Development of Eco-Friendly Brake Friction Composites Containing Flax Fibers

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ABSTRACT: Eco-friendly brake friction composites with good friction performance were developed. The raw materials utilized were selected according to eco-friendly criterion that natural products should be preferably chosen. The formulations are composed of plant flax fiber, mineral basalt fiber, and wollastonite as reinforcements, natural graphite as solid lubricant, zircon as abrasive, vermiculite and baryte as functional and space fillers, and cardanol based benzoxazine toughened phenolic resin as binder. To isolate the flax fibers, chemical and physical methods including drying, room temperature alkaline solution, and acid steam treatment were performed and fibers with micro-fibrillated structure on the surface were formed. A new cardanol based benzoxazine synthesized by the reactions among cardanol, aniline, and formaldehyde was used as toughening for phenolic resin. The effects of both the content of treated flax fibers and friction temperature on friction performance, friction coefficient and specific wear rate, of the friction composites were evaluated by the extension evaluation method.

KEY WORDS: Brake Friction Composites, Friction Performance, Flax Fibers

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INTRODUCTION

The organic brake friction composites are typically composed of multiple ingredients including fiber reinforcements, abrasives, lubricants, space and functional fillers, and phenolic binders [1,2]. Most popularly used reinforcements are steel wool, aramid pulp, and ceramic fibers, abrasives are alumina, zircon, and silicon carbide, lubricants are graphite and metal sulfides, functional and space fillers are vermiculite, cordierite, mica, potassium titanate, calcium sulfate, and baryte. The first generation of modern brake friction composites was asbestos reinforced composites. Due to the environmental problem connected to asbestos fibers [3], the asbestos containing friction composites were replaced by the semi-metallic [4] and non-asbestos organic (NAO) composites [5]. As the new types of NAO composites, both ceramic [6] and eco-friendly phenolic bounded composites [7] with more comfortable properties were developed recently to solve the environmental problems caused by the toxicity and the small size wear debris containing copper and brass, metal sulfides, whiskers and nano-particles, and those to be harmful to water resources, atmosphere, soil, and human body [8, 9]. In order to partly address the problems mentioned above, natural plant fibers, whose character predetermine them to be eco-friendly material, have been added into brake friction composites [10-13].

For the strategic development of eco-friendly brake friction composites, we have considered following important issues: (1) screening of new raw materials from renewable natural fibers, non-toxic mineral fibers and powders, plant powders (nut shells), and bio-mineral powders (seashells), particularly, the thermal stability of natural fibers and nut shells must be enhanced to reach as possible the level of phenolic binder; (2) design of the eco-friendly friction composites containing multiple components including abrasives, lubricants, reinforcement fibers, noise reduction agents, and low cost space fillers; (3) optimization of the composition of friction composites reinforced by natural fibers to meet the requirements of automotive brake linings; and (4) study of the friction mechanisms related to eco-friendly friction composites.

In this paper, chemical and physical treated flax fibers were used in developing eco-friendly brake friction composites. The main purpose of utilizing natural plant fibers is to replace aramid pulp in NAO or steel wool in semi-metallic friction composites. Cardanol based benzoxazine was synthesized from cardanol, a product from natural resource, aniline, and formaldehyde [14] using as toughening for phenolic resin. Benzexazine is an open-ring polymerized phenolic resin and it has been used as binder to replace phenolic resin in brake friction materials [15,16]. The synthesis and curing reactions of cardanol based benzoxazine are shown in Figures 1a and 1b, respectively [14]. Due to the long flexible methylene side chain in the cardanol based benzoxazine, it can be used as toughing for phenolic resin. Also the cardanol based benzoxazine can be co-cured with phenolic resin and the possible reaction mechanism is shown in Figure 1c [14].

All ingredients in the formulations designed, except the phenolic resin, are eco-friendly and non-toxic raw materials. The friction performance of the composites was tested by a drag type friction tester and the friction performance was evaluated by an extension evaluation method [13,17].

EXPERIMENTAL

Chemical and Physical Treatments of Flax Fibers

Flax fibers as received (Figure 2a) were treated by drying at 80 °C for 30 min, 12% NaOH solution at room temperature for 1 h, and 1M HCl steam for 30 min [18].

Raw Materials Used and Formulations Designed

All raw materials used were selected according to their biodegradable and non-toxic properties as well as from natural resources, except the phenolic binder because phenolic resin is not a biodegradable binder. They are treated flax fibers (Figure 2d) as organic reinforcement, basalt fibers (Figure 3a) and wollastonite with needle shape (Figure 3b) as inorganic reinforcements, zircon (Figure 3c) as abrasive, vermiculite (Figure 3d) as noise reduction agent, natural graphite (Figure 3e) as lubricant, baryte as space filler (Figure 3f), cardanol based benzoxazine as toughening for phenolic resin, and phenolic resin as binder.

The formulations of the eco-friendly composites designed are shown in Table 1. The formulations consist of three groups of materials. The first group is phenolic resin and carbanol based benzoxazine and their volume fraction is kept constant. The second group is represented by flax fibers and its volume fraction is increased from 0 to 23.6 vol.%, and the third group is composed of all the remaining materials and their volume fraction is decreased proportionally.

