Graphite–Epoxy Graded Material by Centrifugation

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ABSTRACT: A graded distribution of graphite particles in epoxy resin matrix was obtained using a centrifugation technique. By varying the centrifugation time the graded profile could be effectively controlled. Scanning electron microscopy and optical microscopy revealed the graded dispersion of graphite particles in the epoxy matrix, which is sensitive to centrifugation time. Electrical or wear properties can accurately estimate the property profile of graded material. The abrasive wear test also provided a quick estimation of the extent of gradient formed in the sample. The increased centrifugation time increased the compaction of graphite particles in the graphite-rich phase of graded material that could be correlated with the increased capacitance of the sample. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 550–556, 2005

Key words: centrifugation; graded material; epoxy resin; dielectric properties; morphology

INTRODUCTION

To achieve the desired properties for encapsulating electronic devices, such as thermal expansion coefficients and elastic modulus, a spatially desired distribution of particulate modifiers is required.[1] The spatial gradient in concentration can be produced in sedimentation of particles that differ in density from the polymer when it is in a fluid state.[2] Assuming an ideal case, under the force of gravity, particles of uniform geometry and size suspended in a fluid would start moving toward the bottom. The particles, which are independent of local concentration, would attain the same velocity. However, at the bottom region these particles cannot move because of both boundary restriction and other particles. The viscosity in this region increases so much that suspension behaves like a solid. Above this zone a middle zone appears that has almost uniform distribution of particles with the original concentration. The third, top zone is expected to be clear and free from particles. With the progress of sedimentation, the top clear zone and the bottom dense zone increase in thickness whereas the middle zone shrinks. After a certain period only two distinct zones are expected. Considering the differences in particle size, the velocity of particles would thus also be different, which would cause a gradient in concentration. By freezing this gradient in concentration, a graded material can be obtained.

Not only does particle size cause a gradient in concentration but other parameters, such as bulk viscosity, also play a vital role in this regard. The collision and interaction of particles hinder the velocity of particles, and thus the assumption of unhindered travel of particles does not remain valid. This phenomenon would not produce the expected outcome of the three-zone postulate. The suspended particles change the bulk viscosity of fluid and therefore a viscosity profile is formed; this would also help in development of a graded material.

One of the important parameters in particle sedimentation is gravitational force. This gravitational force can be replaced with centrifugal force so that this parameter can be applied with varying degrees of control. Both intensity of force on particles and time of travel could easily be manipulated. A centrifugation technique has recently been used in making graded distribution of carbon fiber in epoxy resin matrix.[3–6] Achievement of a wide spectrum of filler distribution, by varying the centrifugation speed, was reported. Electrical properties varied with the volume content of fibers in the direction of centrifugal force and a graded electrical conductivity was reported.[3]

Graphite, which is another form of carbon, has attained paramount importance because of its lubricating effectiveness and has been well documented with respect to its tribological properties.[7–10] The experimental study on graphite-filled epoxy concludes that the coefficient of friction and wear of graphite–epoxy resin depend on the concentration of graphite powder, sliding time, and applied load. Addition of graphite reduces the coefficient of friction and the wear rate of epoxy by formation of a transfer-lubricating graphite film at the contact interface.[7] Graphite is also widely used as an electrically conducting filler for preparing conducting polymer composites.[11–13] Electrical con-

