Effect of Alkyl Phenol from Cashew Nutshell Liquid on Mechanical and Dry Sliding Wear Behavior of Epoxy Resin

Rajesh Panda,[a,b,]* Jimmy Tjong,[a] Sanjay K. Nayak,[b] and Mohini M. Sain [a,c]

A phenalkamine made from the reaction of alkyl phenol from cashew nutshell liquid (CSNL) and polyamine was added at three different weight percentages (30%, 40%, and 50%) as a diglycidyl ether of bisphenol A (DGEBA) epoxy hardener. This curing agent was compared to a traditional polyamine epoxy hardener. It was observed that an increase in phenalkamine concentration resulted in considerable improvement to impact strength and elongation, which ultimately translated to better wear resistance of the cured epoxy compound. Lancaster–Ratner correlations between mechanical and wear resistance properties were found to be linear. Optical microscope observations were used to understand the wear mechanisms of the cured epoxy materials.

Keywords: Phenalkamine; Sliding wear; Lancaster–Ratner correlation; Cashew nutshell liquid (CSNL)

*Contact information: a: Faculty of Forestry, University of Toronto, 33 Willcocks Street, Toronto, ON M5S 3B3, Canada; b: Advanced Research School for Technology & Product Simulation (ARSTPS), Central Institute of Plastics Engineering & Technology (CIPET), Guindy, Chennai -600 032, India; c: King Abdulaziz University, Jeddah, Saudi Arabia; *Corresponding author:rajesh.panda@mail.utoronto.ca*

INTRODUCTION

Polymers are subjected to adhesive wear in many applications, where two bodies slide over each other and fragments are pulled off from one surface and adhere to other surfaces in successive cycles, causing surface wear and finally failure of the components. The epoxy diglycidyl ether of bisphenol A (DGEBA) has been widely used for many decades as a thermoset resin because of its excellent inherent chemical resistance and adhesive properties; this epoxy is used in a variety of fields, such as binders for adhesives, coatings, and paints in engineering application (Chrysanthosa *et al*. 2011; Lagunas *et al.* 2014; Reddy *et al*. 2014). However, this epoxy's inherent poor impact resistance and stress cracking resistance limits its practical use in tribological applications. To overcome this drawback, researchers have made numerous attempts to physically modify epoxy resins by introducing various reinforcing agents such as glass fiber (Kishore *et al*. 2001), carbon fiber (Suresh *et al.* 2009), and Kevlar fiber (Wu and Cheng 2006), as well as fillers like silica, (Kanchanomai *et al.* 2011), SiC, Al_2O_3, (Ahmed *et al.* 2012) TiO_2, and MoS_2 (Nayak *et al.* 2014). These reinforcing agents can successfully improve the wear resistance of the epoxy resin. The growing concern and awareness over replacing synthetic-based products with bio-based products have attracted researchers to incorporate various natural fibers, such as palm (Shalwan and Yousif 2014), bamboo (Nirmal *et al*. 2012), and rice husk (Rout and Satapathy 2012) to improve the mechanical and wear resistance properties of epoxy resins. The physical modifications of epoxy materials limit their use in various applications, which has attracted researchers to find methods to modify them chemically by incorporating vegetable oil-based polymers.

Cashew nutshell liquid (CSNL; *Anacardium occidentale*) is an abundant and natural source of phenols obtained from renewable, non-food chain biomaterials (Cheng *et al.* 2000; Sato *et al.* 2009). It consists of four major components with an unsaturated aliphatic side chain containing 15 carbon atoms; these components include cardanol, cardol, anacardic acid, and 2-methylcardol. Cardanol is a natural phenol compound with a meta-substituted 15-carbon unsaturated aliphatic side chain that is obtained by vacuum distillation of the CNSL liquid precursor.

Phenalkamine is synthesized from cardonol reacted with formaldehyde and alkylamines *via* the Mannich reaction. The aromatic backbone of phenalkamine is responsible for the rigidity of the epoxy resin network, whereas the aliphatic side chain gives it flexibility when used as a hardener for curing the epoxy resin. The phenolic hydroxyl group makes it very active even at low temperatures, and the alkylamine side chain is responsible for the high cross-linked density (Dai *et al.* 1994; Pathak and Rao 2006). The chemical structures of DGEBA and phenalkamine are shown in Fig. 1.

