties. The composite materials are expected to perform under severe environments involving harsh conditions such as extreme stresses due to thermal, mechanical, or electrical loads over time. The conditions could also be demanding, such as corrosive environment and highly demanding. Thus, the materials are being continuously monitored for tribological applications [6].

3.2 *Methods to access tribological properties*

Table 1 gives the different testing methods for analyzing wear performance and corresponding ASTM standards, sample size, and applications.

Table 1: Different testing methods for analyzing wear performances

Types of Wear Test	ASTM	Preferred Sample Size (mm^3)	Application
Dry sand rubber wheel	G65	70×20×7	Rollers, bushes, tires, and bearings
Pin on drum	A514	-	Conveyer belts
Linear tribo machine	-	-	Door rails, window panels
Block on ring	G137-95, G77	10×20×50	Bearings, cam shafts, and rubber tires
Pin on disc	G99	10×20×20	The particular interest of any two materials always in contact with each other
Block on disc	G99	10×20×20	The particular interest of any two materials always in contact with each other

3.3 *Determination of tribological behavior*

3.3.1 Coefficient of friction

When the rubbing starts between the loaded composite sample and Steel counterface in the tribo tester, the wear properties (i.e., friction and wear) continuously show the values of the tangential force in the monitor. Thus, the frictional force (F_f) value would also be recorded to calculate the coefficient of friction (μ) as given in Equation (1).

$$\mu = \frac{F_f}{F_N} \quad (1)$$

where,
μ = coefficient of friction,
F_f = Frictional force (N) and
F_N = Normal load (N)

3.3.2 Specific wear rate

The specific wear rate (K_s) is another essential tribological property. The K_s can be calculated by using Equation (2)

$$K_s = \frac{\Delta V}{F_N \times L} \quad (2)$$

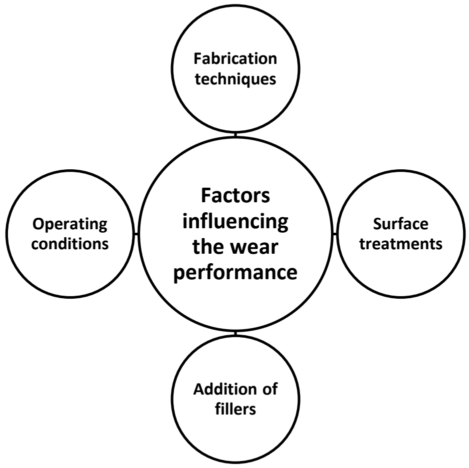


Figure 2: Influencing factors on the wear behavior of composites.

where,
K_s denotes the specific wear rate
ΔV denotes the mass loss (mm^3),
F_N denotes the normal load (N) and
L denotes the sliding distance (m)

4 Wear Performance of Natural-based Thermoplastic Composites

Wear may be addressed as a phenomenon involving material loss from surfaces due to friction. They could be 1) due to relative motion such as sliding, impact, or rolling contact and 2) due to mechanisms such as abrasion, erosion, adhesion, or surface fatigue.

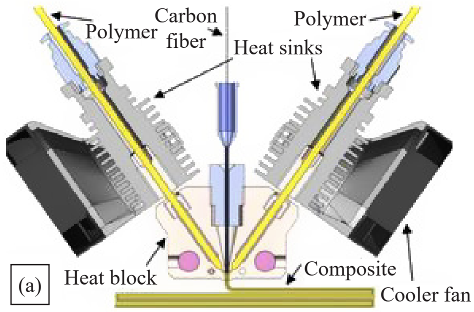
The application of various natural fibers in composites has increased since the last decade due to the demerits of synthetic fibers. The demerits of synthetic fibers include higher energy consumption of their synthesis, high cost, and non-recyclability, which affects the performance of synthetic fiber-based composites in their end applications. In general, when combined with natural fibers to form composites, synthetic fibers improves the performance of the composites remarkably in terms of mechanical performance and wear-resisting behavior. Some of the synthetic fibers that are widely used include Kevlar, glass, and carbon. Figure 2 shows some of the vital factors that affect the wear performance of natural-based thermoplastic composites includes fiber surface treatments, working conditions, etc.

4.1 *Fabrication techniques*

The composite structures generally comprise reinforcement distributed in a matrix. The reinforcements of natural-based composites obtain from different natural resources: animal sources (wool, silk, hair), mineral sources (asbestos, basalt), and plant sources (leaf, stem, and seed). There are numerous techniques for fabricating natural-based thermoplastic composite materials such as injection processing, melt intercalation, blending, solution mixing, in situ intercalative polymerization, screw extrusion, liquid composite molding (LCM), pultrusion [7], and in-situ formation. Though these methods are widely used, optimizing suitable techniques is essential to achieve comparable results. Thus, an essential part of manufacturing activity for wear applications lies in choosing the suitable material and the fabrication method.