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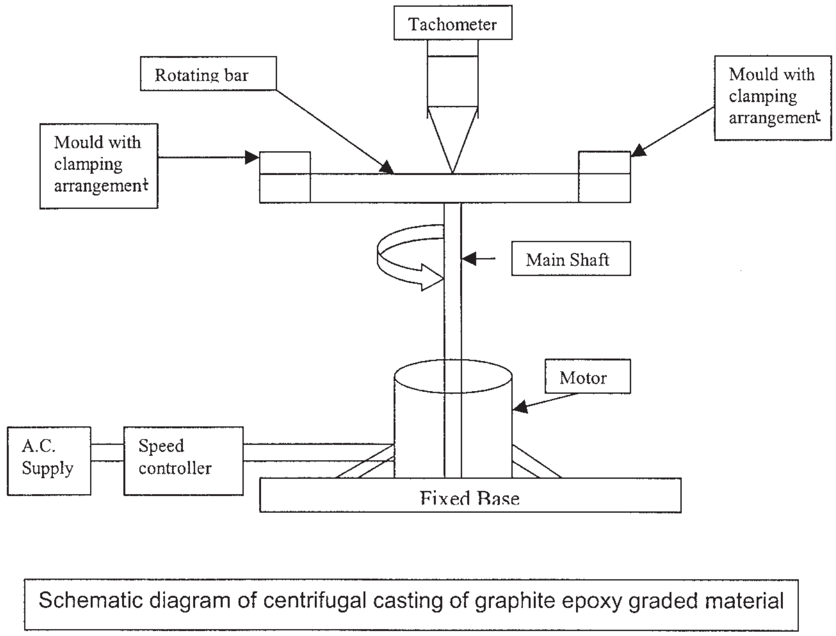

Figure 1 Schematic diagram of centrifugal casting of graphite–epoxy graded material.

ductivity of graphite is of the order of 10^4 S/cm at room temperature. Carbon atoms in graphite are arranged in a layered structure. Graphite–epoxy composites have also shown potential as transducing materials for electrochemical genosensing because of their high sensitivity that results from microelectrode array behavior.[14–16] In the present study, a graded graphite–epoxy material was developed by use of a centrifugation technique. The profile of graded dispersion was evaluated and discussed using morphological, electrical, and wear properties. An attempt was also made to use electrical and abrasive wear test methods to characterize graded materials.

EXPERIMENTAL

Materials

Room-temperature–cured polysulfide modified epoxy resin (Tech Floor grade) used in this study was obtained from M/s Choksey Chemical (Mumbai, India). The density of epoxy resin, cured at room temperature with hardener in the ratio of 2 : 1, was 1.15 g/cm^3. Graphite particles were obtained from M/s HEG (Mandideep, India). The particle size varied from 38 to 45 μm. The density of particles, estimated by relative density (RD) bottle measurement, was 2.23 g/cm^3.

Sample preparation

The simple centrifugal arrangement was developed in the laboratory, as shown schematically in Figure 1.[17] A motor controlled by electrical current was used to rotate the shaft at fixed speed. Sample molds were fixed at both ends of a bar, which was fixed onto the shaft of the motor by appropriate clamping arrangement. A tachometer was attached to observe rpm values of the assembly. Graphite particules were added to a mix of epoxy resin and hardener and were thoroughly mixed. The mix contained 3 phr (parts per hundred parts of resin) graphite particles in the resin system. Equal amounts of graphite particles dispersed in the epoxy resin were transferred to two identical molds. The molds were closed and fitted onto the centrifugal apparatus. The molds were designed to make cylindrical pins of 10 mm diameter. The rotational speed was kept constant at 550 $\pm$ 20 rpm. The distance between the rotor axis and end of the sample was 30 cm. The time of centrifugation was varied at 30, 60, 90, and 120 min. Thereafter, molds were removed from the rotating system and kept at room temperature for 24 h. After removal from the mold, the sample pins were postcured in an oven at 120°C for 2 h, after which the cured samples were subjected to different tests.

Methods

A JSM 5600 scanning electron microscope (JEOL, Tokyo, Japan) was used to observe the worn and fractured surfaces. An optical microscope (Leitz, Wetzlar, Germany) was used to observe the distribution of graphite particles in the graded material.