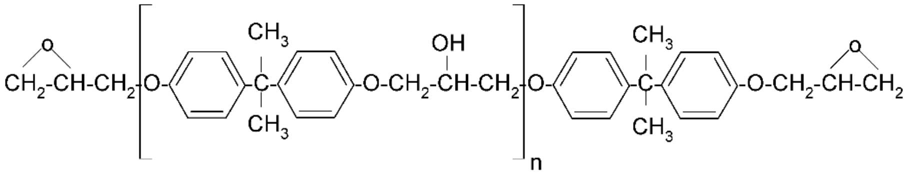

Fig.1. (a)

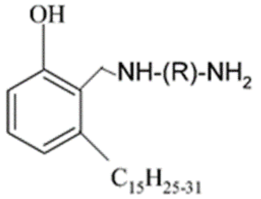

Fig.1. (b)

Fig. 1. Structures of (a) DGEBA and (b) phenalkamine

In this report, an attempt was made to correlate the mechanical and wear properties of a cured epoxy modified with phenalkamine; the results are compared with a traditional epoxy/polyamine material. The main objective of this research was to enhance the mechanical properties of an epoxy resin, which translates to increased wear resistance of the cured epoxy compound.

EXPERIMENTAL

Materials

Phenalkamine, with an amine value of 490 to 550 mg KOH/g and density of 0.99 g/cm^3, was obtained from Cardolite Specialty Chemicals India, Pvt. Ltd. (Mangalore, India). The epoxy resin and polyamine (TETA) curing agent was supplied by Huntsman Advanced Materials India, Pvt. Ltd. (Mumbai, India); the epoxy had an equivalent weight of 183 to 189 g/eq and a density of 1.17 g/cm^3 whereas polyamine had an amine value of 1443 mg KOH/g.

Methods

Diglycidyl ether of bisphenol A (DGEBA) was mixed with the phenalkamine at a weight ratio percentage of 70:30, 60:40, or 50:50. The TETA was mixed with the DGEBA at a weight ratio percentage of 90:10. The suffix labels PKA and EP were used as abbreviations for phenalkamine/DGEBA and triethelenetriamine (TETA)/DGEBA, respectively, while the prefix number labels represent the corresponding weight percentage in the cured epoxy material.

The combination of epoxy resin and hardener was stirred manually to obtain a homogeneous mixture prior to casting the samples. Stainless steel molds having dimensions of 210 x 210 x 40 mm^3 and 50 x 50 x 10 mm^3 were used for casting the sheets. A mold releasing agent (silicon spray) was used for easy removal of the sheets. The sheets were cured for 24 h in the molds, and the sheets were cured an additional 24 h after removal from the molds. The samples were prepared from the cast sheets of all compositions for further testing purposes.

Physical and Mechanical Properties

Densities of all the samples were measured using a precision balance by employing Archimedes' principle of buoyancy. The density data of all the materials prepared in the present study are listed in Table 2.

Tensile tests were conducted according to ASTM D638 (2010) using an Instron universal testing machine. The tests were performed at a crosshead speed of 5 mm/min in room temperature environment. The dimension of specimen was 162 mm x 12 mm x 3.5 mm.

Notched impact strengths of the samples were measured using an impact pendulum tester according to ASTM D256 (2010). The dimension of samples were 64 mm x 13 mm x 3 mm. The impact strength (kJ/m^2) was calculated by dividing the recorded absorbed impact energy by the cross-section area of the samples.

Three measurements were done for each specimen, and the average value is reported for each of the samples (Table 1).

Sliding Wear Studies

A pin-on-disk dry sliding wear testing apparatus (Ducom TR-20LE- M53) was used for evaluating all epoxy components at ambient room temperature and humidity. Table 2 shows the methodology opted for studying tribo-behaviour of the materials. Prior to each test, each specimen was rubbed over a silicon carbide abrasive paper (P-1200 grade) to ensure proper intimate contact between the sliding face of the specimen and the stainless steel counterface. The roughness of the disc was maintained by pressing an abrasive paper (silicon carbide waterproof; E-66 grade) after each test was completed.

The specific wear rate (K) was calculated from Eq. 1,

$$\boldsymbol{K} = \Delta \boldsymbol{W} / \boldsymbol{\rho L D} \text{ (mm}^3\text{/N-mm)} \tag{1}$$

where ΔW is the weight loss (in g), ρ is the density (in g/cm^3), L is the load (in N), and D is the sliding distance (in m).