Golaz *et al.* fabricated thermoplastic polyurethane containing wax using extrusion for compounding and compression molding for processing. The wax acted as a lubricant and the composite also comprised fillers: graphite, TiO_2, MoS_2, microparticles of ZrO_2, and SiO_2 nanoparticles in different weight ratios. A ball-on-plate reciprocating tribometer was deployed to measure the wear characteristics of the thermoplastic-based composites. The researchers explored the matrix-filler interactions using scanning electron microscopy. The obtained results showed 1) variations in the wear rate of the thermoplastic polyurethane based on filler material and their concentration, and 2) the surface morphology of the composites given wear tracks was highly stable [8].

Artur Prusinowski *et al.* used fused deposition modeling (FDM), an additive manufacturing technique involving layering material over the work surface to fabricate the desired composite. A patented system (as shown in Figure 3(a) and (b) with two extrusion channel heads that feed matrix material (acrylonitrile-butadiene-styrene (ABS)) as a 1.75mm diameter wire is mounted on a 3D printer working in FDM technology. Another channel head feeds continuous carbon fiber along the material extrusion axis to the die head where the composite is fabricated. The analysis confirmed a significant difference in composite wear performance compared to dry and wet conditions. The results also showed that 1) the friction value in water was lower than the frictional value in air, and 2) even wear on the surface in a water environment [9].



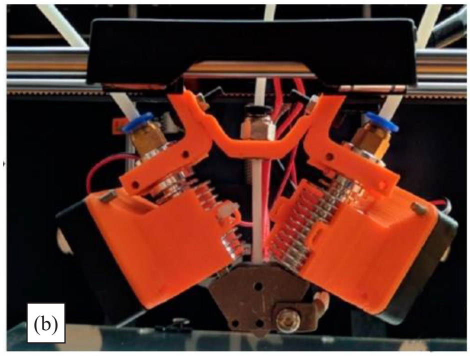


Figure 3: (a) Diagram of FDM fabrication system (b) Prototype of FDM fabrication system [9].

4.2 *Operating conditions*

The blending of discontinuous matrix phases distributed over continuous reinforcement is considered an effective method to fabricate low-cost composite characteristics for applications demanding superior requirements. The multi-phase system could be influenced by operating conditions such as loading parameters, operating temperature, sliding speeds, etc.

Specific wear rate decreased at operating conditions for nettle/polypropylene, sisal/polypropylene, and grewia optiva/polypropylene than its relative pure forms as the applied loads were increased (10–30 N, order of 10 N) at different sliding speeds (1–3 m/s). This indicated that the wear performance of incorporating natural polypropylene fibers has enhanced to a significant level due to delay in the softening process. Also, the fiber reinforcements act as the barrier to prevent material removal [10]. Correa *et al.* explored the wear behavior of Musaceae-polyester, a natural-based composite, in terms of varying the size of the fiber, matrix, and curing agents. A pin-on-disc (POD) tribometer was used to observe the experimental findings. The observed results showed that the composites exhibited better performance on wear than the virgin matrix. Besides, the wear properties were increased when reduced the fiber size. The scanning electron microscopy was analyzed to explore the wear mechanisms of the Musaceae fiber-reinforced composites [11].

Muthukumar *et al.* [12] studied the effect of hybridization on tribological behavior of sisal/coconut sheath polyester matrix composites. The experimental works were conducted using the pin-on-disc machine. The major test conditions: 1) sliding distance, 2) disc velocity, and 3) applied load were 600–3000 mm, 1 m/s, and 10N. As the sliding distance increased, the specific wear rate decreased gradually, while the pure sisal fiber-reinforced composites and sisal/coconut sheath/sisal hybrid composites were increased (after ~2000 mm). The possible reasons for decreasing the wear rate with increasing the sliding distances were 1) change of fiber surfaces from rough surface to smooth surface and 2) reduction of depth-of-penetration. The coefficient of friction was increased with increasing sliding distances due to the increased contact area of polymers, resulting in a new surface area exposed to the abrasive grit. Consequently, the friction heat could be increased and led to a higher coefficient of friction.

4.3 *Treatments*

Plastics, derivatives of fossil fuels, are currently primarily applied in various application-based industrial sectors. Numerous tribological applications require thermoplastic composites because of their inherent advantages, like 1) reduced weight and 2) enhanced chemical compatibility. Research attention for using natural fibers in polymer composites is increasing as they could contribute to sustainability and environmental safety. Also, it is observed that various natural fibers that are chemically treated improve adhesion between the fiber reinforcement and the polymer matrix, which enhances the tribo-performance of natural fiber-based composites [13]. Thus, modifying the natural fibers using chemical treatments has been identified as an effective technique to enhance the tribological properties of polymer composites with natural-based constituents. Other techniques include surface coating, thermal treatment, etc. Irullappasamy *et al.* fabricated a natural-based composite having palmyra fruit fiber, which was chemically treated with NaOH as reinforcement and polyester as the matrix. A POD testing instrument was made use of to investigate the wear performance of the composites and tested against steel counterface for sliding under dry conditions. Result analysis reported that the NaOH-treated fiber composites exhibited improved wear properties than the composite with untreated fiber [14].