A pin-on-disk sliding wear machine (model type TR-20 LE, Ducom, India) was used to characterize the

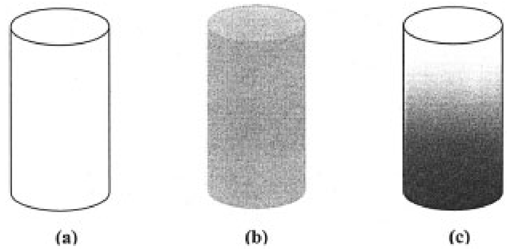

Figure 2 Schematic sample pins: (a) unfilled epoxy resin, (b) uniformly distributed graphite in epoxy resin, and (c) a view of a pin with concentration profile.

sliding wear properties of graded material and epoxy resin. Abrasive wear studies were carried out under multipass conditions to characterize graded material on the same pin on the disk sliding wear machine. Abrasive paper was fixed onto a disc rotating at 80 rpm in a track diameter of 6.5 cm. The graded material sample pin was fixed in a holder and was abraded at a speed of 0.27 m/s at 5 N load for a fixed time of 1 min. Because the composition of material varies with thickness of the studied pin, the wear loss (length loss) could thus be related to the concentration gradient of the graphite–epoxy centrifuged graded material. The length loss was observed using a vernier caliper after each run. To remove particles and other detritus before and after each run, a soft brush was used to clean the samples. The sliding wear data reported herein were also taken on the same equipment. The contact-sliding surface was an EN 21–grade stainless steel disc instead of abrasive paper. The pin was cleaned with acetone before and after wear testing and then dried. In sliding wear measurement the sliding distance length was 816 m.

A 4274A LCR meter (Hewlett–Packard, Palo Alto, CA) was used to estimate the capacitance of graded material, cured epoxy resin, and uniformly distributed graphite in epoxy resin at 1 kHz.

RESULTS AND DISCUSSION

Figure 2 shows a schematic of the three pins: (1) unfilled epoxy resin, (2) uniformly distributed graphite in epoxy resin, and (3) a pin with concentration profile. In the present investigation of graphite distributed epoxy resin graded material, the graphite particles traveled through the epoxy resin under centrifugal force and tended to occupy the farthest position; however, because of the lack of sufficient time, all the particles could not reach to the end and therefore a concentration profile along the thickness of the sample was formed.

The centrifugal force accelerated the movement of graphite particles toward the farthest end of the pin. The concentration profile mainly depends on the process parameters, density of suspension, viscosity of medium, centrifugal force, and time of centrifugation.

Microstructure of graded graphite–epoxy composites

Figure 3 shows the microstructure of graded graphite–epoxy samples as observed by optical microscope un-