Preparation of Eco-friendly Friction Composites

Cardanol based benzoxazine is a viscous matter. It was mixed using agate mortar with barite, zircon, graphite, and vermiculite to form particulates. Resulting particulates were mixed with rest of raw materials in an electric blender (Electrolux EBR-100) for 2 min. The mixture was molded for 6 min at 165 °C under 25 MPa by a hot press (Wanda JFY-60). Post-curing of prepared friction composites was implemented in an oven at 170 °C for 3 h. Then the composites were cut to give the test samples with dimension of 25 mm × 25 mm × 6 mm.

Measurements of Friction Performance

Friction tests were performed using a drag type of friction tester (Wanda JF151) with constant speed of 7.6 m/s and applied normal pressure of 0.98 MPa. The disc is made of the grey cast iron. Friction coefficient during heating process and volume wear rate of the tested samples at 100, 200, 250, 300, and 350 °C, respectively, and friction coefficient during cooling process at 300, 250, 200, 150, and 100 °C, respectively, were measured according to Chinese National Standard GB 5763-2008. In total, 11 friction coefficient data and 6 wear rate data for each sample were obtained.

Morphology of Raw Materials

The morphology of chemical and physical treated flax fibers, vermiculite, and natural graphite was observed by Hitachi S-4700 scanning electron microscopy (SEM). The morphology of basalt fibers, wollastonite, zircon, and baryte was observed by Philips SEM equipped with energy dispersive X-ray microanalysis (EDX) and the SEM images were obtained using back scattered electrons at operating current 25 kV.

RESULTS AND DISCUSSION

Morphology of Treated Flax Fibers

The morphology of treated flax fibers was observed by SEM, as shown in Figures 2b-d. After treatments, the micro-fibrils composed of cellulose from flax fibers were obtained and the hemicelluloses and lignin appeared on the surface of flax fibers were cleaned off.

Friction Performance

The effects of both flax fibers content and temperature on the friction coefficient during both heating and cooling processes during friction tests are shown in Figures 4a and 4b, respectively, and it is evident that the relationships among friction coefficient, composition, and temperature are non-linear. The friction sample without flax fibers shows slightly higher friction coefficient than the samples containing flax fibers at lower temperature. By the addition of flax fibers to the composites, the friction coefficient is depressed with the amount of flax fibers increased. Therefore, the amount of flax fibers has to be optimized. The effect of temperature on friction coefficient indicates that the fade phenomenon appears at higher temperature and higher content of flax fibers (F-14.6 and F-23.6). Therefore, the optimal amount of flax fibers led to the stable and suitable friction coefficient, which are one of the most important demands for friction composites designed for automotive brake linings.

The effects of flax fibers content and temperature on the wear rate of the composites are shown in Figure 5. It shows also non-linear relationships among the wear rate, composition, and temperature. From the Figure 5, it is evident that at higher temperature, the wear resistance of friction samples containing flax fibers was enhanced significantly due to ductile fracture and char formation of the natural fibers at elevated temperature.

Extension Evaluation

In order to evaluate the non-linear relationships between friction performance and compositions of the friction composites, extension evaluation method [13,17] based on Extenics theory [19] was developed. The procedures of the extension evaluation are as follows.

Assuming there is a interval $X = \langle a, b \rangle$ and a point $M \in X$, the dependent degree function of any point $x \in -\infty, +\infty$ with regard to the interval X and the point M is defined by equation (1).

$$K(x) = \begin{cases} \dfrac{x-a}{M-a}, & x \le M \\ \dfrac{b-x}{b-M}, & x \ge M \end{cases} \tag{1}$$

For friction coefficient (μ), let $M = \dfrac{a+b}{2}$ (the middle point of interval X meaning the best friction coefficient is near the middle value shown in Table 2, which is from the testing standard of brake linings for automobiles (GB 5763-2008, China), the dependent degree function is changed into equation (2).

$$K(\mu_i)=\begin{cases}\dfrac{2(\mu_i-a_i)}{b_i-a_i},\ \mu_i\le\dfrac{a_i+b_i}{2}\\ \dfrac{2(b_i-\mu_i)}{b_i-a_i},\ \mu_i\ge\dfrac{a_i+b_i}{2}\end{cases} \qquad (2)$$

For each temperature (heating and cooling), a dependent degree $K(x_i)$ was calculated. And each of eleven measured friction coefficient has equal importance to this evaluation, with a same weight (α_i) described by equation (3). The weighted average dependent degree (equation 3), $\overline{K_\mu(x)}$, can be used to compare and rank different samples. The higher the value of the $\overline{K_\mu(x)}$ is, the better friction stability is.

$$\overline{K(\mu)}=\sum_{i=1}^{11}\alpha_i K(\mu_i)\ ,\alpha_1=\alpha_2=\cdots=\alpha_{11}=\frac{1}{11} \qquad (3)$$

Equations (2) and (3) can be then applied to describe the correlation between the measured friction coefficient at different temperature (Figure 4) and the middle points of the interval adopted based on GB 5763-2008. The dependent degree results calculated are shown in Figure 6 and the rank of good friction stability is F-5.6, F-9, F-14.6, F-23.6, F-0 (Table 3).