Similarly, Ashok *et al.* fabricated composites using both NaOH treated and untreated forms of sisal/glass/epoxy matrix reinforced composites and performed wear analysis using a POD instrument. The testing was carried at a constant load of 10 N with varying sliding velocities ranging from 0.2 mm/s to 4 mm/s. Different length of sisal fiber (1–3 cm) was used for the test with 50 cycles duration. The results reported that the NaOH-treated fiber composites exhibited improved wear resistance than the untreated fiber composites [15]. The optimum result was achieved for a fiber length of 2 cm, where the lowest friction coefficient was recorded for both the fibers treated with NaOH and fibers that are untreated.

In another research work, corn stalk fiber/phenolic matrix composites have been explored by Yucheng *et al.* [16] to analyze the effect of silane treatment on mechanical and tribological properties. The silane concentration was varied from 1 wt% to 13 wt% and analyzed their effects on tribological properties such as friction coefficient and wear rate. The results reported that the friction coefficient was increased from ~0.45 to ~0.60 by increasing the test temperature from 100°C to 150°C. Further increasing the test temperature, the friction coefficient was observed to decline. It was ascribed to the decomposition of organic components. Among the various composites, 9% of silane-treated fiber composites exhibited the lowest friction coefficient (~0.275). Regarding the wear rate, the untreated and silane-treated fiber composites exhibited similar behavior from 100°C to 200°C. However, the wear rate was increased rapidly for untreated fiber composites when the temperature was >250°C. While the silane-treated fiber composites such as 5% and 9% were showed a significant improvement in wear resisting behavior at higher temperatures.

Hence, natural-based thermoset and thermoplastic composites fabricated using chemically treated fibers could be the eco-friendly solution for manufacturing composites with improved tribological performance.

4.4 *Addition of fillers*

Researchers are exploring to find potential tribo-fillers to be added to natural-based thermoplastic composites for achieving required benefits such as quality and behavior in terms of tribological performance. This has enhanced interest in tribo – fillers. Additionally, researchers have listed numerous plasticizers and antimicrobial agents that could be combined with thermoplastics to improve their characterization. Some fillers that are identified as the tribo–fillers are SiC, Al_2O_3, or CuO [17].

Sawan Kumar *et al.* [18] analyzed the effect of various wood-plastic composites such as babool/polypropylene, mango/polypropylene, sheesham/polypropylene, and mahogany/polypropylene on mechanical and tribological behaviors. The particle size of the wood dust was maintained as 600 μ, and the wood loading was varied (10, 15, and 20% by weight) in polypropylene for fabricating the wood-plastic composites. The obtained results indicated that increasing the wood dust concentration in polypropylene exhibited a lesser wear rate. Among the various composites, Mahogany/polypropylene and Mango/polypropylene composites showed a superior wear performance. Sandeep Kumar *et al.* utilized the agro–waste and bio particulate obtained from mustard cake and pine needles as fillers to form composite samples of sisal fiber in the polyester matrix. The observations showed remarkable wear performance at 40 wt% sisal and 5 wt% pine needles, thus demonstrating a viable eco–friendly futuristic option [19]. Thus, the fillers improve the tribological performance of polymer composites, but their compatibility with fiber and matrix is an essential factor in determining the composite.

In other study, the effect of adding Cu_2O and Melamine-formaldehyde coated sisal fibers in Polylactic acid (PLA) was examined recently by Krishnasamy *et al.* [20]. Besides, the tribological characteristics were analyzed by varying the working temperatures, such as 35°C and 65°C. Though the PLA/ Cu_2O (at 10 pph) composites exhibited a lower coefficient of friction, by increasing the Cu_2O content, the coefficient of friction was observed to increase. These results were confirmed by the optical micrographs by exhibiting smooth and precise surfaces. On the contrary, a reversed phenomenon was observed for the Melamine-formaldehyde coated sisal fiber reinforced PLA matrix composites. Besides, the researchers reported that the Melamine-formaldehyde coated sisal fiber (20 and 30 ppm) reinforced PLA matrix composites were not suitable to reduce the wear volume and/or specific wear rate behaviors.

5 Lubrication

Lubrication is a phenomenon to reduce wear and friction between contacting surfaces by applying any substance (lubricant) or in the presence of any lubricating medium (water, oil, etc.). When the polymer composite is operated in a lubricated condition such as water-lubrication, the lubricant dissipates the heat-induced due to friction. Hence, it compensates for self-lubrication. However, for conditions involving high applied normal load, the lubricants cannot compensate for the lack of self-lubricity. Yousif and Nirmal reported that the wear behavior of polymer composites immersed in engine oil and diesel was better than the polymer composites immersed in water and saltwater environments [21].

6 Conclusions

The current global scenario requires developing new bio-based materials due to the demand for replacing ecologically hazardous synthetic material. Though such replacements cannot happen suddenly, this perspective review has given the scope of adding more natural-based components in the composition of thermoplastic materials to hybrid composites through the advances in processing techniques. These have resulted in significant improvement in their tribological performances. Also, it has acted as a solution to overcome the shortfalls of bio-based fibers, polymers, and composites. The application of natural-based materials contributes to enhancing sustainability and minimizing waste, and bringing down the emission of toxic substances, which will lead us all to acquire an eco-friendly environment.

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