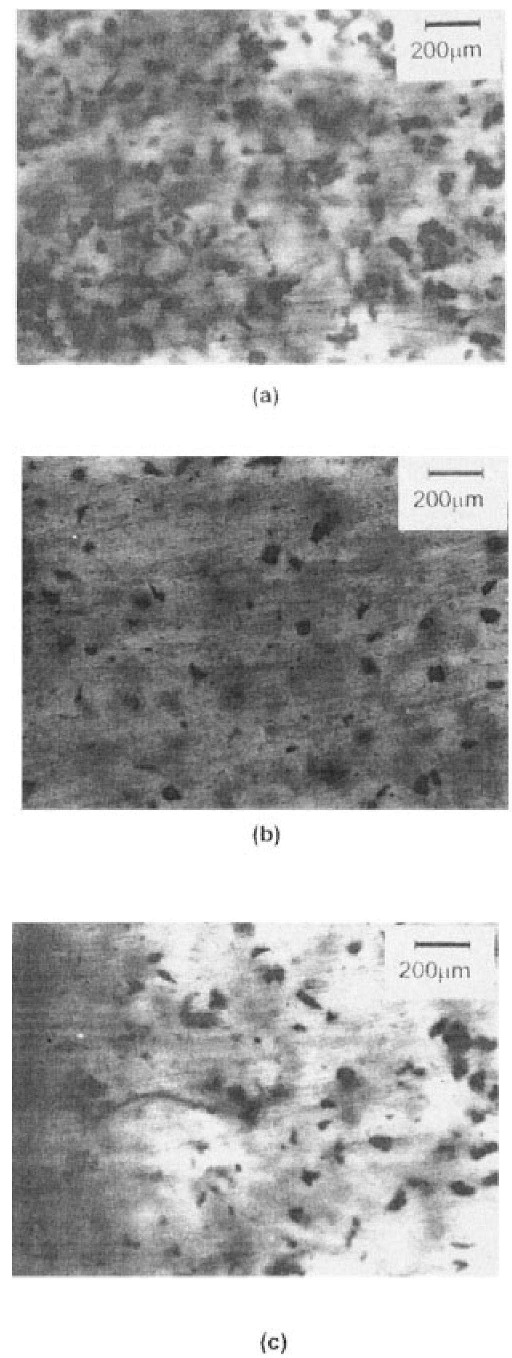

Figure 3 Optical micrographs of graded materials: (a) transition zone (graded zone) of a sample centrifuged for 30 min; (b) 10 mm from graphite-rich phase; (c) near graphite-rich region in a sample centrifuged for 2 h.

der transmission mode. The centrifugation speed used was 550 rpm and initial concentration of graphite content was 3 phr. The specimen pins were cut in such a way as to observe the distribution of particles in the sample from the bottom to the top of the pin. For this purpose thin plates were cut parallel to the centrifugal force. A dense layer of graphite particles at the end (bottom) of the sample was observed in all three samples, corresponding to different times of centrifugation. The thickness of this layer, however, was different in different samples. The thickness of the graphite layer increased with centrifugation time. Just above this layer a transition zone appeared, showing a graded concentration of graphite in the epoxy resin. The concentration profile of graphite can be observed in Figure 3(a), in which graphite particles show a higher concentration at the left side. It can be observed that the concentration of particles decreases at the right side of this micrograph. This micrograph represents a sample that was centrifuged for 30 min. Figure 3(b) shows another micrograph of the same sample taken at 10 mm distance from bottom. This shows an almost uniform distribution of graphite with substantially less particle density in this region. Figure 3(c) shows a micrograph of a sample centrifuged for 2 h. The black area on the left represents a dense graphite particle region that does not allow light to pass through the sample. The right portion of this micrograph shows graphite particles distributed in the transition region. The sharp, irregularly shaped particles are graphite particles those focused properly, but the profiles present in planes other than the focused plane are slightly diffuse. At a high concentration of graphite particles light could not be transmitted, as observed in Figure 3(c).

SEM was used to observe the fractured surfaces of samples. Figure 4(a) shows a sample centrifuged for 2 h. The bottom portion clearly shows the highly dense graphite particles in the sample. The upper part of this fractograph shows the epoxy matrix in which few graphite particles are also observed. Figure 4(b) shows the distribution of graphite in the transition region.