For wear rate (ω): let $M = a = 0$ (the left ending point of interval X meaning the best wear rate is 0), the dependent degree function is changed to equation (4).

$$K(\omega_j)=\begin{cases}\dfrac{\omega_j-a_j}{b_j-a_j},\ \omega_j<a_j\\ 1,\qquad \omega_j=a_j\\ \dfrac{b_j-\omega_j}{b_j-a_j},\ \omega_j>a_j\end{cases} \qquad (4)$$

The weight for wear rate (β_j) is equal (equation 5) and the weighted average dependent degree (equation 5), $\overline{K_\omega(x)}$, can be utilized to evaluate the wear rate of the composites (Figure 5). The greater the $\overline{K_\omega(x)}$ is, the better wear resistance is. The dependent degree results are shown in Figure 6 and the rank of good wear resistance is F-14.6, F-23.6, F-5.6, F-0, F-9 (Table 3).

$$\overline{K(\omega)}=\sum_{j=1}^{6}\beta_j K(\omega_j)\ ,\ \beta_1=\beta_2=\cdots=\beta_6=\frac{1}{6} \qquad (5)$$

To assess the friction coefficient and wear rate comprehensively with equal weight (w_i), the extension evaluation was performed according to equation (6) and the results are shown in Table 2. The parameters i=1-6 are dependent degree of friction coefficient measured during heating process, i=7-11 are dependent degree of friction coefficient measured during cooling process, and i=12-17 are dependent degree of wear rate. The greater the $\overline{K(x)}$ is, the better comprehensive friction performance is. The best value of the dependent degree is 1 and the worst value is 0. Therefore, the five samples ranked from best to worst are F-5.6, F-9, F-14.6, F-23.6, F-0. It means that the optimal formulation is F-5.6.

$$\overline{K(x)} = \sum_{i=1}^{17} w_i K(x_i)\ ,\ w_1 = w_2 = \cdots = w_{17} = \frac{1}{17} \tag{6}$$

CONCLUSIONS

A new type of eco-friendly brake friction composites containing flax fibers was developed and the ranking of the prepared samples based on their friction-wear performance was carried by extension evaluation method. The friction samples are composed of natural plant fibers (flax), mineral fibers (basalt and wollastonite), mineral fillers (natural graphite, zircon, vermiculite, and baryte), and cardanol based benzoxazine toughened phenolic resin. Flax fibers were treated by chemical and physical methods and the micro-fibrils were obtained. The effects of flax fibers content and temperature on friction performance were evaluated. Based on the results obtained using extension evaluation method, the optimized amount of flax fibers in the composites is 5.6 vol.% (F-5.6). The role of flax fibers in the composites is to stabilize the friction coefficient and to improve the wear rate at high temperature.

ACKNOWLEDGEMENTS

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REFERENCES

1. Lu, Y. (2006). A Combinatorial Approach for Automotive Friction Materials: Effects of Ingredients on Friction Performance, *Composites Science Technology*, 66, 591-598.
2. Lu, Y. (2002). Combinatorial Approach for Automotive Friction Materials: Combined Effects of Ingredients on Friction Performance, *Polymer Composites*, 23, 814-823.
3. Chan, D. and Stachowiak, G.W. (2004). Review of Automotive Brake Friction Materials, *Proceedings of the Institution of Mechanical Engineering Part D: Journal of Automotive Engineering*, 218, 953-966.
4. Lu, Y., Tang, C.F. and Wright, M.A. (2002). Optimization of a Commercial Brake Pad Formulation, *Journal of Applied Polymer Science*, 84, 2498-2504.
5. Ma, Y., Martynkova, G.S., Valaskova, M., Matejka, V. and Lu, Y. (2008). Effects of $ZrSiO_4$ in Non-metallic Friction Materials on Friction Performance, *Tribology International*, 41, 166-174.
6. Han, L., Huang, L., Zhang, J. and Lu, Y. (2006). Optimization of Ceramic Friction Materials, *Composites Science Technology*, 66, 2895-2906.
7. Lu, Y., Suo, B., Lu, Y. and Wang, H. (2008). Preparation of Eco-friendly Brake Friction Materials, CN Patent Application 2008102278317.
8. Grag, B.D., Cadle, S.H., Mulawa, P.A. and Groblicki, P.J. (2000). Brake Wear Particulate Matter Emission, *Environmental Science Technology*, 34, 4463-4469.
9. Fubini, B. and Arean, C.O. (1999). Chemical Aspects of the Toxicity of Inhaled Mineral Dusts, *Chemical Society Review*, 28: 373-381.
10. Drach, V. and Drucker, P. (2001). New Process and Reinforcing Fibers for Friction Materials Based on Renewable Raw Materials, *Proceedings of 18th Annual Brake Colloquium Exhibition* (SAE Paper No. 2001-01-3129), 43-47.
11. Sloan, M., Savage, L., Evans, K. and Hooper, B. (2006). Natural Fibers in Friction Materials, *Proceedings of 24th Annual Brake Colloquium Exhibition* (SAE Paper No. 2006-01-3187), 17-27.
12. Xu, X., Chen, G.X. and Liu, F.Q. (2007). Friction Properties of Sisal Fiber Reinforced Resin Brake Composites, *Wear*, 262, 736-741.
13. Yun, R., Lu, Y. and Filip, P. (2010). Application of Extension Evaluation Method in Development of Novel Eco-friendly Brake Materials, *SAE International Journal of Materials*

and Manufacture, 2(2), 1-7.