Table 1. Methodology Opted for Studying Tribo-behaviour of the Material

<table>
<tr><td colspan="10">Tribosystem-1</td></tr>
<tr><td colspan="8">Load (N)</td><td>Sliding Velocity (m/s)</td><td>Sliding Distance (m)</td></tr>
<tr><td colspan="2">10</td><td>30</td><td colspan="2">50</td><td colspan="2">70</td><td>90</td><td>3</td><td>7000</td></tr>
<tr><td colspan="10">Tribosystem-2</td></tr>
<tr><td colspan="8">Sliding Distance (m)</td><td>Load (N)</td><td>Sliding Velocity (m/s)</td></tr>
<tr><td colspan="2">1000</td><td>2000</td><td colspan="2">3000</td><td colspan="2">4000</td><td>5000</td><td>30</td><td>3</td></tr>
<tr><td colspan="8">Tribosystem-3</td><td></td><td></td></tr>
<tr><td colspan="8">Sliding velocity (m/s)</td><td>Load (N)</td><td>Sliding Distance (m)</td></tr>
<tr><td>1</td><td>2</td><td>3</td><td>4</td><td>5</td><td>6</td><td>7</td><td>8</td><td>30</td><td>7000</td></tr>
</table>

RESULTS AND DISCUSSION

As shown in Table 2, the ultimate tensile strength of epoxy/PKA was reduced with the increases of phenalkamine concentration due to reduction of aromatic epoxide group in the network. The elongation at break and impact strength was increased with the concentration of phenalkamine percentage due to the long aliphatic side chain in the molecular structure makes it flexible.

Table 2. Mechanical and Physical Properties of DGEBA+TETA and DGEBA+Phenalkamine Epoxy Resin

Sample	Density (g/cm^3)	Ultimate Tensile Strength (MPa) σ_u	Elongation (%)ϵ_u	Impact Strength (kJ/m^2)
DGEBA+TETA	1.50	55.52±4.44	5.39± 1.99	13.68± 0.01
DGEBA+30% PKA	1.45	55.76±3.02	8.88± 2.57	13.92± 0.01
DGEBA+40% PKA	1.43	40.15±2.63	13.72± 0.47	17.21± 0.02
DGEBA+50% PKA	1.41	39.71±4.14	15.73±1.36	27.48± 0.02

Figure 1(a) shows schematic representation of adhesive wear mode, whereas Fig. (b) shows the abrasive wear mode during dry sliding wear process. The small triangles in Fig. (b) represent abraded particles, which accelerate the wear process of the materials. It was observed that the adhesive and abrasive wear modes were dominant in the studied material removal process. Moreover wear modes changed from one to another for reasons that included change in surface material properties and dynamic surface response caused by frictional heating and chemical film formation. Adhesive and abrasive wear modes are generated under plastic contact. In adhesive wear modes, the crack is brought about as the result of strong adhesion at the contact interfaces, whereas in abrasive wear the micro cutting of softer material occurred due to the harder and sharp materials. The phenalkamine cured epoxy compound switch over from adhesive wear to abrasive was delayed due to strong intermolecular adhesion between molecules. The abraded particles were observed also to be softer compared to TETA cured epoxy compound.

Fig. 1. (a) Adhesive wear and (b) abrasive wear mechanism during dry sliding wear process

Figure 2 shows the specific wear rate *vs*. the normal load in dry sliding wear mode. Up to 60 N normal load, the specific wear rate increased slightly for all samples, whereas beyond 60 N, the wear rate increased drastically. This can be attributed to the materials' limiting load capacity for bearing applications. The wear resistance (inverse of specific wear rate) of the epoxy was much improved by the addition of phenalkamine, which may be due to good inter-particle adhesion; this better inter-particle adhesion may increase the energy absorption behavior of the epoxy matrix and may delay the micro-cutting and micro-plowing wear mechanisms.