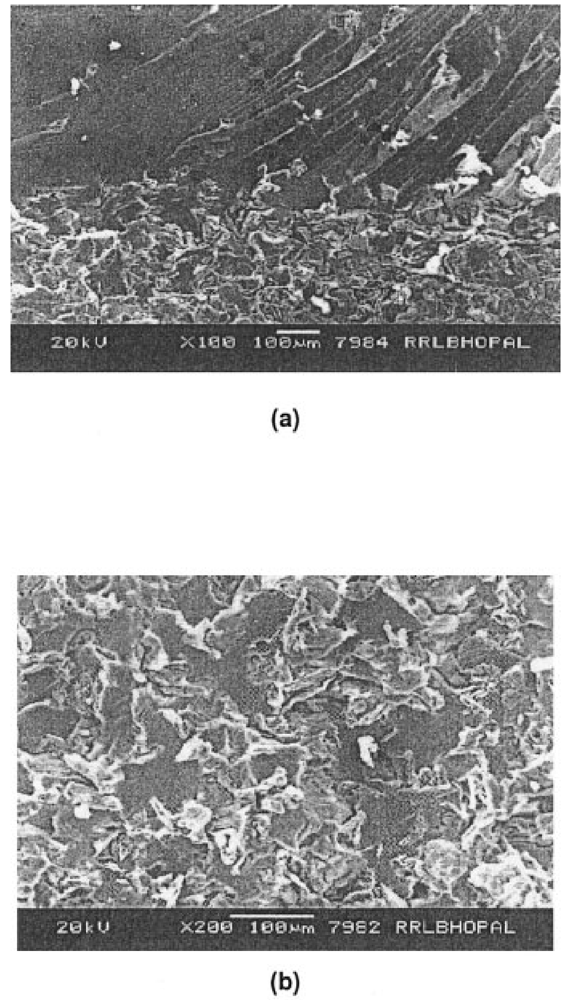

Figure 4 SEM microphotographs of fractured surface of sample centrifuged for 2 h.

Electrical properties

Capacitance (C) of epoxy, uniformly distributed graphite in epoxy and graded graphite–epoxy materials, was determined by using an LCR meter at 10 kHz and at fixed room temperature. Capacitance is related to the dielectric constant (k) thickness of sample (d), the cross-sectional area of flat surface of sample (A), and constant of permittivity for free space (ε_0) by the following relation:

$$C = \varepsilon_0 A/(d/k) \quad (1)$$

Capacitance is an important electrical property of material that varies with composition. The concentration-graded material can therefore be characterized by observing changes in capacitance.

In the present case three different samples were taken to determine capacitance: (1) the epoxy resin, (2) 3 phr uniformly distributed graphite particles in epoxy resin, and (3) centrifuged samples of graphite–epoxy graded material. The test pin diameter was 10 mm and sample length was originally 30 mm, although the tests were conducted on the 5-mm sample after removing the top resin-rich part of the pin. First observations of the 5-mm-thick sample on the LCR meter were taken. Removal of the resin-rich top layer reduced the sample thickness and the sample was then tested for electrical capacitance. The process of thickness reduction was continued and measurements were taken until the last sample, having a thickness of 1.5 mm, was tested. The same procedure was adopted for all three types of samples.

These results are plotted for comparison in Figure 5. The plot represents the relationship between capaci-