14. Lu, Y. (2009). Synthesis of Cardanol Based Benzoxazine and Its Application in Friction Materials (MS Thesis, Beijing University of Chemical Technology).
15. Lu, Y. (2003). A Golden Section Approach to optimization of Automotive Friction Materials, *Journal of Materials Science*, 38, 1081-1085.
16. Lu, Y., Tang, C.F., Zhao, Y. and Wright, M.S. (2004). Optimization of a Semimetallic Friction Material Formulation, *Journal of Reinforced Plastics and composites*, 23, 1537-1545.
17. Yun, R., Martynkova, G.S. and Lu, Y. (2011). Performance and Evaluation of Nonasbestos Organic Brake Friction Composites with SiC as an Abrasive, *Journal of Composite Materials*, 45, 1585-1593.
18. Wang, H., Huang, L. and Lu, Y. (2009). Preparation and Characterization of Micro- and Nano-fibrils from Jute, *Fibers & Polymers*, 10, 442-445.
19. Yang, C. and Cai, W. (2007). *Extenics Engineering* Science Press, Beijing.

Table captions

Table 1. Eco-friendly friction formulations designed (volume fraction).

Table 2. Allowed values of friction performance (GB 5763-1998).

Table 3. Ranks of friction performance by extension evaluation method.

Table 1. Eco-friendly friction formulations designed (volume fraction).

	F-0	F-5.6	F-9	F-14.6	F-23.6
Wollastonite	0.326	0.303	0.289	0.266	0.230
Basalt fibers	0.090	0.084	0.080	0.074	0.063
Zircon	0.090	0.084	0.080	0.074	0.063
Baryte	0.146	0.136	0.130	0.119	0.103
Vermiculite	0.056	0.052	0.050	0.046	0.039
Natural graphite	0.090	0.084	0.080	0.074	0.063
Phenolic	0.146	0.146	0.146	0.146	0.146
Cardanol based benzoxazine	0.056	0.056	0.056	0.056	0.056
Flax fibers	0	0.056	0.090	0.146	0.236

Table 2. Allowed values of friction performance (GB 5763-1998).

	100°C	150°C	200°C	250°C	300°C	350°C
μ	0.25-0.65	0.25-0.70	0.25-0.70	0.25-0.70	0.25-0.70	0.20-0.70
V, $\times 10^{-7}$cm^3• (Nm)$^{-1}$	≤0.50	≤0.70	≤1.00	≤1.50	≤2.50	≤3.50

Table 3. Ranks of friction performance by extension evaluation method.

Parameters	F-0	F-5.6	F-9	F-14.6	F-23.6
$\overline{K_{\mu}(x)}$	0.692	0.898	0.880	0.729	0.710
Rank (μ)	5	1	2	3	4
$\overline{K_{\omega}(x)}$	0.636	0.660	0.576	0.779	0.677
Rank (ω)	4	3	5	1	2
$\overline{K(x)}$	0.672	0.814	0.773	0.747	0.698
Rank (μ &ω)	5	1	2	3	4

Figure Captions

Figure 1. Synthesis (a), curing (b) of cardanol based benzoxazine and co-curing reaction between cardanol based benzoxazine and phenolic resin (c) [14].

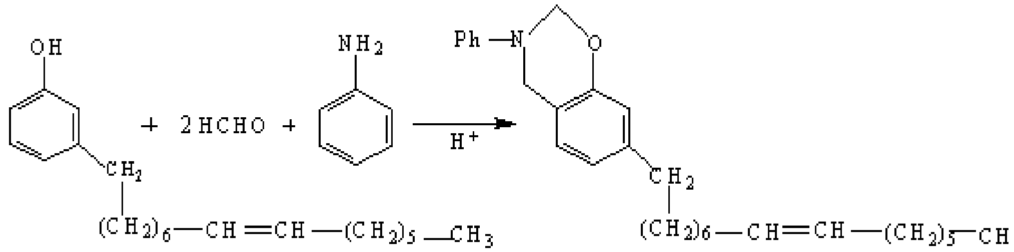
Figure 2. Morphology of flax fibers (a) photograph as received sample, SEM images after (b) drying, (c) room temperature alkaline, and (d) acid steam treatment.

Figure 3. SEM and EDX images of raw materials used: (a) basalt fibers, (b) wollastonite, (c) zircon, (d) baryte, and (e) natural graphite.

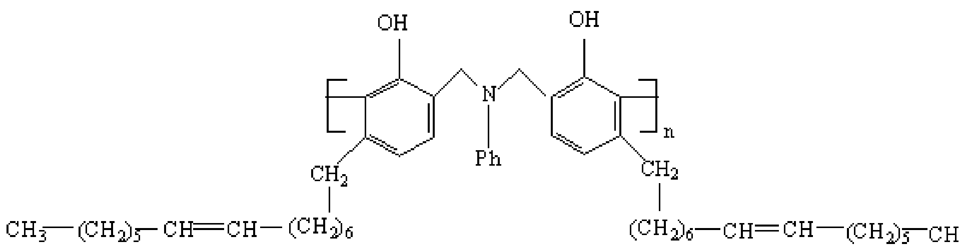
Figure 4. Effects of flax fibers content and temperature on friction coefficient measured (a) during heating process and (b) during cooling process.