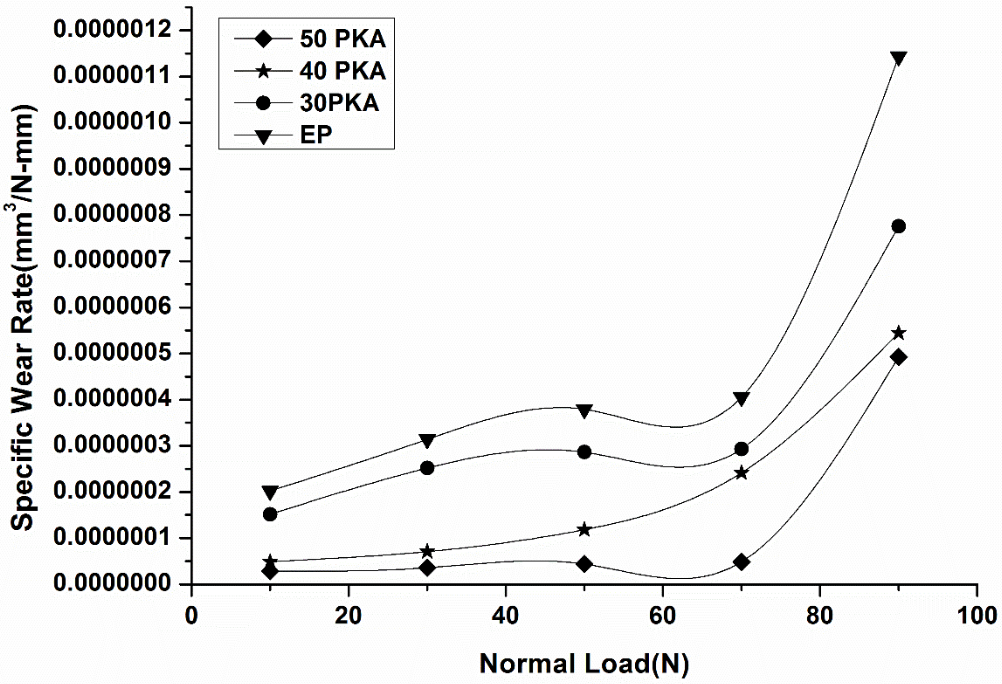

Fig. 2. Specific wear rate *vs*. normal load at a sliding velocity of 3 m/s and a sliding distance of 7000 m

Figure 3 shows the effect of increasing the sliding distance on the sliding wear of the same epoxy resin series. Wear drastically increased as the sliding distance increased above 3000 m (while the applied load and the sliding velocity were kept constant). The wear resistance rate increased as the PKA content in the cured epoxy material increased.

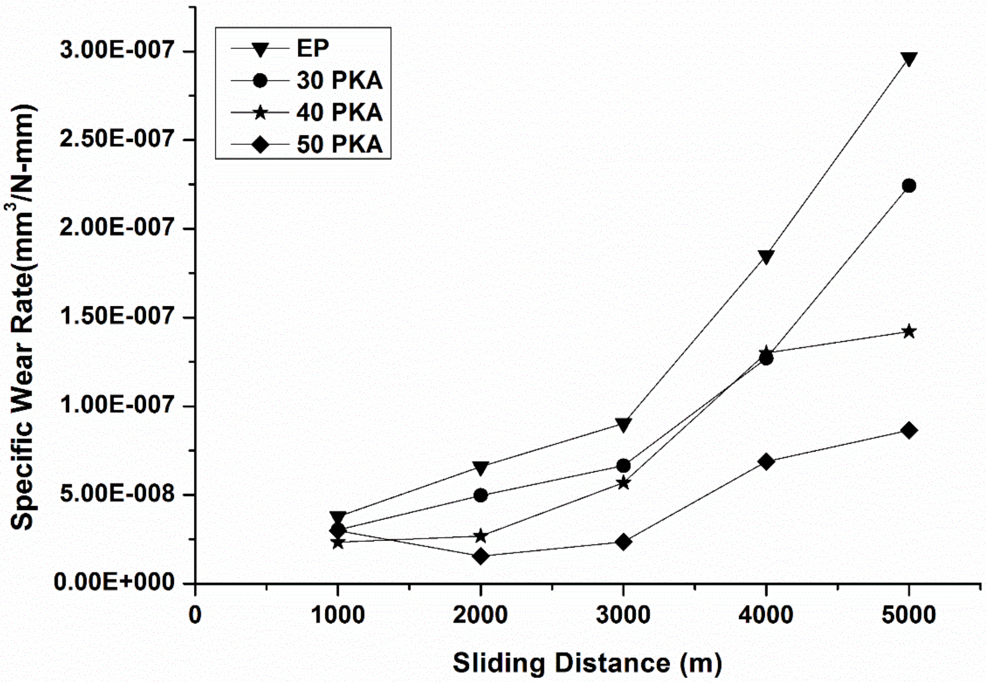

Fig. 3. Specific wear rate *vs*. sliding distance at a sliding velocity of 3 m/s and a normal load of 30 N