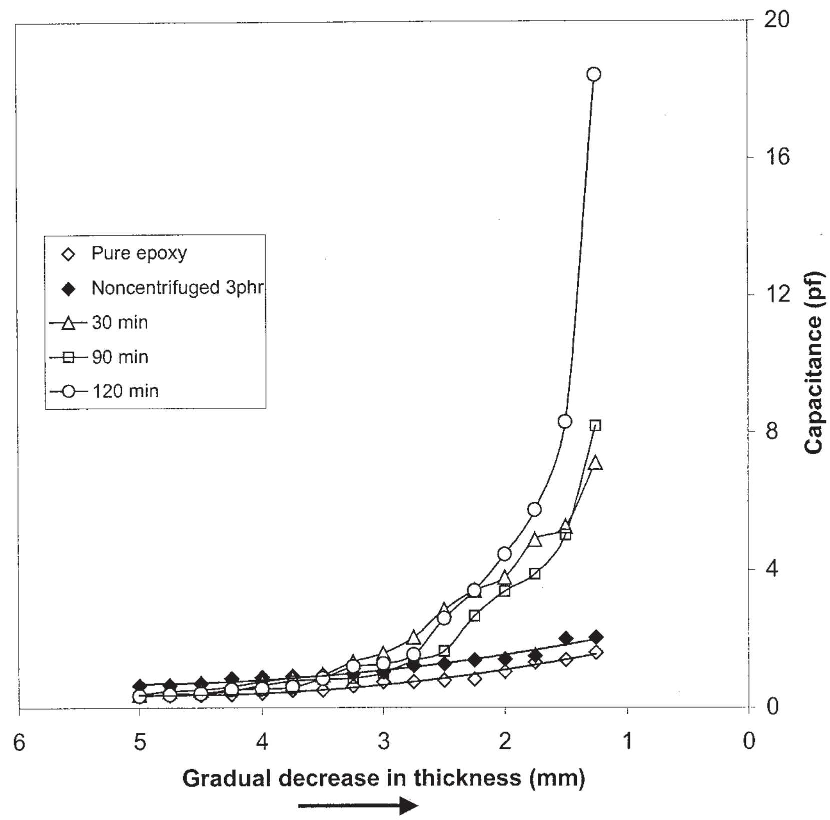

Figure 5 Plot between capacitance and gradual decrease in thickness of sample.

tance and gradual decrease in thickness of sample. The concentration of graphite increases in the graded sample upon moving positive in the x-direction in Figure 5. The lowest curve shows variation in capacitance of epoxy resin with thickness. The capacitance increases slowly and uniformly with reduction of sample thickness. This is in line with the relation given in eq. (1). The unfilled epoxy pin is a uniform material having a fixed dielectric constant and thus the observed capacitance is inversely proportional to the sample thickness. Parallel to and above this curve another curve is shown in Figure 5 that tracks the uniformly distributed graphite–epoxy material. The capacitance is higher compared to that of the epoxy resin because of the addition of graphite in this sample, although the nature of the curve is identical to that of epoxy resin. This curve also shows uniformly increased capacitance with reduction in the thickness of the sample. Important inferences could be drawn from the curves: (1) addition of graphite particles increases capacitance of the material; (2) the nature of the curve of uniformly distributed graphite in epoxy does not vary compared to that of the matrix material while changing the thickness of sample. Armed with these results and by comparing three additional curves that tracked centrifuged samples of 30, 90, and 120 min, it was clearly demonstrated in Figure 5 that the capacitance of graded material initially falls between the two curves. On reducing the thickness of sample from the resin-rich end, the capacitance of material of remaining thickness increases. Capacitance of the graded sample crosses over the upper curve tracking the 3 phr graphite distributed uniform sample at different thicknesses. In other words, capacitance of the graded material at the point of crossover is equivalent to that of the uniformly distributed 3 phr graphite–epoxy resin. On further reduction of the resin-rich phase a significantly increased capacitance of the remaining gradient material was observed. This confirms the formation of a concentration profile in the sample.

Interestingly, the effect of centrifugation time on capacitance of graded materials is also substantial. The graphite-rich phase shows the highest value of capacitance in all cases: this is attributed to the high concentration of graphite in epoxy. Over and above the high capacitance value of the sample, which was centrifuged for a longer time, may be attributed to densely packed graphite particles, thus increasing the capacitance value of material corresponding to centrifugation time.

Wear studies

Sliding wear data of graded graphite–epoxy material show an excellent lubrication effect of graphite in the