Figure 5. Effects of flax fibers content and temperature on wear rate.

Figure 6. Dependent degree calculated for the five composites.



(a)



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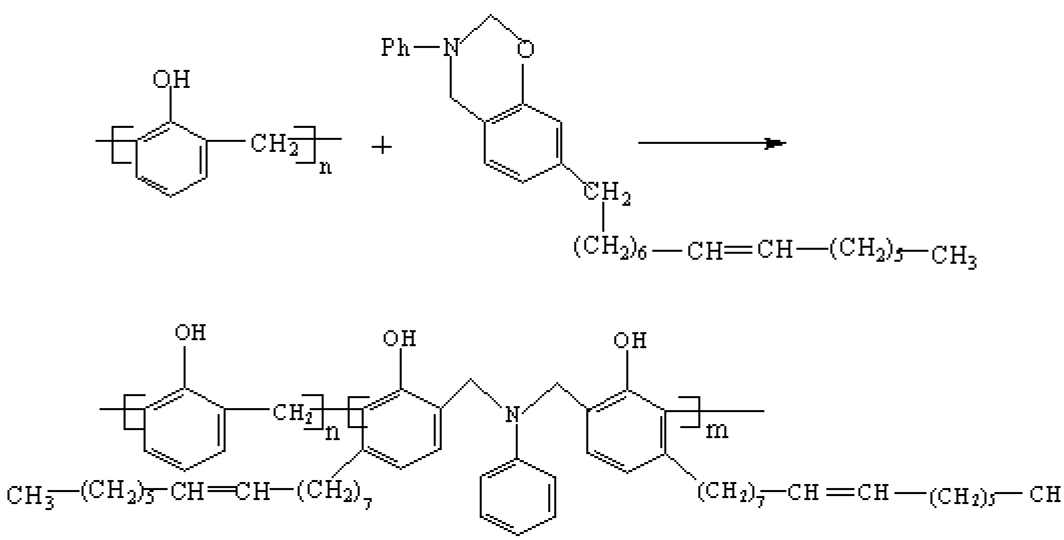

(c)

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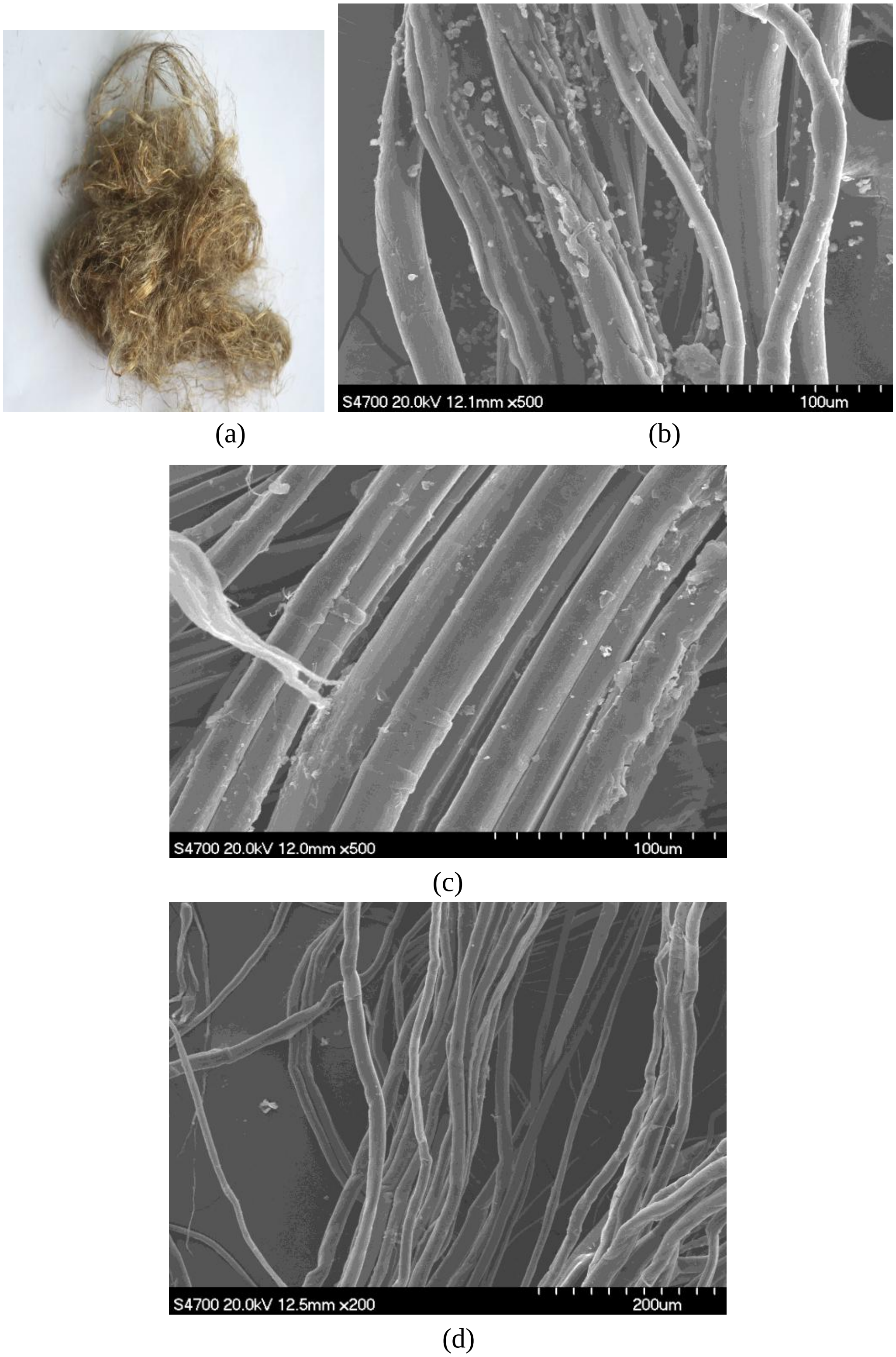