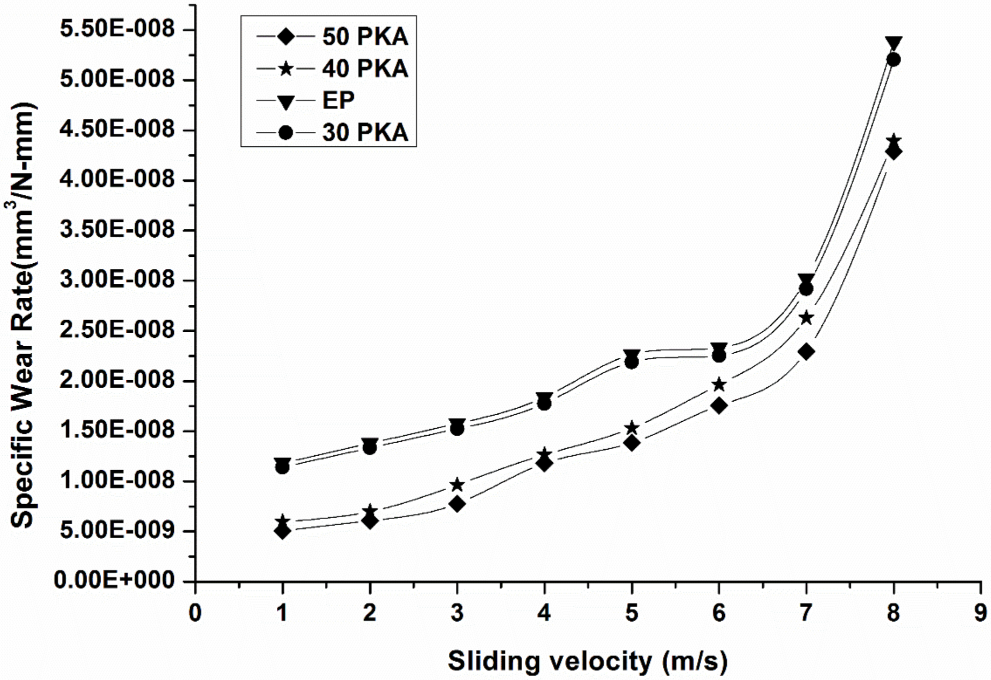

Fig. 4. Specific wear rate *vs*. sliding velocity at a sliding distance of 7000 m and a normal load of 30 N

Figure 4 shows the effect of increasing sliding velocity on the dry sliding specific wear rate of the same cured epoxy samples. The specific wear rate was lowered with the increase of phenalkamine percentage. The specific wear rate drastically increased after 6 m/s for all the samples.

Figure 5 shows the correlation between impact strength and wear-resistance (*i.e.*, the inverse of wear rate) for the cured epoxy compounds under standard room temperature and humidity conditions. It is clear from the figure that the impact strength of the cured epoxy compounds has a direct correlation with the wear resistance. Chand *et al.* (2010) reported a similar relationship between impact strength and wear resistance for other polymeric composites. The enhancement of the impact strength in comparison to the TETA cured network may be attributed to the long aliphatic side chain of the phenalkamine. Another reason for the improvement in the wear resistance could be better particle-to-particle adhesion in the phenalkamine cured epoxy compound because the hydrophobic side chain in its molecular structure can cause steric hindrance to hydroxyl and oxygen-containing groups absorbing moistures in the curing reaction.