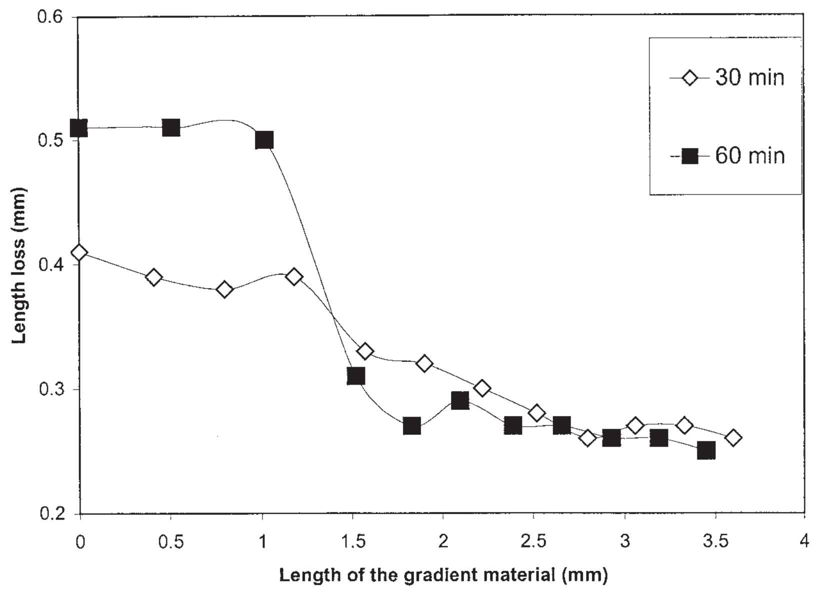

Figure 6 Plot between length loss and length of graded material.

epoxy matrix. The effectiveness of lubrication is attributed to buildup of a transferred layer on the sliding surface.[7–9] In the present case, the wear rate of epoxy resin and graphite-rich epoxy graded pin (bottom zone that contains highest the concentration of graphite) was 3.445×10^{-3} and 0.3178×10^{-3} mm^3/m, respectively, whereas the experiment was conducted at 400 rpm and at 20 N applied load for overall 816 m traveled distance. This shows that sliding wear results are in line with available published literature.[7–10] In the present article, the possibility of characterizing concentration gradient was attempted by using the wear technique for a quick estimation. For this purpose a multipass abrasive wear test was conducted. Multipass abrasive wear has been successfully used to characterize polymer composites.[18] Abrasion produces loose graphite wear particles, which are retained within the interface until their attachment or escape. On a rough surface, such as abrasive paper, the loose worn particles fill the valleys of surface topography and, as wear proceeds, start to reduce the effectiveness of abrading asperities.[7] A few tests were initially conducted to observe the sample running to a minimum distance, sufficient to provide measurable wear. The sample pins were abraded against the same abrasive paper in the same track for a distance of 16.3 m.

The wear observations are shown in Figure 6. The length loss resulting from abrasion of the cylindrical pin is plotted against the concentration profile of graded materials. The concentration of graphite decreases in the sample on moving positive in the x-direction in the figure. Figure 6 shows the data for two samples, each from 30- and 60-min centrifugation. The initial part of this curve tracks the graphite-rich graded material. The length loss, which is an indicator of abrasive wear loss, is higher in this portion compared to that in the remaining part of the curve. Thereafter, the length loss decreases corresponding to the concentration gradient formed by graphite particles. After a length of nearly 2.5 mm, a nearly constant length loss was observed. By summarizing and correlating the introductory discussion with these results, mainly three zones are observed: a nearly uniform graphite-rich bottom zone, a concentrated graded zone, and a resin-rich top zone. The resin-rich top zone shows minimum abrasive wear, the graded zone shows increased wear with the increased concentration of graphite, and the dense graphite zone shows maximum wear loss. These results clearly established that the abrasive wear test provides a quick estimation of gradient formation. With respect to abrasive wear loss results and results of sliding wear, it is reported in the literature that composites that show good performance in sliding wear exhibit poor abrasion resistance. Unfilled polymer shows better abrasion resistance than that of filled polymers. Similar results were observed in the present case in which higher loading of graphite in epoxy resulted in higher wear loss compared to that of lower-concentration graphite–epoxy material. The reduction in abrasive wear length is related to the reduced graphite content in different sections of the pin, as shown in Figure 6.

CONCLUSIONS

This experimental study yielded the following conclusions:

- Graded distribution of graphite in epoxy resin can be obtained using a centrifugation technique by controlling the centrifugation time.
- Morphological, electrical, and wear tests can be used to characterize the concentration gradient of material.
- The abrasive wear test provides a quick estimation of the concentration gradient of graded materials.

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