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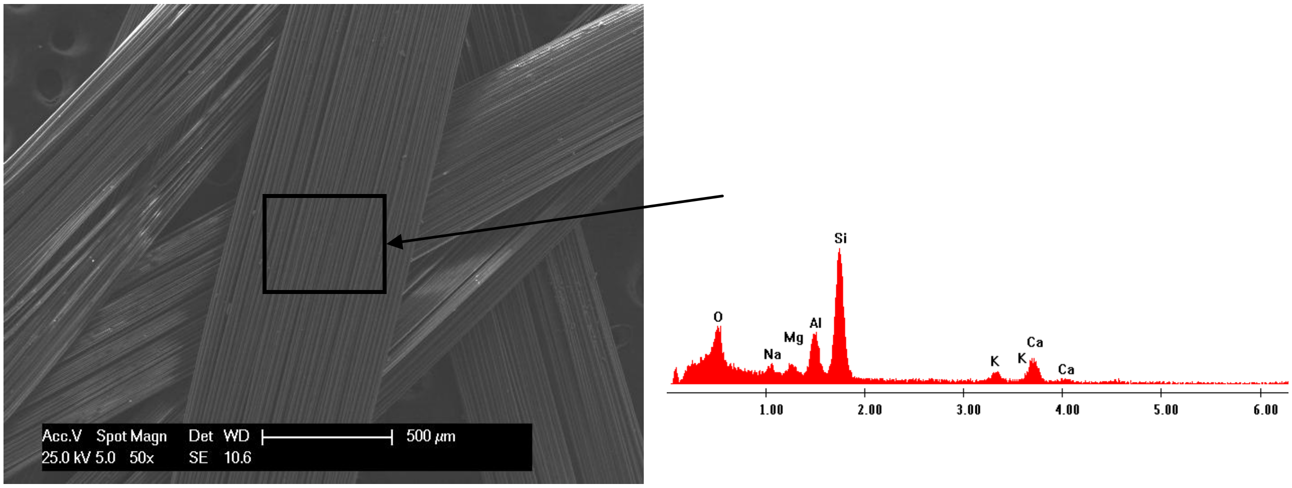
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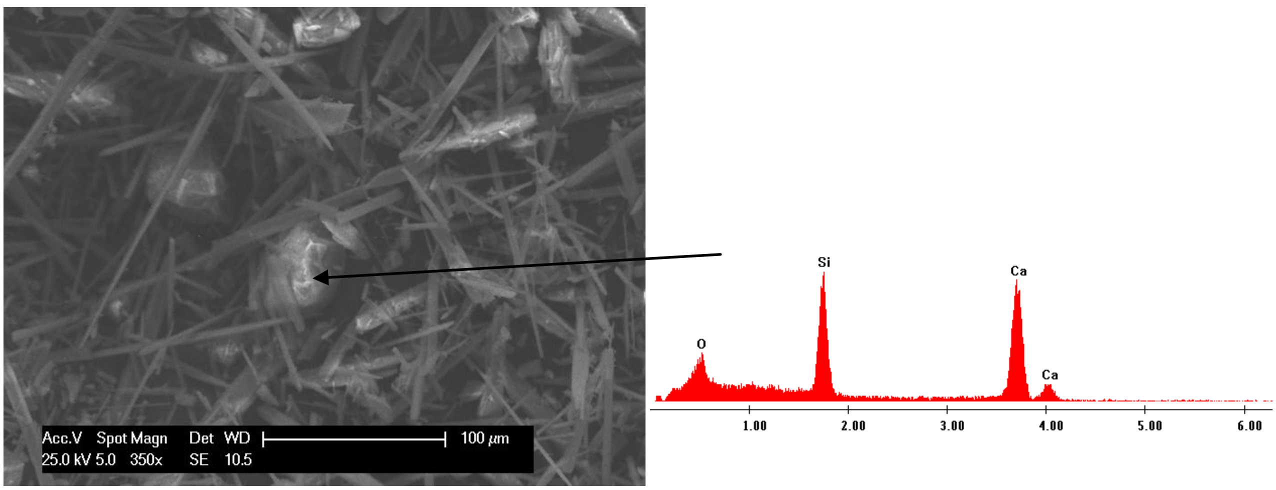
(a)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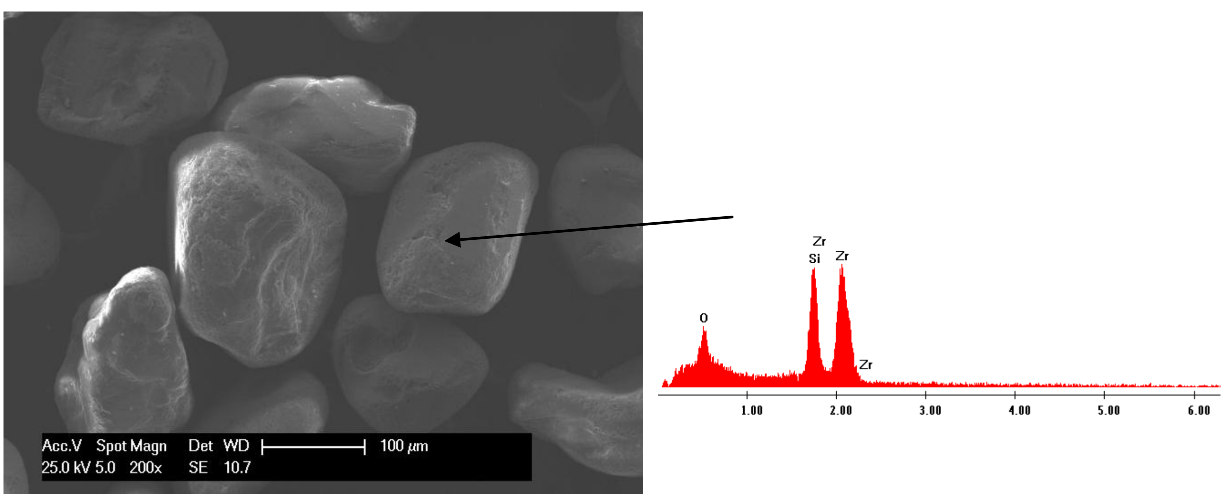
(b)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Zr
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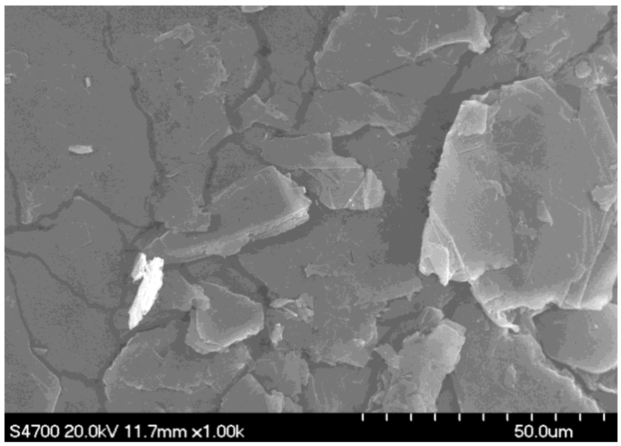
(c)