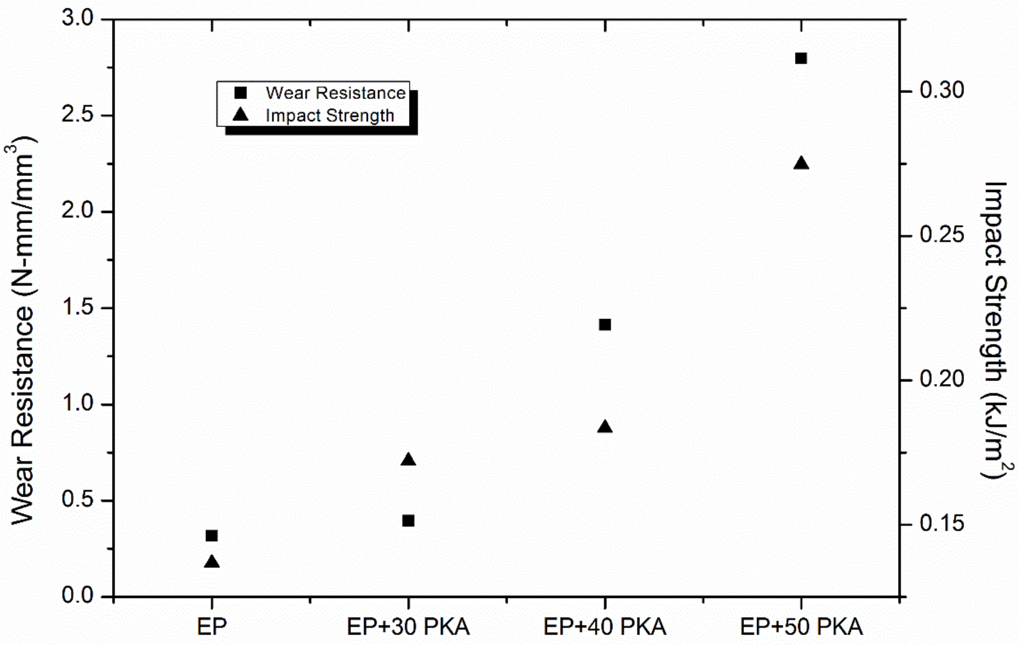

Fig. 5. Correlation between impact strength (x10^{-2} kJ/m^2) and wear resistance (×10^7 N-mm/mm^3) of the cured epoxy compounds

To explain the wear rate of polymer and polymer composites, it has been established in the literature that the specific wear rate varies in proportion to $1/\sigma_u{*}\varepsilon_u$, where σ_u is the ultimate tensile stress and ε_u is the corresponding strain or elongation (Ratner *et al*. 1967). This correlation, generally referred to as the Lancaster–Ratner correlation, was used to characterize the epoxy resins examined in this study.

Lancaster–Ratner correlations and the wear resistances for the epoxy series are compared in Fig. 6. The trends are similar to the trends shown in Fig. 5 for impact strength. Interestingly, these correlations were found to be linear for the cured epoxy compounds in this study. These correlations were responsible for the wear behavior of the cured epoxy compounds. A higher $\sigma_u*\varepsilon_u$ value (*i.e.*, a lower $1/\sigma_u*\varepsilon_u$) indicates an epoxy with better wear resistance because of the high energy absorption behavior (Lancaster *et al.* 1968). The most likely explanation for the increase in wear resistance with the higher content of phenalkamine resin hardener is the greater elongation and better particle-to-particle adhesion when compared to traditional polyamine-cured epoxy resins (Chand *et al*. 2010).

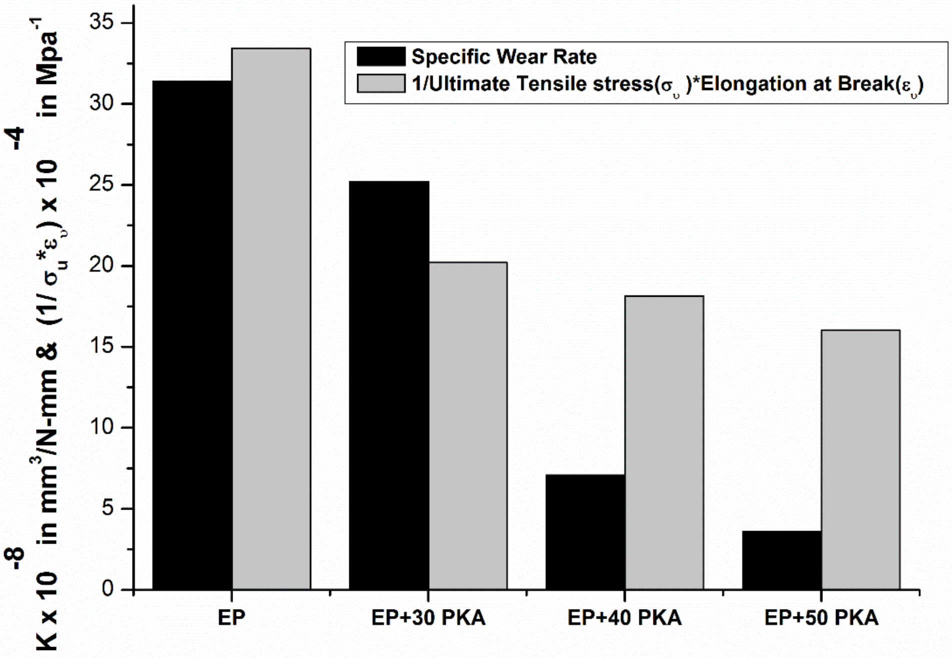

Fig. 6. Lancaster–Ratner correlations between mechanical properties and specific wear rate

Optical micrographs of the worn surfaces of epoxy/phenalkamine and epoxy/TETA compounds are shown in Fig. 7 (a) and (b), respectively.

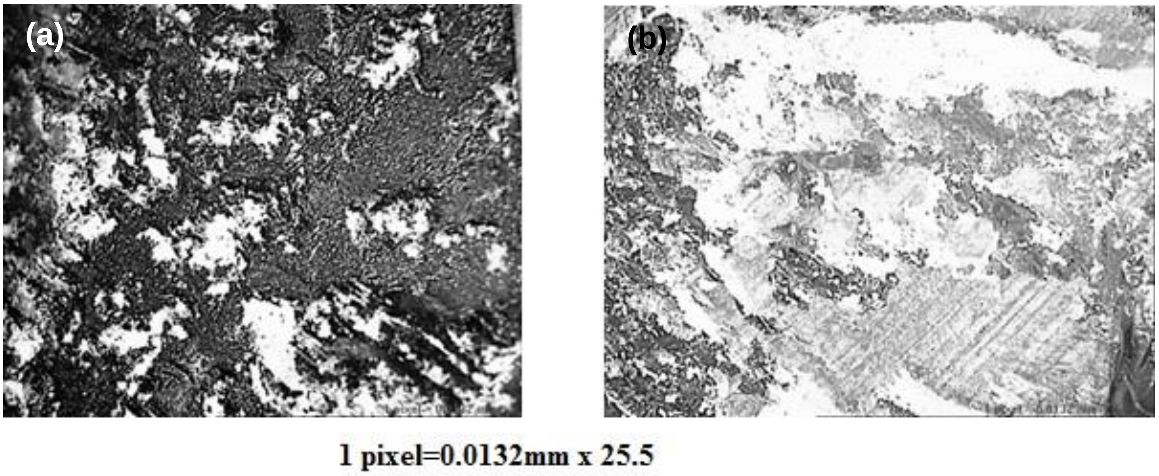

Fig. 7. Optical microscope images of (a) epoxy/phenalkamine and (b) epoxy/TETA wear tracks

The tribological conditions of the compounds first showed micro-cracks developing, then crack propagation to join other cracks, followed by larger groove formation. The abraded particles that were chipped off from the base material acted as a third body abrasive to generate micro-plowing marks on the base material along the grooves generated. With the addition of phenalkamine, there was less micro-crack generation and propagation because of the enhancement of energy absorption. The wear debris of phenalkamine-cured epoxy resins were softer compared to its TETA-cured counterpart, so the specific wear rates of phenalkamine-cured epoxy resins were reduced in relation to TETA-cured epoxy.

CONCLUSIONS

The phenalkamine as a resin hardener has immense potential for enhancing the tribological properties of cured epoxy compounds. The mechanical properties of epoxy composites can be improved by using phenalkamine instead of polyamine as an epoxy hardening/curing agent. The salient results presented in this study are as follows:

1. Wear resistance of cured epoxy compounds increased considerably with the addition of phenalkamine.
2. Impact strength and elongation of the cured epoxy compounds improved with the addition of phenalkamine.
3. Lancaster–Ratner correlations among the impact properties and wear resistances of phenalkamine-cured epoxy compounds were found to be linear.

ACKNOWLEDGEMENTS

The authors acknowledge the Green Transportation Network (GREET) CoE Project for the financial assistance provided by the Department of Chemicals and Petrochemicals (DCPC), Govt. of India, and Centre for Biocomposite and Biomaterial Processing (CBBP), University of Toronto.

REFERENCES CITED

Ahmed, K. S., Khalid, S. S., Mallinatha, V., and Amith Kumar, S. J. (2012). "Dry sliding wear behavior of SiC/Al_2O_3 filled jute/epoxy composites," *Mater. Design* 36, 306-315. DOI: 10.1016/j.matdes.2011.11.010

ASTM D256 (2010). "Standard test methods for determining the izod pendulum impact resistance of plastics," ASTM International, West Conshohocken, PA. DOI: 10.1520/D0256-10

ASTM D638 (2010). "Standard test method for tensile properties of plastics," ASTM International, West Conshohocken, PA. DOI: 10.1520/D0638-10

Chand, N., Sharma, P., and Fahim, M. (2010). "Correlation of mechanical and tribological properties of organosilane modified cenosphere filled high density polyethylene," *Mat. Sci. Eng. A-Struct.* 527(21-22), 5873-5878. DOI: 10.1016/j.msea.2010.06.022

Cheng, C. W., Bedner, D., and Wang, H. (2000). "Phenalkamine derivatives, their use as curing agents in epoxy resin compositions and curable epoxy resin compositions containing them," World Patent #WO 00/01659.