(d)



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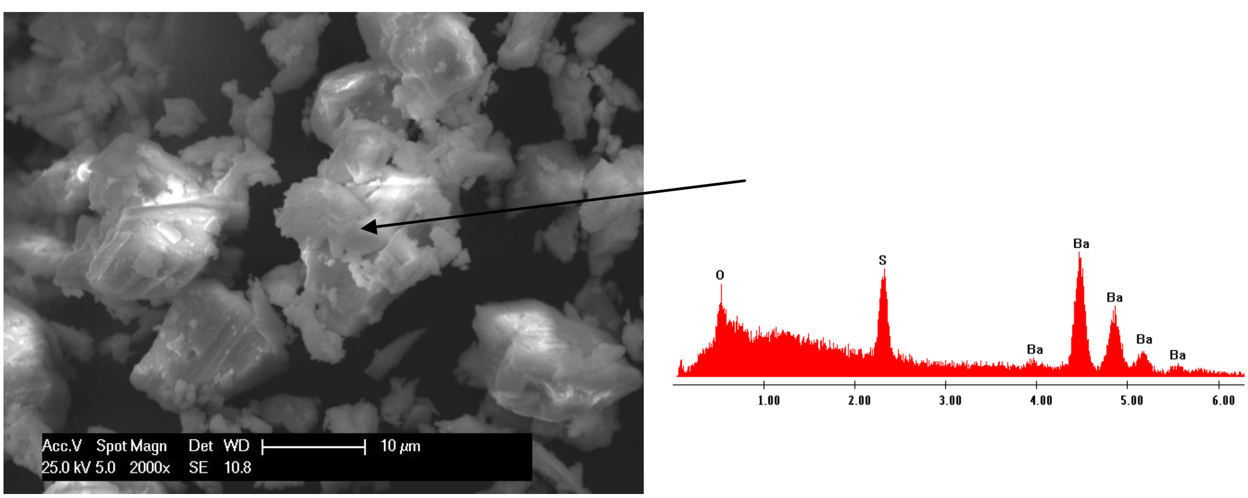

(f)

Figure 3. SEM and EDX images of raw materials used: (a) basalt fibers, (b) wollastonite, (c) zircon, (d) vermiculite, (e) natural graphite, and (f) baryte.