Chrysanthos, M., Galy, J., and Pascault, J.-P. (2011). "Preparation and properties of bio-based epoxy networks derived from isosorbide diglycidyl ether," *Polym.* 52(16), 3611-3620. DOI: 10.1016/j.polymer.2011.06.001

Dai, Z., Constantinescu, A., Dalal, A., and Ford, C. (1994). "Phenalkamine multipurpose epoxy resin curing agents," Cardolite Corporation, Newark, NJ, reprinted from EPI-ERF Conference, Sept. 1994.

Kanchanomai, C., Noraphaiphipaksa, N., and Mutoh, Y. (2011). "Wear characteristic of epoxy resin filled with crushed-silica particles," *Compos. Part B-Eng.* 42(6), 1446-1452. DOI: 10.1016/j.compositesb.2011.04.046

Kishore, Sampathkumaran, P., Seetharamu, S., Murali, A., and Kumar, R. K. (2001). "On the SEM features of glass–epoxy composite system subjected to dry sliding wear," *Wear* 247(2), 208-213. DOI: 10.1016/S0043-1648(00)00537-8

Lagunas, C., Fernandez-Francos, X., Ferrando, F., Flores, M., Serra, A., Morancho, J. M., Salla, J. M., and Ramis, X. (2014). "New epoxy thermosets modified with amphiphilic multiarm star polymers as toughness enhancer," *React. Funct. Polym.* 83, 132-143. DOI: 10.1016/j.reactfunctpolym.2014.07.022

Lancaster, J. K. (1968). "Relationship between the wear of polymers and their mechanical properties," *Proc. Inst. Mech. Eng.* 183(1968), 98-106.

Nayak, R. K., Dash, A., and Ray, B. C. (2014). "Effect of epoxy modifiers (Al_2O_3/SiO_2/TiO_2) on mechanical performance of epoxy/glass fiber hybrid composites," *Procedia Mater. Sci.* 6, 1359-1364. DOI: 10.1016/j.mspro.2014.07.115

Nirmal, U., Hashim, J., and Low, K. O. (2012). "Adhesive wear and frictional performance of bamboo fibres reinforced epoxy composite," *Tribol. Int.* 47, 122-133. DOI: 10.1016/j.triboint.2011.10.012

Pathak, S. K., and Rao, B. S. (2006). "Structural effect of phenalkamines on adhesive viscoelastic and thermal properties of epoxy networks," *J. Appl. Polym. Sci.* 102(5), 4741-4748. DOI: 10.1002/app.25005

Ratner, S. B., Farberoua, I. I., Radyukeuich, O. V., and Lure, E. G. (1967). "Correlation between wear resistance of plastics and other mechanical properties," in: *Abrasion of Rubber*, D. I. James (ed.), MacLaren, London, pp. 145-154.

Reddy Paluvai, N., Mohanty, S., and Nayak, S. K. (2014). "Synthesis and modifications of epoxy resins and their composites: A review," *Polym-plast Technol.* 53, 1723-1758. DOI: 10.1080/03602559.2014.919658

Rout, A., and Satapathy, A. (2012). "Analysis of dry sliding wear behaviour of rice husk filled epoxy composites using design of experiment and ANN," *Procedia Eng.* 38, 1218-1232. DOI: 10.1016/j.proeng.2012.06.153

Sato, S., Shah, S., Bueno, R. C., Moon, R., and Ferreira, A. (2009). "Phenalkamine and salted amine blends as curing agents for epoxy resins," World Patent #WO 2009/080209.

Shalwan, A., and Yousif, B. F. (2014). "Influence of date palm fibre and graphite filler on mechanical and wear characteristics of epoxy composites," *Mater. Design* 59, 264-273. DOI: 10.1016/j.matdes.2014.02.066

Suresh, B., Siddaramaiah, P., Kishore, Seetharamu, S., and Sampath Kumaran, P. (2009). "Investigations on the influence of graphite filler on dry sliding wear and abrasive wear behaviour of carbon fabric reinforced epoxy composites," *Wear* 267(9-10), 1405-1414. DOI: 10.1016/j.wear.2009.01.026

Wu, J., and Cheng, X. H. (2006). "The tribological properties of Kevlar pulp reinforced epoxy composites under dry sliding and water lubricated condition," *Wear* 261(11-12), 1293-1297. DOI: 10.1016/j.wear.2006.03.014

Article submitted: October 13, 2014; Peer review completed: December 19, 2014;
Revised version received and accepted: January 9, 2015; Published: May 21, 2015.
DOI: 10.15376/biores.10.3.4126-4136