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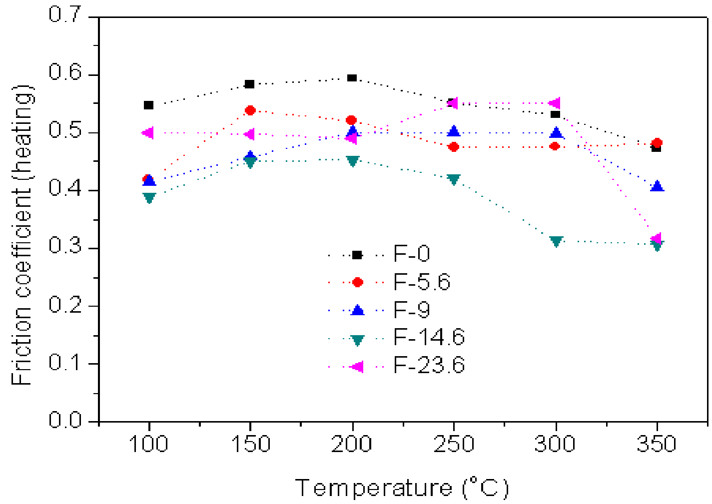
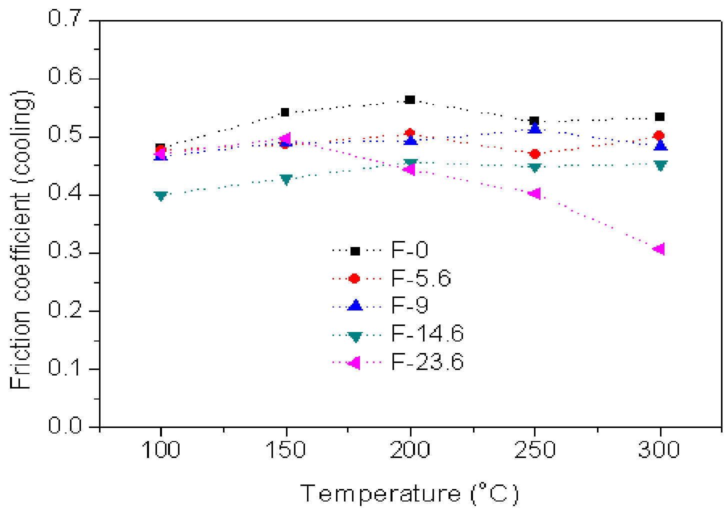


(a)



(b)

Figure 4. Effects of flax fibers content and temperature on friction coefficient measured (a) during heating process and (b) during cooling process.

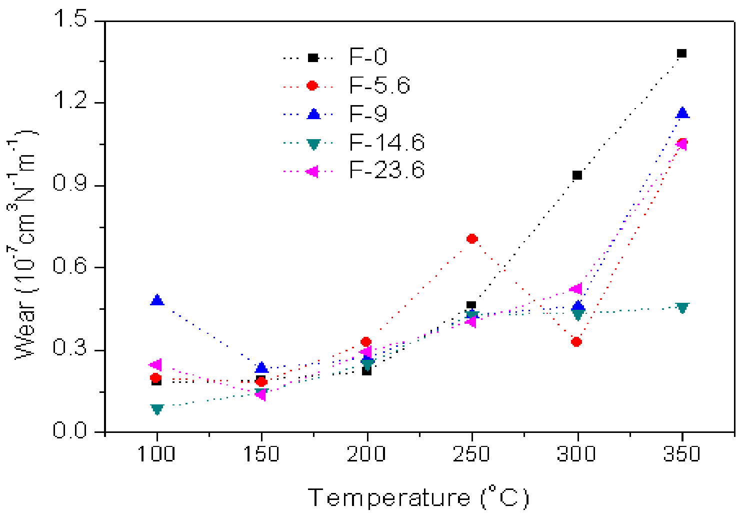
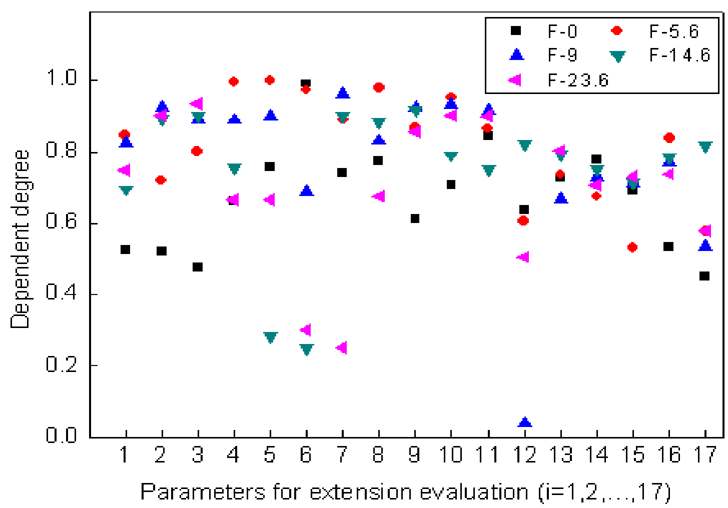


Figure 5. Effects of flax fibers content and temperature on wear rate.



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